

# Studies of Influence of Naphthalene Mono/Disulfonic Acid Dopant on Thermal Stability of Polypyrrole

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**ABSTRACT:** Thermal stability of polypyrrole (PPY) synthesized by *in situ* doping polymerization in the presence of different naphthalene mono/disulfonic acid dopant like  $\alpha$ -naphthalene sulfonic acid ( $\alpha$ -NSA),  $\beta$ -naphthalene sulfonic acid ( $\beta$ -NSA), and 1,5-naphthalene disulfonic acid (1,5-NDSA) has been systematically investigated by thermogravimetric analysis (TG). It was found that the thermal stability of as-resulted PPY was greatly affected by type and concentration of dopant. In general, the order of their thermal stability was PPY-( $\beta$ -NSA) > PPY-( $\alpha$ -NSA)  $\approx$  PPY-(1,5-NDSA). And high concentration of dopant (e.g., 1.2 mol/L) had a negative effect on the thermal stability. Among those three dopants, 1,5-NDSA had a unique influ-

ence on thermal stability and crystallinity of as-resulted PPY. In addition, all of room-temperature conductivity and crystallinity of PPY-(1,5-NDSA) changed dramatically after aging for 9 h under N<sub>2</sub> atmosphere and at 230°C, which may be due to a partly dedoping process. These results were confirmed by elemental analysis, FTIR, X-ray photoelectron spectroscopy (XPS), and X-ray powder diffraction (XRD). © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 997–1001, 2008

**Key words:** polypyrrole; conducting polymer; thermogravimetric analysis; thermal properties; a dedoping process

## INTRODUCTION

Polypyrrole (PPY) is one of the well studied intrinsically conducting polymers (ICPs) along with polycetylene (PA) and polyaniline (PANI). It has a good stability in air and an excellent reversible redox property and therefore has many attractive potential applications. For example, sensor, micro-actuator, anticorrosion paint and battery, which are made of PPY, have been developed and studied in the past several decades.<sup>1–7</sup> However, its long-term thermal stability in working condition is prerequisite to a successful commercialization. So far, there are many reports<sup>8–12</sup> that show the stability of PPY is closely related to synthetic condition, dopant and aging condition. Moreover, its degradation mechanism has been investigated too.<sup>9,13–15</sup>

In our group, research has been focusing on controlling micro/nano-size morphology of ICPs special for PANI and PPY in the past decade.<sup>16–23</sup> Because it is believed that nanotube/hollow-ball of ICPs can be applied in drug delivery system and other advanced

materials.<sup>24</sup> Moreover, nanofiber of ICPs has shown higher room-temperature conductivity than common ones.<sup>25,26</sup> Until now, different morphologies of PANI and PPY like tube, fiber and so on can be prepared in our lab. One of interesting results is that we can tune the morphology from fiber to tube and control its diameter simply by a combination of different type of dopants and proper concentrations.

Among these dopants, naphthalene sulfonic acid is a super dopant. Many related works have been carried out and been published so far.<sup>16–21</sup> For naphthalene sulfonic acid, it is found that the position and number of sulfonic acid group on naphthalene (Fig. 1) have great effect on morphology, crystallinity, and the other properties of as-resulted PPY. For example, in  $\beta$ -naphthalene sulfonic acid ( $\beta$ -NSA) dopant system, nano-/micro-tube can be prepared; in the other two dopants systems like  $\alpha$ -naphthalene sulfonic acid ( $\alpha$ -NSA) and 1,5-naphthalene disulfonic acid (1,5-NDSA), the same morphology is hardly observed. In addition, we recently have reported PPY with unusual crystallinity, which is synthesized by *in situ* polymerization in the presence of 1,5-naphthalene disulfonic acid as dopant.<sup>27</sup>

