



Properties of Polyaniline Synthesized in Ionic Liquid (1-Ethyl-3-methylimidazolium-ethyl sulphate)

Qiaofang Shi, Ya Zhang, Guolin Jing, and Jinqing Kan*
School of Chemistry and Chemical Engineering, Yangzhou University,
Yangzhou, 225002, P.R. China

Received 27 March 2007; accepted 7 July 2007

ABSTRACT

The electroactive polyaniline at high pH was electrochemically synthesized in a solution containing 0.2 mol.dm⁻³ aniline and ionic liquid, 1-ethyl-3-methylimidazolium-ethyl sulphate (EMIES). The cyclic voltammograms of the polyaniline were performed in 1.0 mol.dm⁻³ KCl in a range of pH from 8.0 to 12.0 between 0.0 and 1.2 V at 60 mV.s⁻¹. The results indicated only 14.4% decay of the electrochemical activity when the polyaniline was moved from pH 8.0 to 10.0. The polyaniline still retains good electrochemical activity at pH 12.0. The results of UV-visible and FTIR spectrum reveal that the framework of polyaniline synthesized in EMIES is similar to that of polyaniline synthesized in HCl. The thermal behaviour of the polyaniline prepared in EMIES shows a three-step weight loss process, they are at about 100°C, 200-300°C and over 350°C, respectively. The conductivity of polyaniline synthesized in EMIES is 0.011 S.cm⁻¹. After immersion of polyaniline into 1.0 mol.dm⁻³ HCl or 1.0 mol.dm⁻³ KCl for one hour, its conductivity enhances to 0.53 or 0.052 S.cm⁻¹, respectively. Based on the results of osmometry, the average molecular weight of the polyaniline is about 4.97×10⁴. The polyaniline can be dissolved in DMF and other common organic solvents but little in water, which is very favourable to structural analysis and applications of polyaniline.

Key Words:

ionic liquid;
electroactive;
polyaniline;
synthesis;
EMIES.

INTRODUCTION

Among conducting polymers polyaniline has attracted significant interest due to its high conductivity, good redox reversibility, swift change of colour with potential and stability in an aqueous solution and in air. These properties are favourable in such applications as rechargeable batteries [1,2], elec-

trocatalysis [3], electrochromic devices [4], sensors [5], and conversion of light to electricity [6]. However, the properties of polyaniline are strongly affected by pH value, which restricts its applications in a certain extent. Polyaniline is also a good material to immobilize enzymes, however, the low

(*) To whom correspondence to be addressed.

E-mail: jqkan@yzu.edu.cn

electrochemical activity of polyaniline is a disadvantage to electron transfer at $\text{pH} > 4$ for the enzymes with high isoelectric points, such as uricase or galactose oxides [7].

Ionic liquids have excellent thermal stability, low volatility, and wide electrochemical potential windows, and are excellent solvent. They are widely applied in batteries, capacitors, electropolymerization and the like. Synthesis of polyaniline in some ionic liquids has also been investigated, for example, Miao et al. prepared polyaniline nanofibrous networks in ionic liquid (1-hexadecyl-3-methylimidazolium chloride) [8], and Gao et al. also fabricated polyaniline nanoparticles in an aqueous/ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate) interfacial [9]. Innis et al. synthesized the polyaniline in 1-ethyl-3-methylimidazolium bifluoromethanesulphone imide [10]. Zhang et al. reported the synthesis of polyaniline in ionic liquid (1-methyl-3-butylimidazolium hexafluorophosphate) and found that the electrochemical activity of the polyaniline synthesized in the ionic liquid with CF_3COOH can be improved [11]. Synthesizing polyaniline of different properties is still a topic of general interest based on different purposes.

Based on the facts that polyaniline has relatively high electrochemical activity up to $\text{pH} 12$ and easy synthesis, low-cost and environmental stability of ionic liquid, 1-ethyl-3-methylimidazolium-ethyl sulphate (EMIES) [12], the synthesis of polyaniline in the EMIES is being reported for the first time. The polyaniline synthesized is characterized by cyclic voltammetry (CV), FTIR spectrum, UV-visible spectrum and thermogravimetric analysis (TGA). The conductivity and the molecular weight of polyaniline are measured by a four-probe technique and by osmometry, respectively.

EXPERIMENTAL

Aniline (reagent grade) was distilled until colourless under reduced pressure prior to use. All other reagents used were of analytical reagent grades and used without further purification. All solutions were prepared with double distilled water.

