# Journal of Chemical and Pharmaceutical Research, 2014, 6(9):313-321



**Research Article** 

ISSN : 0975-7384 CODEN(USA) : JCPRC5

# Thermal stability and electrical properties of self-doped N-substituted carboxyl polyaniline

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# ABSTRACT

*N*-substituted carboxyl polyaniline (NPAN) is readily prepared through chemical oxidative polymerization of *N*-phenylglycine in hydrochloric acid solution. Techniques such as Fourier transform infrared spectroscopy, <sup>1</sup>H-NMR spectrometry, UV-vis spectrophotometry, and X-ray diffraction are employed to characterize the structure of the prepared NPAN. The <sup>1</sup>H-NMR spectra indicate that the ratio of the aromatic protons to methylene protons in pristine NPAN chains is 4:1, which suggests that only a  $-CH_2COONH_4$  group remains after both monomers react. Elemental analysis experiments demonstrate that the benzene rings in the polymer backbone transfer into the quinone units through a process of decarboxylation during the polymerization. The solubility of NPAN in most polar solvents is outstanding in comparison with that of polyaniline, and NPAN exhibits solvatochromic properties in different solvents. Moreover, the conductivity of NPAN changes in the range of  $4.7 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$  to  $1.49 \times 10^{-1} \text{ S} \cdot \text{cm}^{-1}$  as the acidic medium in the reaction system is changed. The minimal temperature of the derivative thermogravimetry curve is shifted to a substantially higher temperature by approximately 186 °C in the case of pure NPAN. The thermogravimetric analyses reveal that pure NPAN exhibits better thermal stability than polyaniline.

Key words: N-substituted carboxyl polyaniline, solubility, thermal stability, conductivity

# INTRODUCTION

Polyaniline (PANI) is unique among the family of conjugated polymers because of its good environmental stability, unique electrical and optical properties, and facile synthesis<sup>1-3</sup>. It has been extensively studied for potential use in numerous applications, including electrochromic devices<sup>4-5</sup>, electrocatalysis<sup>6</sup>, light-emitting devices<sup>7</sup>, battery electrodes<sup>8</sup>, biosensors<sup>9-10</sup> and corrosion inhibitors<sup>11-12</sup>. These applications involve reversible modulation through redox or protonation procedures due to the presence of alternating single and double bonds in the  $\pi$ -orbital system of aromatic amine conducting polymers<sup>13-14</sup>. However, the practical use of PANI is inhibited by two major drawbacks: it has low solubility in most organic solvents and it degrades before melting, which results in poor processability<sup>4</sup> due to the stiffness of its highly conjugated backbone and the strong hydrogen-bonding interactions between adjacent chains<sup>15</sup>. Therefore, various procedures have been adapted to improve its processability, especially its solubility. For example, one approach has been to introduce a macromolecular organic acid, such as dodecyl benzene sulfonic acid, camphor sulfonic acid, or p-toluene sulfonic acid, to weaken the hydrogen-bonding interactions between polymer chains<sup>16</sup>. Consequently, such modified polymers exhibit better solubility in cresol or toluene and almost the same conductivity as non-modified PANI. In addition, chemical modification is also an effective method for improving the solubility of PANI. On the basis of its molecular structure, three active sites can be substituted in the structure of PANI chains: the ortho- and para-positions of the phenyl ring and the nitrogen of the secondary aromatic amine. Notably, these sites are capable of incorporating certain groups, such as sulfonic acid, alkyl, alkoxy, or halogen groups, at the ortho- and para-positions of the benzene ring<sup>17-23</sup> as well as at the nitrogen of the secondary aromatic amine<sup>24-26</sup>. The modified PANI with a large and/or better group attached to the benzene ring exhibits remarkably improved solubility in conventional organic solvents and even in aqueous solution.

However, the conductivity of the modified PANI decreases, presumably due to damage of the  $\pi$ -conjugated backbone structure.