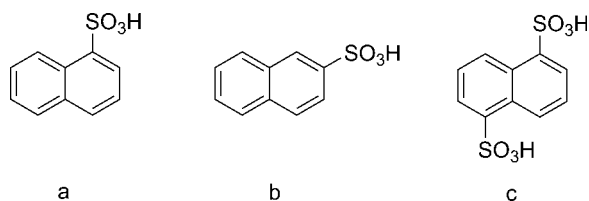
However, for these PPY with controlling nano/micro-size morphologies and with many potential applications, we hardly do any fundamental research about their thermal stability. How do the position and number of sulfonic acid group on naphthalene affect thermal stability of as-synthesized PPY after

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**Figure 1** Molecular structure of naphthalene mon/disulfonic acid: (a)  $\alpha$ -naphthalene sulfonic acid, (b)  $\beta$ -naphthalene sulfonic acid, (c) 1,5-naphthalene disulfonic acid.

we knew they had great effects on morphology and crystallinity?

In this article, PPY doped with different naphthalene mono/disulfonic acid was synthesized by *in situ* doping polymerization, and their thermal stability has been systematically studied by thermogravimetric analysis (TG). Particularly, influence of the thermal treatment under  $N_2$  atmosphere and at high temperature (e.g.,  $230^\circ C$ ) on crystallinity and room-temperature conductivity of PPY-(1,5-NDSA) was carefully investigated because of its unique thermogram. In addition, elemental analysis, FTIR, X-ray photoelectron spectroscopy (XPS), and X-ray powder diffraction (XRD) were applied to collect more support information.

## EXPERIMENTAL

### Sample preparation

Pyrrole was distilled under reduced pressure before using. Ammonium peroxydisulfate (APS),  $\alpha$ -NSA,  $\beta$ -NSA, and 1,5-NDSA were used without any further purification.

A synthetic procedure was similar to the previous report.<sup>20,21,27</sup> In a typical preparation,  $9.6 \times 10^{-3}$  molar 1,5-NDSA and  $5.8 \times 10^{-3}$  molar pyrrole were added into 8 mL deionized water with stirring. The above mixture was cooled in ice/water bath. Next 6.7 mL APS (0.52 mol/L) was added slowly into above mixture with stirring. After reacted for 10 h in ice/water bath, filtered off the solvent, and washed the solid product with deionized water and methanol for several times, respectively, until the filtered solvent became colorless. Finally, as-resulted PPY powder was dried overnight under vacuum at  $60^\circ C$ .

As-resulted PPY powder was put into tube furnace and aged for 9 h under  $N_2$  flow (5 mL/min) and at  $230^\circ C$  to get enough samples for investigation of effect of such thermal treatment on its crystallinity and its room-temperature conductivity.

### Instrumentation

TG was performed on Perkin-Elmer, TG7, under  $N_2$  flow (20 mL/min) and the scanning rate was  $20^\circ C$ /min. The Fourier transform infrared (FTIR) absorp-

tion spectrum of the polymers was measured by using a Shimadzu FTIR 8101 M spectrophotometer. Powder samples were first dispersed in KBr and then pressed into pellets. Bulk analysis of C, H, N, and S element was carried out by using a Perkin-Elmer 2400 Series II CHNS/O analyzer. Powder X-ray data were collected at  $25^\circ C$  on RINT 2000 wide-angle goniometer with employing Ge monochromated  $CuK\alpha_1$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The XPS measurements were made on a VG ESCALAB MkII spectrometer (VG Scientific) with Mg KR X-ray source (1253.6 eV photons). The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). Throughout the measurements, the pressure in the analysis chamber was maintained at  $10^{-8}$  mbar or lower. To compensate for the surface charging effect, all binding energies (BE) were referenced to the C (1s) neutral carbon peak at 284.6 eV. In peak calculation and curve synthesis, the line widths (full width at half-maximum) of the Gaussian peaks were maintained constant for all components in a particular spectrum.