According to the literature [12], 1-ethyl-3-

methylimidazolium-ethyl sulphate (EMIES) was synthesized. The prepared process was as follows: firstly, diethyl sulphate (0.221 mol) was added dropwise to a solution consisting of 1-methylimidazole (0.221 mol) and toluene (100 mL) in an ice-bath at a controlled rate to maintain reaction temperature below 40°C . After addition of diethyl sulphate, the reaction mixture was stirred at room temperature for 1h. Ionic liquid phase was washed with toluene, followed by removal of toluene and finally it was dried under reduced pressure at 75°C .

The electrochemical polymerization of aniline was carried out at 1.2 V in EMIES solution containing $0.2 \text{ mol}\cdot\text{dm}^{-3}$ aniline. The electrolysis cell consisted of two platinum sheets and a reference electrode. Two platinum sheets were used as working electrode and counter electrode, respectively. The area of working electrode was $4 \times 3 \text{ mm}^2$. A saturated calomel electrode (SCE) was used as reference electrode, and all potentials given here were referred as SCE. Electrochemical polymerization of aniline was performed on a CMBP-1 bipotentiostat/galvanostat. Yellow polyaniline film was formed on the working electrode in the freshly prepared solution after 4 h. The film thickness increased with increasing time. The obtained polyaniline was washed with double distilled water and dried at $50\text{--}60^\circ\text{C}$ for 48 h.

UV-Vis spectra of polyaniline were recorded by using *N,N*-dimethylformamide (DMF) as solvent. A Shimadzu UV-2550 spectrophotometer was used to record the electronic absorption spectra in the range of $300\text{--}800 \text{ nm}$. The structural characteristics of the polyaniline were investigated by a Tensor 27 spectrometer in the range of $400\text{--}4000 \text{ cm}^{-1}$ by KBr pellet method. TGA was performed using a SDT Q600 instrument (USA), at a heating rate of $10^\circ\text{C}/\text{min}$, under nitrogen, from room temperature (about 25°C) to 800°C . The conductivity was measured by a conventional four-point technique on pellets compressed from polyaniline powders at $8 \times 10^5 \text{ Pa}$ with a manual hydraulic press at 25°C . The thickness of polyaniline pellets obtained was 1.2 mm. The molecular weight of polyaniline was determined by osmometry. An amount of 10.0 mg of polyaniline was completely dissolved in 100 mL DMF, the osmometry instrument consisted of a capillary of $d = 4 \text{ mm}$ and a semipermeable membrane of chicken intestine. The determina-

tion was carried out at 25°C.

The cyclic voltammograms of polyaniline film synthesized in the EMIES were recorded using a CMBP-1 bipotentiostat/galvanostat and a YEW 3036 X-Y recorder in EMIES, 1.0 mol. dm⁻³ HCl and 1.0 mol dm⁻³ KCl, respectively. The sweeping potential range was set between 0.0 and 1.2 V. The scan rate was 60 mV. s⁻¹ unless otherwise stated. The pH values of solutions were determined using a PXD-12 pH meter. The standard deviation is less than 3.0% in our experiments.

RESULTS AND DISCUSSION

Cyclic Voltammetry (CV)

Figure 1 shows the voltammograms of polyaniline film prepared in EMIES. As soon as polyaniline was prepared in EMIES the electrochemical behaviour of polyaniline film in EMIES was examined by voltammograms in 1.0 mol.dm⁻³ HCl or 1.0 mol.dm⁻³ KCl, respectively. It is observed from Figure 1 that there is no redox peak in these solutions. The result is similar to the polythiophene film prepared in BMIMPF₆ (1-butyl-3-methylimidazolium hexafluorophosphate) by Li et al. [13].

Figure 2 is the cyclic voltammograms of the polyaniline film immersed in EMIES (curve 1), 1.0 mol.dm⁻³ HCl (curve 2) or 1.0 mol.dm⁻³ KCl