An important route to improving the solubility and processability of PANI is the grafting of PANI with other polymers<sup>27,28</sup>. However, this processing method is still a challenge in commercial applications because of the difficulty in controlling the obtained structure and because of the very low conductivity and purity of the resulting copolymers.

Here we demonstrate a facile, effective procedure for the chemical synthesis of N-substituted carboxyl polyaniline (NPAN) through studying the molar ratio between the oxidant and monomer. The obtained polymer was characterized by infrared spectroscopy (IR), UV–vis spectrophotometry, <sup>1</sup>H-NMR spectrometry, and X-ray diffraction (XRD). The thermal stability and degradation behaviors of NPAN were studied by thermogravimetric analysis (TGA).

#### EXPERIMENTAL SECTION

#### 2.1 Materials

*N*-Phenylglycine (NAN; 97%) was purchased from Sigma–Aldrich. All other reagents were analytical reagent grade and were used as received.

#### 2.2 Chemical synthesis of NPAN

The doped NPAN was prepared by chemical oxidative polymerization using  $(NH_4)_2S_2O_8$  as an oxidant in an acidic medium. A typical preparation procedure is as follows: 4.535 g (0.03 mol) of NAN was dissolved in 100 mL of a mixed solution of acetonitrile and deionized water (v/v 1:1). Ammonium persulfate (6.84 g, 0.03 mol) was dissolved in 30 mL of 6 M dopant acid solution. Afterwards, the oxidant solution was slowly dripped into the monomer solution with gentle magnetic stirring. The resulting product (ES) was a dark-green powder that was obtained after 24 h of reaction; the precipitate was subsequently filtered and washed with 95% ethanol several times until the filtrate became colorless. The obtained product was dried at 60°C for 24 h. The emeraldine base (EB), i.e., the pristine NPAN, was prepared via a conventional method of deprotonation with excess 0.1 M NH<sub>4</sub>OH solution.

#### 2.3 Electrochemical synthesis of NPAN

Glassy carbon electrodes (GCEs; diameter = 3 mm) were carefully polished with a 0.05  $\mu$ m alumina slurry on a polishing cloth and were ultrasonically washed in ethanol as well as water for approximately 5 min each. The GCE was activated in 0.1 M H<sub>2</sub>SO<sub>4</sub> using cyclic voltammetry in the potential range of -0.3 V to +1.5 V. We prepared the NPAN film in 0.2 M HClO<sub>4</sub> solution that contained 20 mM NAN by sweeping the potential between -0.5 V and 1.2 V vs. Ag/AgCl for 15 cycles at a scan rate of 50 mV·s<sup>-1</sup>. The NPAN-modified electrode was washed with deionized water to remove physically adsorbed monomer.

#### 2.4 Characterization

The IR spectra were recorded with a PerkinElmer FT-IR spectrometer from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> using KBr pellets. UV–vis spectra of the polymers in *N*-methyl-2-pyrrolidone (NMP) were obtained on a Perkin Elmer Lambda 35 UV–visible spectrometer in the range from 200 nm to 800 nm at a scanning rate of 480 nm·min<sup>-1</sup>. Wide-angle X-ray diffraction of the microparticles was performed with a Bruker Axs D8 Advance X-ray diffractometer (Germany) equipped with a Cu K $\alpha$  radiation source operated at 40 kV and 40 mA; the step width was  $0.02^{\circ}$ . <sup>1</sup>H-NMR spectra were obtained on a Bruker-400 (Germany). The conductivity measurements of NPAN were performed on pressed pellets (10 mm diameter and approximately 2 mm thickness) with an RTS-8 four-probe conductivity setup at room temperature. Electrochemical impedance studies were conducted on a model CHI660C electrochemical station (Chenhua, Shanghai). A conventional three-electrode system was used, with a GCE (diameter = 3 mm) as the working electrode, a length of platinum wire as the auxiliary electrode, and a Ag/AgCl (3 M KCl) electrode as the reference electrode. For the evaluation of polymer solubility, polymer powder (2 mg) was added to 1 mL of solvent and was thoroughly dispersed after being shaken intermittently for 2 h at ambient temperature.