As-resulted polymer powder was pressed into disk for measuring its conductivity. The room temperature conductivity was measured by using the standard four-probe method with a Keithley 196 SYSTEM DM digital multimeter and ADVANTEST R6142 programmable DC voltage/current generator as the current source.

## RESULTS AND DISCUSSION

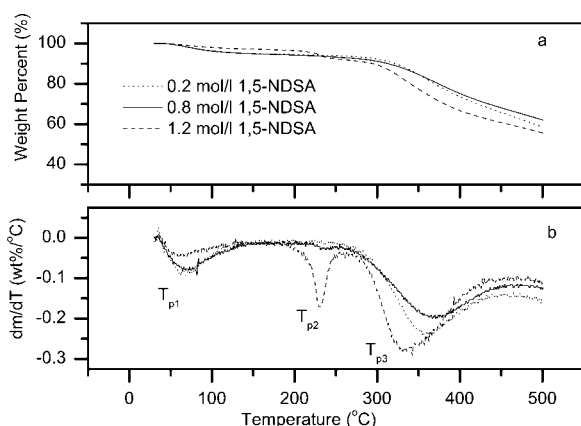
In general, weight loss of PPY doped with naphthalene mono/disulfonic acid can be classified into three steps as its temperature increases. Firstly, it loses some absorbed water and some low molecular-weight organic materials like oligomer at low temperature. Secondly, it loses weight further because of a dedoping process. Finally, it decomposes greatly and becomes carbon black if it was put in nitrogen gas atmosphere. On the last step, the weight loss normally is the largest. Similar phenomena for PANI were also observed by other scientists.<sup>28,29</sup> Some typical thermograms of PPY with naphthalene mono/disulfonic acid are shown in Figures 2 and 3. Since only PPY-(1,5-NDSA) clearly shows the second step, all of its thermograms are presented here.

In Figure 2(b), as concentration of 1,5-NDSA increases from 0.2 to 1.2 mol/L, the second temperature peak ( $T_{p2}$ ) lying between  $T_{p1}$  (the first step temperature) and  $T_{p3}$  (the third step temperature) becomes more obvious. Undoubtedly,  $T_{p2}$  has a direct relationship with dopant's concentration. Since the second step of weight loss of PPY doped with dopant is elimination of dopant, in another words, it is a dedoping process, doping level of as-synthesized PPY will determine the weight loss. When 1,5-NDSA

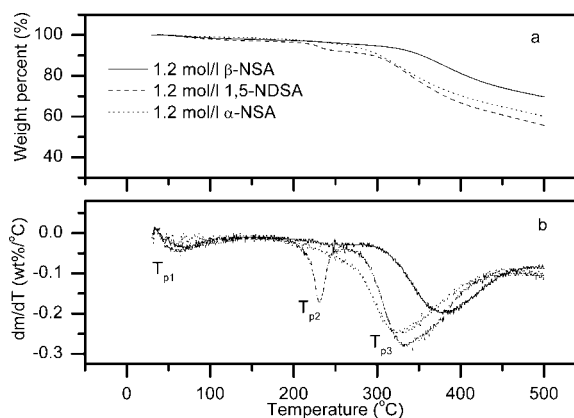
is 0.2 mol/L, S element content of as-resulted PPY is 7.27 wt %; When it increases to 0.8–1.2 mol/L, S element content increases to 8.20 wt % or 8.30 wt %, respectively, (See Table I). This means that doping level of PPY increases as 1,5-NDSA concentration increases. So,  $T_{p2}$  peak becomes stronger. The room temperature conductivity of as-resulted PPY-(1,5-NDSA) partly supports the above result too (See Table I). When 1,5-NDSA increases from 0.2 to 0.8 mol/L, the conductivity increases from 1.4 to 2.4 S/cm. However, when 1,5-NDSA increases up to 1.2 mol/L, the conductivity decreases a little to 1.0 S/cm. The main reason is a certain amount of 1,5-NDSA will not dope with PPY since there exists the maximum of doping level for conducting polymers. And part of these undoped 1,5-NDSA will adsorb on its surface although as-resulted PPY-(1,5-NDSA) is washed by deionized water and methanol for several times, respectively. This will cause a small decrease of room-temperature conductivity of the product.