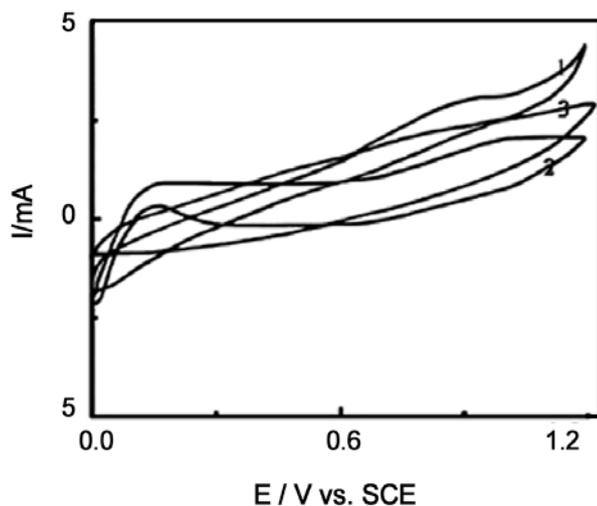


Figure 1. Cyclic voltammograms of polyaniline film synthesized in EMIES at 60 mV.s⁻¹, from 0.0-1.2 V. (1) EMIES, (2) 1.0 mol.dm⁻³ HCl, and (3) 1.0 mol.dm⁻³ KCl (pH 6.9).

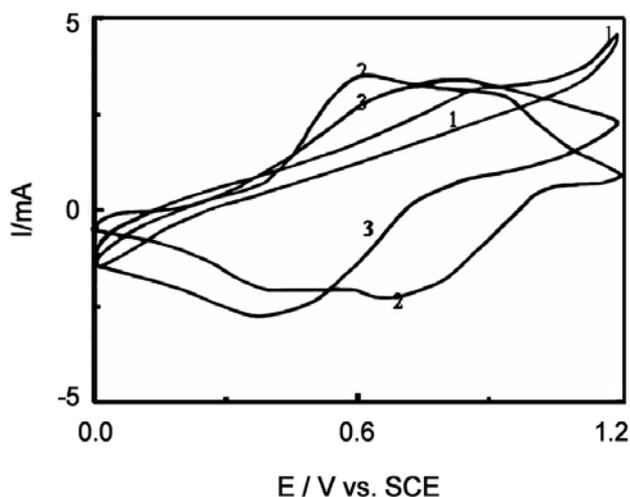


Figure 2. Cyclic voltammograms of polyaniline synthesized in the EMIES at 60 mV.s⁻¹ from 0.0 to 1.2 V. (1) EMIES; (2) immersed in 1 mol.dm⁻³ HCl for 1 h; (3) immersed in 1 mol.dm⁻³ KCl (pH 6.9) for 1 h.

(curve 3, pH 6.9) for 1 h, respectively. It is observed in curve 2 that there are two pairs of redox peaks at 0.60 V and 0.84 V in 1.0 mol.dm⁻³ HCl. The first one (0.60 V) may be associated with the presence of *ortho*-coupled polymers [14] or with the degradation of polyaniline (soluble species such as benzoquinone and hydroquinone) [15], and the second one (0.84 V) corresponded to the interconversion between emeraldine to pernigraniline. There is just a pair of peaks in 1.0 mol.dm⁻³ KCl (pH 6.9) at about 0.87 V, it is also caused by the interconversion between emeraldine to pernigraniline [16]. From the cyclic voltammograms represented in curves 1, 2 and 3, we can observe that the oxidation and reduction potentials are different for different dopant types. This fact is attributed to the electrostatic interaction of those dopants with the chemically flexible -NH- group of polyaniline [17].

Figure 3 shows the voltammograms of the polyaniline films in 1.0 mol.dm⁻³ HCl at 6 mV.s⁻¹ (curve 1) and 60 mV.s⁻¹ (curve 2), respectively. It is observed from curve 1 that there are three couples of peaks on the voltammogram, which is similar to that of polyaniline synthesized in HCl solution [18]. The first peak of 0.56 V is associated with the oxidation of the leucoemeraldine to emeraldine [19]; the third peak (at about 0.95 V) is the further oxidation of the polyaniline to the form of quinoid diradical dications of *para*-phenylene amine polymer units (bipolaron state) or to

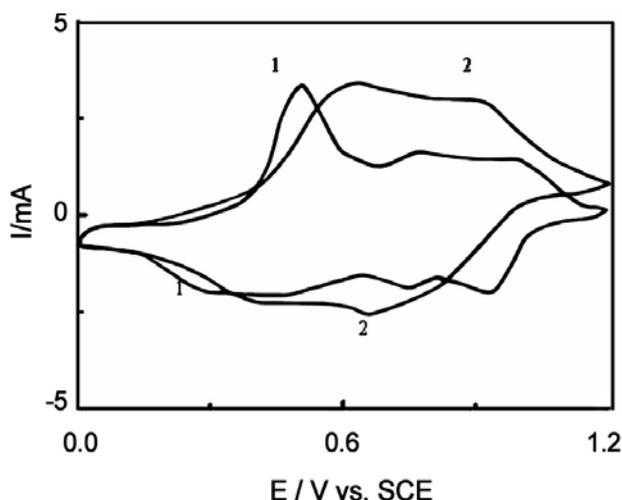


Figure 3. Cyclic voltammograms of polyaniline film in 1 mol.dm⁻³ HCl, 0.0-1.2 V. (1) 6 mV.s⁻¹; and (2) 60 mV.s⁻¹.