# **RESULTS AND DISCUSSION**

#### 3.1 Structure characterization of NPAN

The different IR vibration spectra of HCl–NPAN (a), EB–NPAN (b), and HCl–PANI (c) are shown in Fig. 1, and the different absorption bands and their corresponding structure are listed in Table  $1^{29}$ . As shown in Fig. 1(a), in the spectrum of the HCl-doped NPAN powder sample, the broad peaks at approximately 3400 cm<sup>-1</sup> are the stretching vibrations of N–H. The small absorption peak at 3228 cm<sup>-1</sup> in the spectrum of HCl–NPAN (Fig. 1a) is assigned to a stretching vibration of a carboxyl group O–H, whereas this absorption peak disappears in the spectrum of

EB–NPAN (Fig. 1b), which may be due to the reaction of –COOH with the ammonia water to form a carboxylic acid ammonium salt. The typical absorption bands in HCl–PANI (Fig. 1c) assigned to N=Q=N stretching vibrations at 1589 cm<sup>-1</sup> and to N–B–N stretching vibrations at 1498 cm<sup>-1</sup> shifted to higher frequencies after the PANI was modified with N-substituted –CH<sub>2</sub>COOH. This result is attributed to the electron-withdrawing effect of the carboxylic group, and it shows that the introduction of the carboxyl group on the polymer molecular chain directly affects the structure of the conjugated polymer. The absorption peaks at approximately 1300 and 1240 cm<sup>-1</sup> are assigned to N–H bending and C–N stretching vibrations, respectively. The absorption peak from 700 cm<sup>-1</sup> to 900 cm<sup>-1</sup> is assigned to a  $\gamma$ (C–H) absorption peak, and it is very useful for discerning the substituted structure of the aromatic ring.

#### Table 1 Main IR vibrational frequencies (cm<sup>-1</sup>) and the corresponding assigned modes of samples EB–NPAN, HCl–NPAN, and HCl–PANI

EB-NPAN	HCl-NPAN	HC1-PANI	Stretching mode
3396	3444	3449	N-H stretching
1650	1659		C=O stretching
1595	1589	1568	N=Q=N stretching
1487	1498	1487	N-B-N stretching
1302	1304	1299	N–H bending
1240	1241	1242	C-N stretching
1166	1154	1111	<b>D</b> $\mathbf{M}\mathbf{H}^+$ <b>D</b> or $^{a}\mathbf{O}-\mathbf{M}\mathbf{H}^+$ <b>D</b>
1107	1110	1111	B-NH-BOI Q-NH-B
824	818	798	Out-of-plane C-H bending

(<sup>a</sup>Q denotes quinoid units of PANI; B denotes benzenoid units of PANI)

Table 2 Elemental content of different monomers and EB-polymers oxidized by different molar ratios of oxidant

Samula	Elemental content (%)			
Sample	С	Н	Ν	
Aniline	77.38	7.57	15.04	
NAN	63.56	9.26	6.00	
NPAN-1	68.62	13.15	11.59	
NPAN-2	71.32	8.77	13.22	
NPAN-3	71.22	7.68	12.53	

(NAN denotes N-phenylglycine; NPAN-1, NPAN-2, and NPAN-3 denote oxidant/monomer molar ratios of 0.85, 1, and 1.25, respectively, during the polymerization reaction.)

Sample	HCl-doped		HNO <sub>3</sub> -doped		HClO <sub>4</sub>	HClO <sub>4</sub> -doped	
	PANI	NPAN	PANI	NPAN	PANI	NPAN	
Conductivity (S·cm <sup>-1</sup> )	1.35	$4.7  imes 10^{-3}$	$3.5  imes 10^{-1}$	$1.49  imes 10^{-1}$	$4.57  imes 10^{-2}$	$1.93 \times 10^{-2}$	