On the other hand,  $T_{p3}$  shifts to lower temperature, from 370 to 334°C, as an increase of dopant's concentration [Fig. 2(b)]. This suggests that sulfonic acid group has negative effect on thermal stability of PPY. The more sulfonic acid exists, the less stable as-resulted PPY is.

For the other two dopants:  $\alpha$ -NSA and  $\beta$ -NSA,  $T_{p2}$  does not appear clearly even at high concentration (1.2 mol/L) [Fig. 3(b)]. This may be related to unique crystal structure of PPY-(1,5-NDSA) which is reported earlier.<sup>27</sup> In addition, this also indicates that  $T_{p2}$  of as-synthesized PPY varies with different dopants. From Figure 3(a), it is safe to make a conclusion that PPY-( $\beta$ -NSA) has the highest thermal stability among three dopants. When the weight loss is 10%, corresponding temperature of PPY-( $\beta$ -NSA), PPY-( $\alpha$ -NSA) and PPY-(1,5-NDSA) is 357, 302, and 295°C, respectively, [Fig. 3(a)].



**Figure 2** Thermogram of PPY-(1,5-NDSA): (a) TG and (b) DTG. The test conditions: under  $N_2$  flow (20 mL/min) and the scanning rate was 20°C/min.



**Figure 3** Thermogram of PPY doped with naphthalene mono/disulfonic acid: (a) TG and (b) DTG. The test conditions: under  $N_2$  flow (20 mL/min) and the scanning rate was 20°C/min.

On the basis of all above thermogravimetric results, only PPY-(1,5-NDSA) has the clear second step: a dedoping process. In addition, its decomposing temperature (at least 334°C) is 100°C higher. It is, therefore, very convenient for us to investigate what exactly happens at 230°C isothermal situation and under nitrogen gas atmosphere. Since PPY-(1,5-NDSA) has unusual crystallinity, we have another instrument like XRD to collect information.

Data of elemental analysis and room-temperature conductivity of PPY-(1,5-NDSA) aging for 9 h under  $N_2$  and at 230°C are listed in Table I. From Table I, it is clear that room-temperature conductivity of all of aged PPY-(1,5-NDSA) decreases dramatically to  $10^{-5}$  S/cm. In general, decrease of room-temperature conductivity of PPY doped with mineral anions in inert atmosphere is related to instability of these anions like reaction with polymer backbone, volatilization and so on. In our study, 1,5-NDSA has less volatilization and does not react with polymer backbone either. This is supported by results of elemental analysis (Table I) and FTIR (Fig. 4). There is not great different in the weight percent of S elemental and FTIR spectra after aging for 9 h under  $N_2$  and at 230°C. Weight percent of S element in polymer does not change greatly and keeps around 8 wt % no matter what 1,5-NDSA concentration is. Furthermore, no any change is detected in their FTIR spectra either (Fig. 4). The band at  $3420\text{ cm}^{-1}$  is the characteristic of N–H stretching vibration, pyrrole ring fundamental vibration occurs at  $1550$  and  $1460\text{ cm}^{-1}$ , and =C–H in-plane deformation vibration at  $1310$  and  $1180\text{ cm}^{-1}$ , and =C–H out-of-plane vibration at  $790$  and  $920\text{ cm}^{-1}$ .<sup>30,31</sup> Meanwhile, intensity and shape of band at  $1180$  and  $1040\text{ cm}^{-1}$  could be due to S=O asymmetric stretching vibration and S=O symmetric stretching vibration of sulfonic acid group.<sup>32</sup> So weight loss at 230°C could not be assigned to

**TABLE I**  
**Data of Elemental Analysis and Room-Temperature of Aged or Not Aged**  
**PPY-(1,5-NDSA) Synthesized in Different 1,5-NDSA Concentration**