the further oxidation of polyaniline from emeraldine to nigraniline [20]. The second peak (at about 0.75 V) is attributed to the presence of *ortho*-coupled polymers [14] or to the degradation of polyaniline (soluble species such as benzoquinone and hydroquinone) [21]. However, there are only two redox peaks on the voltammogram when the rate of potential sweep was set at 60 mV.s⁻¹ (curve 2) the two oxidation peaks are at 0.60 V and 0.84 V, the two reduction peaks at 0.35 V and 0.65 V, respectively. The difference between curve 1 and curve 2 was caused by rate of potential sweep [22]. It is very common that some redox peaks decrease or vanish with increasing sweep rate for the complex electrode reactions [23]. It is somewhat analogous to the cyclic voltammograms of polyaniline synthesized in the HCl solution. This implies that the framework of polyaniline synthesized in EMIES is similar to that of polyaniline synthesized in the HCl solution.

In order to gain further insights into the electrochemical activity of the polyaniline at high pH, the cyclic voltammograms of the polyaniline film were completed in 1.0 mol.dm⁻³ KCl solution from pH 8.0 to 12.0 (Figure 4) at 60 mV.s⁻¹. From the curves (1-5) of Figure 4, we can observe a couple of peaks, the oxidation peak at 0.87 V and the reduction peak at 0.40 V, at different pHs. The anodic and cathodic peak currents in Figure 4 (curves 1-5) decrease slowly with increase in pH from 8.0 to 12.0.

It is well known that the plot of I-E on the cyclic

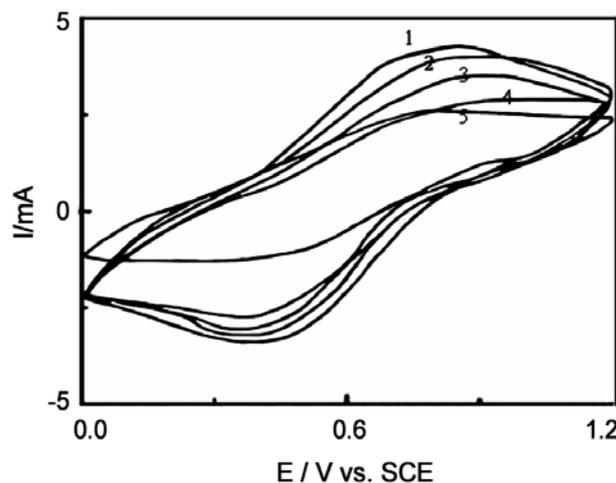


Figure 4. Cyclic voltammograms of polyaniline film at different pHs in 1.0 mol.dm⁻³ KCl, 0.0-1.2 V, 60 mV.s⁻¹, pHs: (1) 8.0, (2) 9.0, (3) 10.0, (4) 11.0, and (5) 12.0.

voltammogram is equivalent to that of current versus time. That is, the area of the cyclic voltammograms represents the quantity of electricity. Based on the cyclic voltammograms of the polyaniline of curve 2 in Figure 2 and curves 1, 3 and 5 in Figure 4, the electrochemical activity of the polyaniline was only 0.4%, 14.5% and 22.4% decreased in KCl solutions of different pHs, respectively. The results from the repeated experiment confirmed that electrochemical activity of the polyaniline film has good reproducibility in 1.0 mol.dm⁻³ KCl (pH 12.0). Polyaniline maintains very good electrochemical activity under such high pH condition (pH 12.0) that is seldom observed. Although the framework of polyaniline synthesized in EMIES is similar to that synthesized in HCl, the improvement of the electrochemical activity of the polyaniline film may be the reason that the EMIES of doped into polyaniline during electropolymerization is partly replaced by HCl or KCl, which has been confirmed by FTIR spectra.