Table 4 Solubility of different polymers in common solvents

	Solubility <sup>[a]</sup> and solution color <sup>[b]</sup>					
Sample	NMP	DMSO	CH <sub>3</sub> CN	THF	CHCl <sub>3</sub>	$H_2O$
	$(6.7)^{[c]}$	$(6.5)^{[c]}$	$(5.8)^{[c]}$	$(4.2)^{[c]}$	$(4.1)^{[c]}$	$(10)^{[c]}$
HC1-PANI	MS, db	MS, dg	IS,	SS, lg	SS, lg	IS
HCl-NPAN	S, db	S, dg	PS, lg	MS, g	SS, dg	PS, dg
EB-NPAN	S, db	S, db	MS, b	S, db	SS, p	MS, b

[a] IS: insoluble; MS: mainly soluble; PS: partially soluble; S: soluble; SS: slightly soluble. [b] db: dark blue; b: blue; dg: dark green; lg: light green. [c] Polarity index of the solvents.

In addition, the spectrum of the HCl–NPAN sample shows an absorption peak attributed to the stretching vibration absorption of a carboxylic C=O at 1659 cm<sup>-1</sup>, which indicates that a carboxyl group has been inserted into the modified PANI molecular chains. By comparison, only a weak shoulder peak is observed at the same location in the spectrum of the EB–NPAN (i.e., the neat NPAN), which demonstrates the possibility of a reaction of the carboxyl group with ammonia to form a carboxylate, consistent with the results of the previous analysis. The absorption peak at 1111 cm<sup>-1</sup> for HCl–PANI is consistent with the vibration absorption of B–NH<sup>+</sup>–B and Q=NH<sup>+</sup>–B, whereas a new peak at 1154 cm<sup>-1</sup>, which is attributed to the vibration absorption of B–NH<sup>+</sup>(CH<sub>2</sub>COOH)–B, can be observed after a –CH<sub>2</sub>COOH group was introduced onto the imine nitrogen, probably due to the induction effect of the carboxyl group. However, the band at 1110 cm<sup>-1</sup> for Q=NH<sup>+</sup>–B remains unchanged, indicating that the quinoid structure can be formed during the polymerization process.

The different polymers were dissolved in N-methyl pyrrolidone, and their UV-vis spectra are shown in Fig. 2. The absorption spectrum of HCl-PANI shows two distinct absorption bands located at 328 and 630 nm. The former band

corresponds to the  $\pi$ - $\pi$ \* transition of the aromatic structure, whereas the absorption at 630 nm is assigned as an  $n-\pi$ \* characteristic transition absorption of the C=N bond in the quinone segment<sup>30,31</sup>. Different absorption peaks of band gaps can reflect the degree of electron delocalization between adjacent benzene rings<sup>24</sup>. Compared with the absorption peak corresponding to the  $n-\pi$ \* characteristic transition absorption of C=N, the absorption peaks of HCl-NPAN and EB-NPAN were blue shifted by 11 and 22 nm, respectively. These blue shifts indicate that the degree of charge delocalization of polymerization decreases with the introduction of the carboxyl group due to the decrease in the amount of quinoid units in the polymer chains with the introduction of the carboxyl group onto the PANI backbone<sup>15,32</sup>. In fact, the formation of the quinoid structure is caused by the elimination of the hydrogen ion at the imine nitrogen during the polymerization process of the acidic-doped polyaniline. In contrast, the quinoid unit structure can be formed by the deviation of the carboxyl group in the N-substituted carboxyl polymerization process, and elimination of the carboxyl group is more difficult than elimination of a hydrogen cation in polymer backbone chains.



Fig. 1 FTIR spectra of HCl doped NPAN (a), EB-NPAN (b), and HCl-doped PANI (c)



Fig. 2 UV-vis spectra of HCl-NPAN (a), EB-NPAN (b), and HCl-PANI (c) dissolved in NMP



Fig. 4 Polymerization mechanism of N-substituted carboxyl polyaniline during chemical oxidative polymerization



Fig. 5 Wide-angle X-ray diffraction patterns of different polymers



Fig. 6 Electrochemical impedance spectra of H<sup>+</sup>−PANI (a), EB−PANI (b), H<sup>+</sup>−NPAN (c), and EB−NPAN (d) in an aqueous solution containing 0.5 M KCl and 2.0 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>]



