



Preparation and performance of different acid-doped polyaniline

Xiao Hua Wang*, Chuan Qiang Li, Qi Tang and Yuan Hua Mu

Department of Applied Chemistry, School of Science, Chongqing Jiaotong University, Chongqing, China

ABSTRACT

Polyaniline(PANI) doped with hydrochloride (HCl), dodecylbenzene sulfonic acid (DBSA) or amino sulfonic acid ($\text{NH}_2\text{SO}_3\text{H}$) were prepared by in-situ polymerization. Effects of acid content, reaction time, oxidant ammonium persulfate(APS) dosage and reaction temperature on conductivity of PANI were studied. The presser resistance and thermal stability of them were compared. Results show that the conductivity of HCl-PANI was the largest 198 s.m^{-1} under the $C(\text{HCl}) 0.5 \text{ mol.L}^{-1}$, reaction time 6.0 h, $n(\text{APS}):n(\text{aniline})=1.0$ among them; The conductivity of $\text{NH}_2\text{SO}_3\text{H}$ -PANI was 26 s.m^{-1} under the $C(\text{NH}_2\text{SO}_3\text{H}) 1.0 \text{ mol.L}^{-1}$, reaction time 6.0 h, $n(\text{APS}):n(\text{aniline})=2.0$; The conductivity of DBSA-PANI was 98 s.m^{-1} under the $C(\text{DBSA}) 1.0 \text{ mol.L}^{-1}$, reaction time 8.0 h, $n(\text{APS}):n(\text{aniline})=2.0$. The presser resistance of HCl-PANI was the least 10Ω , and that of $\text{NH}_2\text{SO}_3\text{H}$ -PANI was the largest 120Ω . The order of their thermal stability is DBSA-PANI > $\text{NH}_2\text{SO}_3\text{H}$ -PANI > HCl-PANI before 350°C , and the order is HCl-PANI > $\text{NH}_2\text{SO}_3\text{H}$ -PANI > DBSA -PANI after 350°C .

Key words: Polyaniline, Acid doping, Conductivity, Resistance, Thermal stability

INTRODUCTION

Polyaniline(PANI) is a conductive polymer with good properties such as electric properties, excellent environmental stability, easy preparation and low monomer price, which is considered as one of the most promising conducting polymer in practical applications [1-5]. However, the conductivity of eigenstate polyaniline is very low because of the strong interaction among its rigid chains. H^+ can be easy to inject polyaniline molecular chain, which makes delocalization degree and conductance of molecules increase [6]. Moreover, the conductivity of polyaniline can be improved 12 orders of magnitude through the proton acid doping reported in the literature [7]. Therefore, polyaniline(PANI) doped with HCl or $\text{NH}_2\text{SO}_3\text{H}$ or dodecyl- benzenesulfonic acid(DBSA) were prepared by in-situ polymerization. Effects of acid content, reaction time, oxidant ammonium persulfate (APS)dosage and reaction temperature on conductivity of PANI were studied. The presser resistance and thermal stability of them were compared.

EXPERIMENTAL SECTION

Materials and instruments: Aniline(An, analytically pure) was purchased from Guangzhou Chemical Reagent Factory. Ammonium persulfate [$(\text{NH}_4)_2\text{S}_2\text{O}_8$, APS], hydrochloride (HCl), amino sulfonic acid ($\text{NH}_2\text{SO}_3\text{H}$) and dodecylbenzene sulfonic acid (DBSA) were obtained from Chongqing Chuandong Chemical Reagent Factory.

Four-point probe digital resistance instrument(SX-1934, Shanghai precision instruments Co., LTD), multimeter, thermal analyzer(WCT-2C)

Preparation of acid-doped polyaniline: The proton acid-doped PANI was prepared by adding 100 mL acid solution and 1 mL aniline into a three mouth flask, stirring in the conditions of ice-water bath under the reaction temperature of $0\sim 5^\circ\text{C}$, dropping 50 mL 1 mol.L^{-1} ammonium persulfate (APS)solution(color from transparent to

blue black), stopping stirring after 4 hours, laying it all the night, filtrating, washing with acetone and drying it under 45°C.

Performance testing:

Conductivity: Conductivities of samples were tested in four-point probe after milled powder with mortar and pressed into pieces [8-9].

Presser resistance: Resistances of samples were tested in multimeter after pressing solid product to diameter 10.0 mm, thickness 2.0 mm discs.