Figure 5 demonstrates the relationship between the peak currents of the polyaniline film prepared in EMIES and scan rates ($v^{1/2}$) in 1.0 mol.dm⁻³ KCl (pH 10.0). It is observed from Figure 5 that two straight lines are obtained in the range of 10 to 90 mV.s⁻¹. This means that the rate of electrode reaction of the polyaniline film is controlled by mass transfer in KCl solution. The relationship between peak current of the polyaniline film and scan rates ($v^{1/2}$) in 1.0 mol.dm⁻³

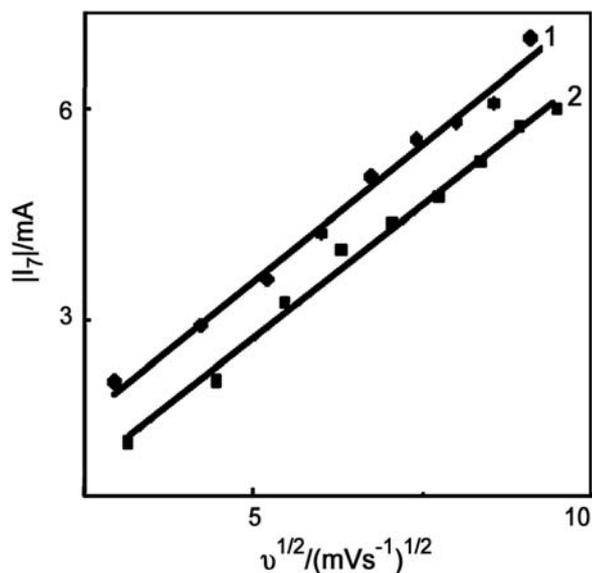


Figure 5. The relationship between peak current and cyclic voltammogram of polyaniline in 1.0 mol.dm⁻³ KCl (pH 10.0) and $v^{1/2}$: (1) I_{a_1} ; and (2) I_c .

HCl solution is also linear (the cyclic voltammograms were omitted).

Conductivity and Molecular Weight

The conductivity of polyaniline synthesized in EMIES is 0.011 S.cm⁻¹. After immersion in 1.0 mol.dm⁻³ HCl or 1.0 mol.dm⁻³ KCl for 1 h, its conductivity increases to 0.53 and 0.052 S.cm⁻¹, respectively. It is well known that smaller dopants have quicker rate of transfer, and at the same time smaller dopants can change the steric effect of EMIES in polyaniline chains. The improvement in conductivity may be the reason that the EMIES doped into polyaniline during electropolymerization is partly replaced by HCl or KCl, which has been confirmed by FTIR spectra. More studies are needed to be carried out to better understand the relationship between conductivity and structure of polyaniline.

Based on the result of osmometry, the relative molecular weight of the polyaniline is calculated to be 4.97×10^4 . Compared with that of polyaniline synthesized in HCl (1140 000-170 000 g.mol⁻¹) [24], the polyaniline synthesized in EMIES has a relative low molecular weight and the EMIES of doped into polyaniline can affect the interaction between polyaniline chains. They may be the reason that the polyaniline synthesized in EMIES can be dissolved in

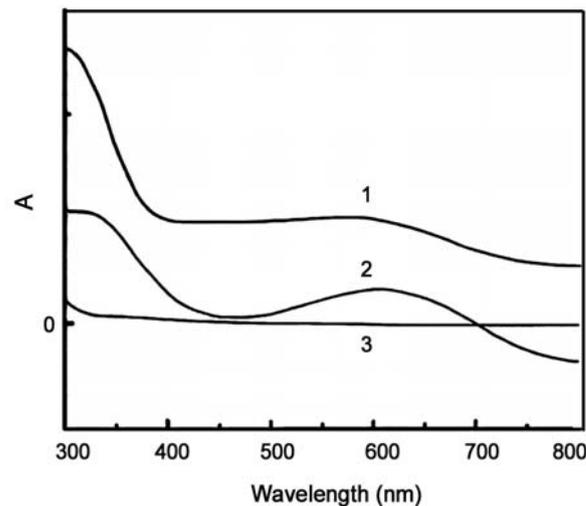


Figure 6. UV-Visible absorption spectra of PANI: (1) PANI-HCl; (2) PANI-EMIES; and (3) EMIES.

DMF and other common organic solvents.