Fig.7. TGA curves and DTG curves (inset) of PANI and NPAN as a function of temperature

To further investigate the structure of pristine NPAN (EB–NPAN), we employed <sup>1</sup>H-NMR to analyze the protons of the phenyl ring and the methylene of the polymer. As shown in Fig. 3, the <sup>1</sup>H-NMR spectrum of EB–NPAN exhibits a broad absorption peak from 6.3 ppm to 7.7 ppm range, which is associated with the aromatic protons. The band in the region from 2.8 ppm to 3.2 ppm is assigned to the protons of methylene and is split into two peaks, possibly because of the electrophilic carboxyl group on the polymer molecular chains. However, the absorption peak, which is attributed to the carboxyl proton, is not observed due to the formation of an ammonium salt by the reaction between NH<sub>4</sub>OH and –COOH during the de-doping process. The ratio of the aromatic protons to the methylene proton is 4:1 based on the peak area in <sup>1</sup>H-NMR spectra, which indicates that only a –CH<sub>2</sub>COO<sup>-</sup> group remains after the reaction of both monomers. The <sup>1</sup>H NMR result is consistent with the IR and UV–vis spectra.

To further confirm the case of decarboxylation during the polymerization process, elemental analyses of the monomer and the polymers were performed. As shown in Table 2, a significant decrease in the C and N contents was found in the EB–NPAN polymers compared to those in aniline; however, they were greater than those in NAN. This result implies that the benzene rings on the polymer backbone will transfer to the quinone units via decarboxylation during polymerization, which is similar to a dehydrogenation process in the classical PANI reaction. Simultaneously,

the decarboxylation reaction is affected by the molar ratio between the monomer and oxidant. An increase in the oxidant-to-monomer molar ratio from 0.85 to 1 tends to result in an increase in the carbon content. Subsequently, the carbon content remains unchanged as oxidant-to-monomer molar ratio is increased further. This result suggests that the chain growth is accompanied by the decarboxylation reaction, which might be due to the partial conversion of the B-N-B structure into the Q=N-B structure via the decarboxylation reaction. The IR spectra, UV–vis, and conductivity measurements for the polymer confirm the formation of the quinoid structure. On the basis of the change in carbon content during the polymerization process, a possible polymerization mechanism is presented in Fig. 4.

The crystal structure and composition of EB-PANI, HCI-PANI, EB-NPAN, and HCI-NPAN powder samples were also investigated by powder XRD measurements. To the best of our knowledge, a matrix of polymer chains generally includes both amorphous and crystalline domains; more highly ordered systems can exhibit a metallic-like conductivity state. As shown in Fig. 5, a broad reflection peak centered at  $2\theta = 19.2^{\circ}$  is observed in the XRD pattern of the pure PANI, whereas three additional sharp diffraction peaks are observed at  $2\theta = 14.4^{\circ}$ , 20.7°, and 25.3° in the case of HCl-PANI. These results reveal that the ordering is greater in HCl-PANI powders than in pure PANI powders. This fact indicates that the structure of the PANI chains will tend to organize the polymer chains in highly ordered arrays when the PANI is doped with HCl. In the case of NPAN, the XRD pattern of the N-substituted EB-NPAN shows a diffraction peak centered at  $2\theta = 18.2^{\circ}$ , which is a somewhat smaller angle than that of the corresponding peak in the XRD pattern of EB-PANI. The smaller angle of this peak indicates that the N-substituted EB-NPAN has greater interplanar crystal spacing according to the Bragg equation:  $2d\sin\theta = n\lambda$ . Where d is the interplanar spacing,  $\theta$  is the Bragg angle,  $\lambda$  is the wave of incident light. This crystal surface structure favors the diffusion of solvent molecules into the polymer molecular chains, which results in improved solubility. However, one broad and three sharp diffractive peaks at  $2\theta = 20.5^{\circ}$ ,  $17.8^{\circ}$ ,  $23.5^{\circ}$ , and  $26^{\circ}$ , respectively, are observed in the XRD pattern of NPAN doped with HCl. The three sharp diffraction peaks imply that the doped NPAN exhibits local crystallization and that the ordered arrays among the polymer molecular chains exhibit short-range order<sup>33</sup>.