Thermal stability: Thermogravimetric analysis(short for TG) were carried out on WCT-2C thermal analyzer with 10°C/min speed, TG range 10mg, DTA range 2mg/min and N₂ atmosphere [2].

RESULTS AND DISCUSSION

Effect of acid content: Effect of acid content on conductivity of PANI is shown in figure 1.

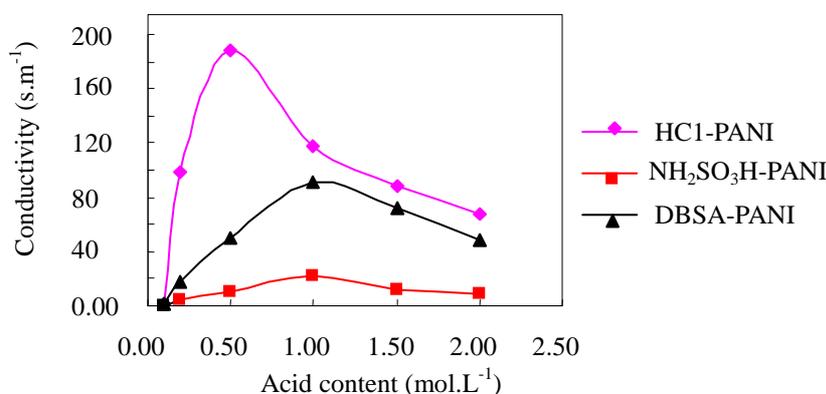


Fig. 1 Effect of acid content on conductivity of PANI

Preparation conditions: reaction time 4.0 h, n(APS)/n(aniline)=1.0, reaction temperature 2 °C

The conductivity of PANI increases with the increasing of acid content firstly. This is the reason that the ionized H⁺ content will be increased with the increasing of acid content, which makes the doped H⁺ content on nitrogen atom of PANI be increased correspondingly. In order to remain electric neutrality of composite film, the anionic quantity getting into PANI molecular chain will be increased correspondingly, which makes the conductivity of PANI be increased. The conductivity of HCl-PANI reaches the maximum of 188 s.m⁻¹ under the condition of C(HCl) 0.5 mol.L⁻¹, and the conductivity of NH₂SO₃H-PANI or DBSA-PANI reaches the maximum of 22 or 91 s.m⁻¹ under the condition of C(NH₂SO₃H) 1.0 mol.L⁻¹ or C(DBSA)1.0 mol.L⁻¹ respectively. However, the aniline monomer will be excessive oxidized when acid content is too high, which will make its big conjugate structure be damaged and its conductive ability will be reduced [10].

Effect of reaction time: Effect of reaction time on conductivity of PANI is shown in figure 2.

The conductivity of PANI increases with the increasing of reaction time at first. The conductivity of HCl-PANI or NH₂SO₃H-PANI reaches the maximum of 188 or 22 s.m⁻¹ under the condition of reaction time 6h respectively, and the conductivity of DBSA-PANI reaches the maximum of 98 s.m⁻¹ under reaction time 8h. However, the aniline monomer will be excessive oxidized when reaction time is too much, which makes the PANI conjugate chain be fractured and the relatively perfect doping system be destroyed, then its conductivity will be decreased correspondingly.

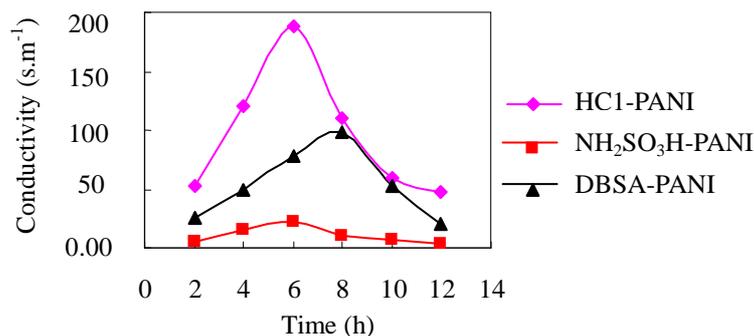


Fig. 2 Effect of reaction time on conductivity of PANI

Preparation conditions: acid content 1 mol.L⁻¹, $n(\text{APS})/n(\text{aniline})=1.0$, reaction temperature 2 °C

Effect of $n(\text{APS})/n(\text{aniline})$: Effect of APS content on conductivity of PANI is shown in figure 3.