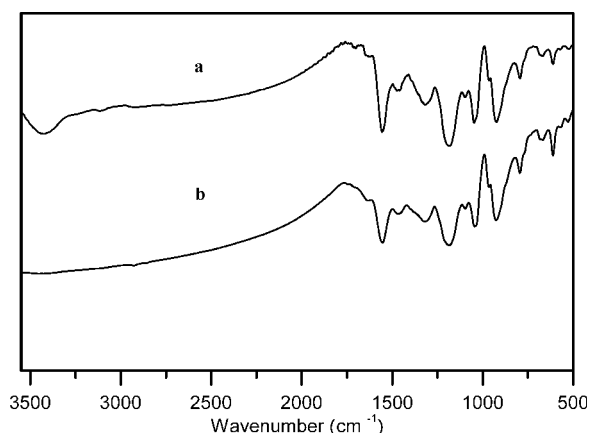
Sample	1,5-NDSA Concen. (mol/L)	Aging <sup>a</sup>	$\sigma_{RT}$ (S/cm)	Elemental analysis (wt. %)			
				C	H	N	S
1	0.2	no	1.4	53.38	3.76	12.25	7.27
2	0.2	yes	$6.8 \times 10^{-5}$	53.68	3.13	12.54	8.01
3	0.8	no	2.4	55.93	4.26	11.95	8.20
4	0.8	yes	$1.2 \times 10^{-4}$	54.97	3.22	11.75	8.10
5	1.2	no	1.0	54.02	4.51	11.52	8.30
6	1.2	yes	$8.6 \times 10^{-6}$	56.34	3.41	11.18	8.70

<sup>a</sup> Aging condition was under N<sub>2</sub> and at 230°C for 9 h.

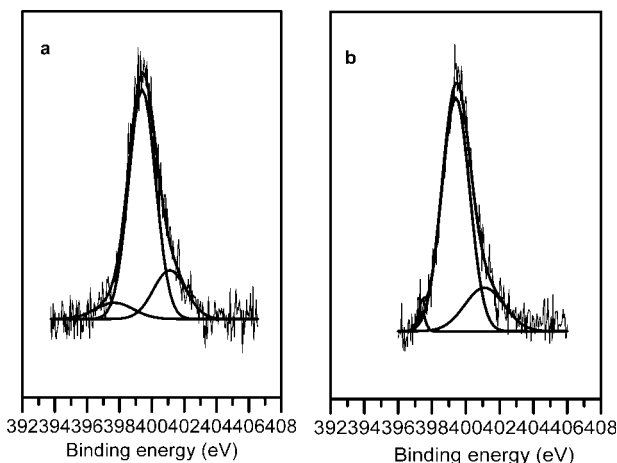
decomposition or reaction of polymer backbone chain. This further supports our above thermogravimetric discussion about  $T_{p2}$ . And decrease of PPY-(1,5-NDSA)'s conductivity after aging for 9 h under N<sub>2</sub> and at 230°C may be due to a dedoping process.

If a dedoping process took place when PPY-(1,5-NDSA) aged for 9 h under N<sub>2</sub> and at 230°C, the relative content of the high binding energy of N(1s) component should decrease. This is consistent with the results obtained from X-ray photoelectron spectroscopy (XPS) measurement. Figure 5 shows influence of aging on the N(1s) core-level spectra of PPY-(1,5-NDSA). As shown in Figure 5, a single major component at 399.7 eV, a high BE tail at 401.1 eV and a low BE at 397.7 eV appear in these spectra, which is the characteristic of the pyrrolidine nitrogen (—NH— structure), the positively charged nitrogen and nitrogen in —C=N—, respectively.<sup>15</sup> When PPY-(1,5-NDSA) aged for 9 h under N<sub>2</sub> and at 230°C, the high binding energy (401.1 eV) component decreases from 18.0% to 14.2%. In addition, the low binding energy (397.7 eV) is clearly observed in the spectra of aged samples. All of these indicate that the positively charged nitrogen decreases. In