# **3.2 Electrical properties of NPAN**

The electrical conductivities ( $\sigma$ ) of the PANI and NPAN doped with HCl, HNO<sub>3</sub>, and HClO<sub>4</sub> were measured using an RTS-8 four-probe conductivity measurement system on pellets pressed from powder; the average conductivities are presented in Table 3. The conductivities of PANI doped with HCl, HNO<sub>3</sub>, and HClO<sub>4</sub> are 1.35,  $3.5 \times 10^{-1}$ , and  $4.57 \times 10^{-2}$  S·cm<sup>-1</sup>, respectively. The electrical conductivities tend to decrease with increasing size of the anion of the acid dopant. However, the conductivities of N-substituted polyaniline doped with HCl, HNO<sub>3</sub>, and HClO<sub>4</sub> are 4.7  $\times 10^{-3}$ ,  $1.49 \times 10^{-1}$ , and  $1.93 \times 10^{-2}$  S·cm<sup>-1</sup>, respectively. The change in the conductivities is greater than that in the case of the traditional polyaniline in HCl medium. This result indicates that the conductivity of N-substituted polyaniline depends on the oxidative properties of the acidic media because the decarboxylation is easier in an oxidative acidic medium. These results are consistent with an increase in the amount of oxidant during the polymerization process.

The conductivity of polymers is also reflected in the electrochemical impedance spectra (EIS) of polymer films. EIS allows the redox reaction resistance, the equivalent series resistance, and the maximum power density ( $P_{max}$ ) of a supercapacitor to be investigated. The EIS data show the frequency response of the electrode/electrolyte system, which is represented as a plot of the imaginary component (Z') of the impedance against the real component (Z')<sup>34</sup>. Fig. 6 shows the electrochemical impedance spectra of ES–PANI (Fig. 6a), EB–PANI (Fig. 6b), ES–NPAN (Fig. 6c), and EB–NPAN (Fig. 6d) on modified GCEs in K<sub>3</sub>Fe(CN)<sub>6</sub>/K<sub>4</sub>Fe(CN)<sub>6</sub> solution. The interfacial electron-transfer resistance ( $R_{et}$ ) of ES–PANI (Fig. 6c) is 50  $\Omega$ ; these results indicate that the film conductivity of NPAN is lower than that of PANI as a consequence of the addition of carboxyl groups to the nitrogen atom decreasing the degree of electron delocalization. However, the  $R_{et}$  of the GCE modified with EB–NPAN (Fig. 6d) dramatically increases to 4100  $\Omega$ . The electrochemical impedance spectra show a larger semicircular arc, which indicates that the EB–NPAN film in neutral solution and to the lower diffusivity of ions due to the negative charge of –CH<sub>2</sub>COO<sup>-</sup>, which may be formed during the de-doping process. Consequently, electrostatic repulsion occurs between the electrode surface and the solution.

#### 3.3 Solubility and solvatochromism of NPAN

The solubility of NPAN in various solvents with different polarity indexes is listed in Table 4. The de-doped NPAN is soluble in all polar solvents, including NMP, DMSO, THF, and CHCl<sub>3</sub>, and is highly soluble in acetonitrile and water, whereas the  $H^+$ -doped NPAN exhibits low solubility in the most polar solvents, except NMP and DMSO. However,  $H^+$ -doped PANI is mainly soluble in polar solvents such as NMP and DMSO and is only partly soluble in most other polar solvents. These results suggest that the solubility is primarily controlled by the molecular structure. The carboxyl group is likely responsible for the significant variation in the solubility because the introduction of a

carboxyl group on the nitrogen atom increases the distance between molecular chains. In addition, the range of solvents in which de-doped NPAN is soluble is increased; it is even soluble in water. This improved solubility is due to the presence of a carboxylate group, which can form during the de-doping process.