UV-Vis Spectra

Figure 6 shows the UV-visible spectra of EMIES (curve 3) and the polyaniline both prepared in aqueous HCl (curve 1) or EMIES (curve 2), respectively. It is observed from curve 3 of Figure 6 that EMIES has no absorption between 300 to 800 nm. There are two absorption bands in curves 1 and 2 of Figure 6, one location is 320 nm, and the other location is 600 nm. Comparing the polyaniline prepared in EMIES with the polyaniline prepared in aqueous HCl, the 320 nm absorption band was assigned to π - π^* transition, and 620 nm absorption band was assigned to quinoid ring transition in the chain of PANI [25-28]. This shows that framework of the polyaniline synthesized in EMIES is similar to that of polyaniline synthesized in the HCl solution. This is consistent with the result of FTIR spectra.

FTIR Spectra

Figure 7 shows the FTIR spectra of EMIES (curve 3), polyaniline prepared in aqueous HCl (curve 2) and EMIES (curve 1), respectively. Polyaniline has the major bands at about 1580 cm⁻¹, 1490 cm⁻¹, 1295 cm⁻¹, 1140 cm⁻¹, and 800 cm⁻¹, which are attributed to the stretching vibrations of N=Q=N ring, N-B-N ring, C-N, the characteristic of B-NH-Q or B-NH-B bonds, and out-of-plane bending vibration of C-H on the 1,4-disubstituted, respectively (where B refers to

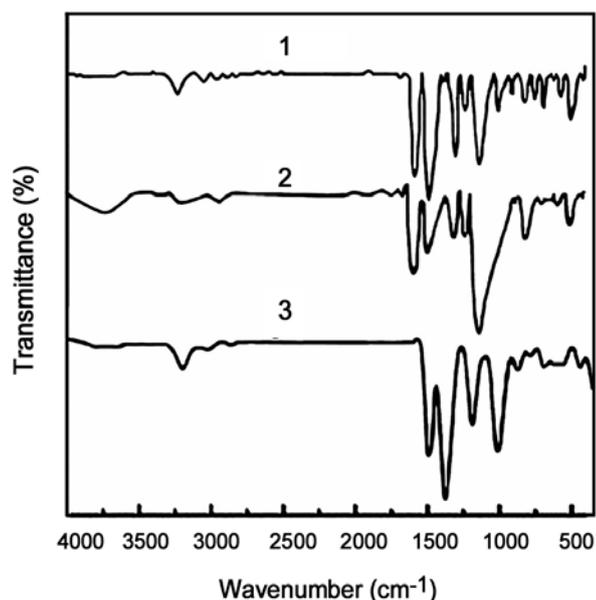


Figure 7. The infrared spectra of PANI: (1) PANI-EMIES; (2) PANI-HCl; and (3) EMIES.

the benzenic-type rings and Q refers to the quinonic-type rings), these bands are in agreement with the references cited [25-28] except for a few shifts in the wavenumbers. In addition, there are two bands located at 3400 cm^{-1} and 3200 cm^{-1} due to N-H bond stretching in Figure 7 (curves 1 and 2). The peaks at 1380 cm^{-1} and 1000 cm^{-1} in curve 1 and curve 3 of Figure 7 are attributed to the EMIES doped into the polyaniline. The peak at 1380 cm^{-1} is attributed to the distortion vibration of $-\text{CH}_3$ and the peak at 1000 cm^{-1} is attributed to the stretching vibrations of $\text{S}=\text{O}$ in the EMIES, respectively. These show that the framework of the polyaniline synthesized in EMIES is similar to that of polyaniline synthesized in the HCl solution. This result is consistent with the UV-visible spectra. It is mentioned that there is EMIES in the polyaniline, this may lead to the improvement of the conductivity and electroactivity of the polyaniline at high pH.

TG Analysis

Figure 8 shows the TGA thermograph of the polyaniline prepared in EMIES (curve 1) or in aqueous HCl (curve 2), respectively. It may be noticed from curve 1 in Figure 8 that the thermal behaviour of the polyaniline prepared in EMIES shows a three-step weight loss process, the first weight loss is at about