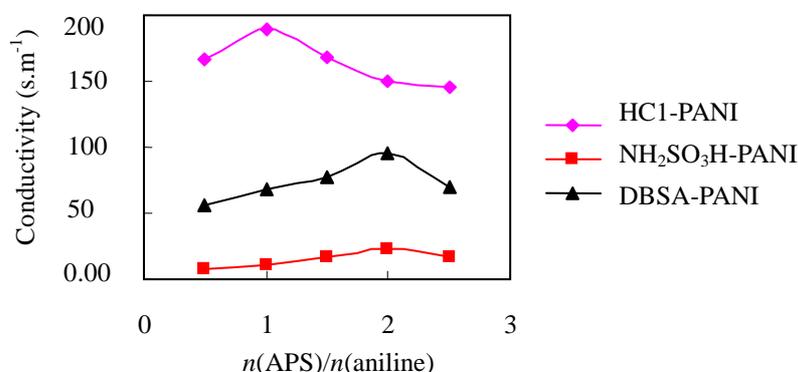


Fig. 3 Effect of APS content on conductivity of PANI

Preparation conditions: acid content 1 mol.L⁻¹, reaction time 6.0 h, reaction temperature 2 °C

The conductivity of PANI increases with the increasing of initiator(APS) content firstly. The conductivity of HCl-PANI reaches the maximum of 190 s.m⁻¹ under the condition of $n(\text{APS})/n(\text{aniline})$ 1.0, and the conductivity of NH₂SO₃H-PANI or DBSA-PANI reaches the maximum of 22 or 96 s.m⁻¹ under the condition of $n(\text{APS})/n(\text{aniline})$ 2.0 respectively. However, the activity center of the system will be relatively more when initiator APS content is too much, which be unfavorable to generate polyaniline with high molecular weight. Moreover, the aniline monomer will be excessive oxidized when initiator(APS) content is too much, which will make its big conjugate structure of π electronic system be destroyed and its carries of displacing charge be reduced, then its conductive ability will be reduced [11-12].

Effect of reaction temperature: Effect of reaction temperature on conductivity of PANI is shown in figure 4.

The reaction can be performed in a wider temperature, and the conductivity of polyaniline reach a maximum under the temperature 1~2 °C. The conductivity of HCl-PANI reaches the maximum of 198 s.m⁻¹ under the optimal temperature 1 °C, and the conductivity of NH₂SO₃H-PANI or DBSA-PANI reaches the maximum of 26 or 96 s.m⁻¹ under the optimal temperature 2 °C respectively. However, the aniline monomer will be excessive oxidized partly, by-products will be increased, the reaction induced period will be shorten, which make the polyaniline molecular weight be dropped and the conjugate degree be reduced when reaction temperature is too high, then its conductivity will be decreased [13].

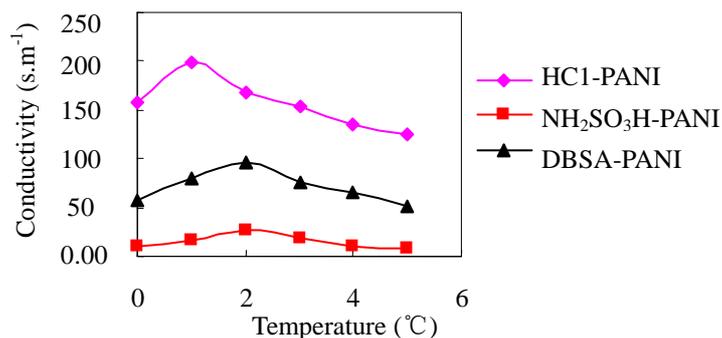


Fig. 4 Effect of reaction temperature on conductivity of PANI
Preparation conditions: acid content 1 mol.L⁻¹, reaction time 6.0 h, $n(\text{APS})/n(\text{aniline})=1.0$

Presser resistance of different acid-doped PANI: Presser resistances of HCl- PANI, NH₂SO₃H-PANI and DBSA-PANI were tested and compared. The result is shown in table 1.