The color of NPAN in a solution depends on the solvent used. As shown Table 3, compared with traditional PANI, the colors of NPAN solutions are the same as those of the traditional PANI solutions: blue and green in NMP and DMSO, respectively. The UV–visible maximum absorption wavelength of the polymer solutions increases steadily when the solvent is changed from NMP or DMSO to THF. This result implies that the polymers exhibit solvatochromic properties because the polymer chains may have different conformations, and therefore different conjugation lengths, in different solvents<sup>35</sup>.

#### 3.4 Thermal stability of NPAN

Thermogravimetric analyses of PANI and NPAN were performed in the temperature range from 25 °C to 800 °C; their thermograms are presented in Fig. 7. For the sample of pure PANI, a slight mass loss begins at approximately 50 °C and continues until 105 °C. The mass loss remains steady up to 350 °C, and then a rapid mass loss of 94.1% occurs until 625 °C. The initial mass loss is due to the loss of water molecules, whereas the next mass loss can be attributed to the loss of oligomer, and the subsequent dramatic mass loss occurs due to the degradation of the polymer chain. Nevertheless, in the case of NPAN, the first step is similar to that of PANI between 50 °C and 105 °C for the expulsion of water molecules, and the dopant (HCl) forms PANI chains. The second step shows a 2% weight loss between 260 °C and 340 °C, which is consistent with the decarboxylation of carboxylic acids on polymer chains. A rapid mass loss of 94.1% occurs between 350 °C and 720 °C due to rapid degradation of the polymer chains. An interesting phenomenon is observed in the derivative thermogravimetry (DTG) curve (inset) of the PANI, which corresponds to the second-step weight loss in the TGA curve. It reveals the presence of two minima rather than one minimum. The first minimum is attributed to the loss of low-molecular-weight polymer, whereas the second minimum is the result of the degradation of high-molecular-weight polymer. However, the degradation trend of NPAN shows a three-step weight-loss process due to the introduction of carboxyl groups onto the polymer chains. Notably, the temperature of PANI at the minimum of the DTG curve is 533 °C; however, the minimum temperature in the case of NPAN is shifted to a substantially higher temperature by approximately 186 °C. This TGA indicates better thermal stability of pure NPAN compared with that of PANI. The better thermal stability of neat NPAN can be explained by the dominance of the benzenoid structure. Alternatively, the inferior thermal stability of pure PANI is due to the presence of a quinoid ring in its structure<sup>36</sup>.

## CONCLUSION

NPAN has been prepared by the oxidative polymerization of NAN using ammonium peroxydisulfate as an oxidant in acetonitrile solution. Structural analysis indicates that the quinoid unit structure is formed by the elimination of the carboxyl group during N-substituted carboxyl polymerization. The decarboxylation reaction is affected by the monomer-to-oxidant molar ratio. The amount of decarboxylation increases with an increase in polymer chain length until only a  $-CH_2COONH_4$  group remains after the reaction of both monomers followed by the de-doping procedure. The conductivity of the polymer, which depends on the oxidizability of the acid, changes only slightly in the range from  $10^{-3}$  S/cm to  $10^{-1}$  S/cm. The de-doped NPAN is soluble in all polar solvents, including NMP, DMSO, THF, and CHCl<sub>3</sub>, and is mainly soluble in acetonitrile and water, whereas the solubility of the H<sup>+</sup>-doped NPAN is low in the most polar solvents, except NMP and DMSO. The color of NPAN in a solution depends on the solvent used, which indicates that the polymer exhibits solvatochromic properties because the polymer chains may have different conformations in different solvents and therefore different conjugation lengths. Consequently, introduction of a carboxyl group on the nitrogen atom of a polymer can not only enhance the solubility of the polymer by altering its chain structure but also increase its thermal stability.

#### Acknowledgements

The study was supported by the National Natural Science Foundation of China (21164001) and the Bureau of Education of Jiangxi Province, China (GJJ13359).

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