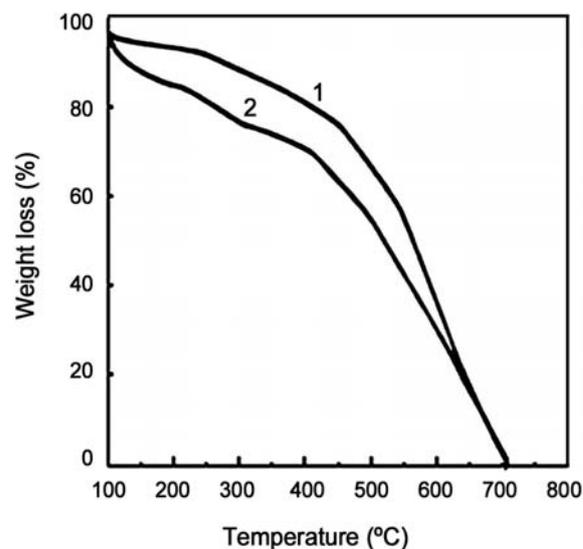


Figure 8. TGA Curves of PANI: (1) PANI-EMIES; and (2) PANI-HCl.

100°C , attributed to the loss of water [29]. The second weight loss at temperatures between 200 and 300°C is believed to be due to the elimination of some low molecules and the third weight loss started at about 350°C is assigned to the thermal decomposition of PANI backbone chains [30]. This implies that the thermal behaviour of the polyaniline synthesized in EMIES is similar to that of the polyaniline synthesized in HCl [31] (curve 2 in Figure 8).

CONCLUSION

Based on the above studied results of cyclic voltammetry, the polyaniline prepared in EMIES has good electrochemical activity in wide pH range. The FTIR and UV-visible spectra indicated that the framework of the polyaniline synthesized in EMIES is similar to that of the polyaniline synthesized in HCl solution. The polyaniline synthesized in EMIES can be dissolved in DMF and common organic solvents but hardly done in water, which is very favourable to structural analysis and applications to polyaniline.

ACKNOWLEDGEMENT

This project was supported by National Science Foundation of China (No. 20673095).

REFERENCES

1. MacDiarmid A.G., Mu S.L., Somasiri N.L.D., Wu W., Electrochemical characteristics of "polyaniline" cathodes and anodes in aqueous electrolytes, *Mol. Cryst. Liq. Cryst.*, **121**, 187-190, 1985.
2. Oyama N., Tatsuma T., Sato T., Sotomura T., Dimercaptan-polyaniline composite electrodes for lithium batteries with high energy density, *Nature*, **373**, 598-600, 1995.
3. Qi X. M., Du Y.F., Zhang G.R., Zhao P., Lu J.X., Electrosynthesis of polyaniline in ionic liquid and its electrocatalytic properties, *Front. Chem. China.*, **3**, 345-349, 2006.
4. Lu W., Andrei G.F., Qi B.H., Elisabeth S., Benjamin R.M., Ding J., Geoffrey M.S., Jakub M., Zhou D.Z., Gordon G.W., Douglas R.M., Stewart A.F., Maria F., Use of ionic liquids for π -conjugated polymer electrochemical devices, *Science*, **297**, 983-987, 2002.
5. Sansinena J.M., Gao J., Wang H.L., High-performance, monolithic polyaniline electrochemical actuators, *Adv. Funct. Mater.*, **13**, 703-709, 2003.
6. Dong Y.H., Mu S.L., Photoelectrochemical behaviour of polyaniline affected by potentials and pH of solutions, *Electrochim. Acta.*, **36**, 2015-2018, 1991.
7. Dia A.F.Z., Logan J.A., Electroactive polyaniline films, *J. Electroanal. Chem.*, **111**, 111-114, 1980.
8. Miao Z., Wang Y., Liu Z., Huang J., Han B., Sun Z., Du J., Synthesis of polyaniline nanofibrous networks with the aid of an amphiphilic ionic liquid, *J. Nanosci. Nanotechnol.*, **6**, 227-230, 2006.
9. Gao H., Jiang T., Han B., Wang Y., Du J., Liu Z., Zhang J., Aqueous/ionic liquid interfacial polymerization for preparing polyaniline nanoparticles, *Polymer*, **45**, 3017-3019, 2004.
10. Innis P.C., Mazurkiewicz J., Nguyen T., Wallace G.G., Macfarlane D., Enhanced electrochemical stability of polyaniline in ionic liquids, *Cur. Appl. Phys.*, **4**, 389-393, 2004.
11. Zhang J., Zhang X., Fang X., Hu F., Effect of polar solvent acetonitrile on the electrochemical behavior of polyaniline in ionic liquid electrolytes, *J. Colloid Interface Sci.*, **287**, 67-71, 2005.
12. Holbrey J.D., Reichert W.M., Swatloski R.P., Broker G.A., Pitner W.R., Seddon K.R., Rogers R.D., Efficient, halide free synthesis of new, low cost ionic liquids: 1,3-Dialkylimidazolium salts containing methyl- and ethyl-sulfate anions, *Green Chem.*, **4**, 407-413, 2002.
13. Shi J.H., Yang C.H., Gao Q.Y., Li Y.F., Studies on electrochemical synthesis of polythiophene in an ionic liquid, *Chin. J. Chem. Phys.*, **17**, 503-507, 2004.
14. Hand R.L., Nelson R.F., Anodic oxidation pathways of *N*-alkylanilines, *J. Am. Chem. Soc.*, **96**, 850-860, 1974.
15. Shim V.B., Won M.S., Park S.M., Electrochemistry of conductive polymers-VIII. In situ spectroelectrochemical studies of polyaniline growth mechanisms, *J. Electrochem. Soc.*, **137**, 538-544, 1990.
16. Motheo A.J., Santos Jr.J.R., Venancio E.C., Mattoso L.H.C., Influence of different types of acidic dopant on the electrodeposition and properties of polyaniline films, *Polymer*, **39**, 6977-6982, 1998.
17. Trivedi D.C., Dhawan S.K., Investigations on the effect of 5-sulfosalicylic acid on the properties of polyaniline, *Synth. Met.*, **58**, 309-324, 1993.
18. Wang B.C., Tang J.S., Wang F.S., Electrochemical polymerization of aniline, *Synth. Met.*, **18**, 323-328, 1987.
19. Huang W.S., Humphrey B.D., MacDiarmid A.G., Polyaniline, a novel conducting polymer-morphology and chemistry of its oxidation and reduction in aqueous-electrolytes, *J. Chem. Soc. Farad. Trans. I.*, **182**, 2385-2400, 1986.
20. Pruneanu S., Veress E., Marian I., Oniciu L., Characterization of polyaniline by cyclic voltammetry and UV-vis absorption spectroscopy, *J. Mater. Sci.*, **34**, 2733-2739, 1999.
21. Shim Y.B., Won M.S., Park S.M., Electrochemistry of conductive polymers.VIII. In situ spectroelectrochemical studies of polyaniline growth mechanisms, *J. Electrochem. Soc.*, **137**, 538-544, 1990.
22. Mu S., Electrochemical copolymerization of aniline and *o*-aminophenol, *Synth. Met.*, **143**, 259-268, 2004.
23. Greef R., Peat R., Peter L.M., Pletcher D., Robimnsn J., *Instrumental Methods in*