Table 1 Presser resistance of different acid-doped PANI

	HCl-PANI	NH ₂ SO ₃ H-PANI	DBSA-PANI
Presser resistance, R (Ω)	10	120	30

The presser resistance of NH₂SO₃H-PANI is the largest among them, the presser resistance of HCl- PANI and that of DBSA-PANI are in the same magnitude. The relationship of their resistance is contrary to that of their conductivity because the relationship between resistance and conductivity is inverse from the formula $G = 1/R = k A/l$ (G : conductance, k : conductivity).

TG analysis of different acid-doped PANI: Heat resistance is an important mark of polymer stability. The using temperature range of polymer can be determined through the thermogravimetric(TG) analysis. The TG curves of HCl- PANI, NH₂SO₃H-PANI and DBSA-PANI are shown in figure 5. The decomposition of HCl- PANI, NH₂SO₃H-PANI or DBSA-PANI starts in 121°C, 182°C and 218°C respectively. Moreover, the decomposing speed of HCl- PANI is very quick and the decomposing speed of NH₂SO₃H-PANI or DBSA-PANI is relatively slow before 350°C. That is to say that the thermal stability of NH₂SO₃H-PANI or DBSA-PANI is better than that of HCl- PANI, and the order of their thermal stability is DBSA-PANI > NH₂SO₃H-PANI > HCl-PANI before 350°C. After 350°C, the thermal stability of HCl- PANI, NH₂SO₃H-PANI and DBSA-PANI is changed, and the order of their thermal stability is HCl-PANI > NH₂SO₃H-PANI > DBSA -PANI.

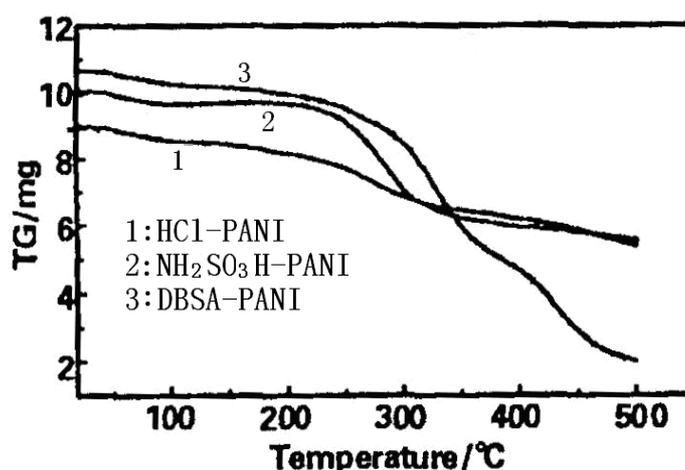


Fig. 5 The TG curves of different acid-doped polyaniline

CONCLUSION

Polyaniline(PANI) doped with HCl or NH₂SO₃H or DBSA were prepared by in-situ polymerization. The conductivity, presser resistance and thermal stability of them were compared. The conductivity of HCl- PANI is the

highest, and that of $\text{NH}_2\text{SO}_3\text{H-PANI}$ is the lowest. On the contrary, the presser resistance of HCl-PANI is 10Ω and the least, and that of $\text{NH}_2\text{SO}_3\text{H-PANI}$ is 120Ω and the largest. The order of their thermal stability is $\text{DBSA-PANI} > \text{NH}_2\text{SO}_3\text{H-PANI} > \text{HCl-PANI}$ before 350°C , the order of their thermal stability is $\text{HCl-PANI} > \text{NH}_2\text{SO}_3\text{H-PANI} > \text{DBSA-PANI}$ after 350°C .

Effects of acid content, reaction time, oxidant ammonium persulfate(APS)dosage and reaction temperature on conductivity of PANI were studied. The conductivity of HCl-PANI was 198 s.m^{-1} under optimal conditions of $\text{C(HCl)} 0.5 \text{ mol.L}^{-1}$, reaction time 6.0 h, $n(\text{APS}):n(\text{aniline})=1.0$; The conductivity of $\text{NH}_2\text{SO}_3\text{H-PANI}$ was 26 s.m^{-1} under optimal conditions of $\text{C(NH}_2\text{SO}_3\text{H)} 1.0 \text{ mol.L}^{-1}$, reaction time 6.0 h, $n(\text{APS}):n(\text{aniline})=2.0$; The conductivity of DBSA-PANI was 98 s.m^{-1} under optimal conditions of $\text{C(DBSA)} 1.0 \text{ mol.L}^{-1}$, reaction time 8.0 h, $n(\text{APS}):n(\text{aniline})=2.0$.

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