- Electrochemistry*, Ellis Harwood, Chichester, *Ch.* **6**, 178-210, 1985.
24. Beadle P.M., Nicolau Y.F., Banka E., Rannou P., Djurado D., Controlled polymerization of aniline at sub-zero temperatures, *Synth. Met.*, **95**, 29-45, 1998.
 25. Epstein A.J., Ginder J.M., Zuo F., Bigelow R.W., Woo H.S., Tanner D.B., Richter A.F., Huang W.S., MacDiarmid A.G., Insulator-to-metal transition in polyaniline, *Synth. Met.*, **18**, 303-309, 1987.
 26. McManus P.M., Yang S.C., Cushman R.J., Electrochemical doping of polyaniline: Effects on conductivity and optical spectra, *J. Chem. Soc. Chem. Commun.*, 1556-1557, 1985.
 27. Li D., Jiang Y.D., Wu Z.M., Chen X.D., Li Y.R., Fabrication of self-assembled polyaniline films by doping-induced deposition, *Thin Solid Films.*, **360**, 24-27, 2000.
 28. Stafström S., Brédas J.L., Epstein A.J., Woo H.S., Tanner D.B., Huang W.S., MacDiarmid A.G., Polaron lattice in highly conducting polyaniline: theoretical and optical studies, *Phys. Rev. Lett.*, **59**, 1464-1467, 1987.
 29. Li Q., Cruz L., Phillips P., Granular-rod model for electronic conduction in polyaniline, *Phys. Rev. B.*, **47**, 1840-1845, 1993.
 30. Pouget J.P., Jozefowicz M.E., Epstein A.J., Tang X., MacDiarmid A.G., X-Ray structure of polyaniline, *Macromolecules*, **24**, 779-789, 1991.
 31. Pielichowski K., Kinetic analysis of the thermal decomposition of polyaniline, *Solid State Ion.*, **104**, 123-132, 1997.