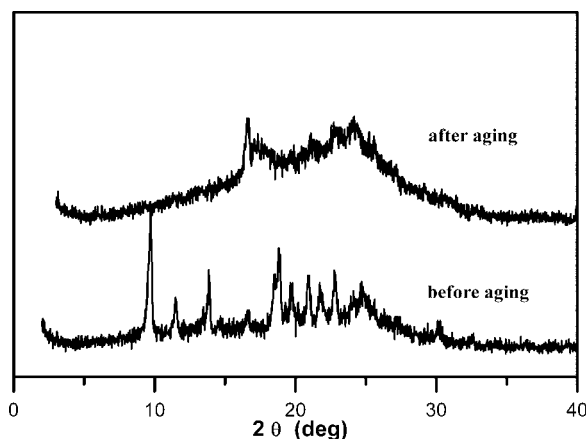
another words, a dedoping process does happen in aging process. As listed in Table I, their room-temperature conductivity decreases from 10<sup>0</sup> S/cm to 10<sup>-4</sup> to 10<sup>-6</sup> S/cm after PPY-(1,5-NDSA) aged for 9 h under N<sub>2</sub> and at 230°C. This also suggests that the dedoping process is not completely in such aging condition. Because the conductivity should be less than 10<sup>-8</sup> S/cm if PPY took a complete dedoping process. Nevertheless, a contradictory thing is that weight percent of S element does not change great before and after aging. According to above thermogram, 1,5-NDSA should dedope from PPY and volatilize at 230°C, and S element content should decrease. The main reasons, we believe, are that firstly, a dedoping process of PPY-(1,5-NDSA) at 230°C is just partly, and its weight loss is further less with consideration of weight loss of low-molecular-weight organic materials at low temperature (<100°C); Secondly, they are treated in quite different conditions although samples are heated in the same temperature and same atmosphere. In TG, quantity of sample is quite small and sample can be treated uniformly to get reproducible data, while it is a quite opposite situation in tube furnace. To get



**Figure 4** FTIR spectra of aged PPY-(1,5-NDSA) for 9 h under N<sub>2</sub> and at 230°C. (a) PPY synthesized in 0.2 mol/L 1,5-NDSA and (b) PPY synthesized in 1.2 mol/L 1,5-NDSA. Other reaction conditions were identical.



**Figure 5** N(1S) XPS core-level spectra of PPY-(1,5-NDSA) synthesized in 1.2 mol/L 1,5-NDSA. (a) Before aging and (b) after aging for 9 h under N<sub>2</sub> and at 230°C.



**Figure 6** X-ray powder diffraction spectra of PPY-(1,5-NDSA) synthesized in 1.2 mol/L 1,5-NDSA before aging and after aging for 9 h under  $N_2$  and at  $230^\circ C$ .

enough samples for all of measurements like element analysis, conductivity, XRD and XPS, at least 2 g sample is put into crucible. Dedoped 1,5-NDSA would diffuse in a long way to escape. This also makes S element content unchangeable.

X-ray diffraction spectra of PPY-(1,5-NDSA) aging for 9 h under  $N_2$  atmosphere and at  $230^\circ C$  show that its crystallinity has destroyed greatly and it becomes amorphous (Fig. 6). On the basis of our discussion of TG, this also means that the order of long-range structure has been broken up when PPY-(1,5-NDSA) dedoped under  $N_2$  and at  $230^\circ C$ . However, there still exists some order of structure in the polymer after aging. This main peak in order of intensity locates at  $2\theta = 16.62^\circ$ ,  $24.10^\circ$ , and  $22.86^\circ$ , respectively. It is quite different from XRD spectrum of as-synthesized PPY-(1,5-NDSA), whose main peaks locates at  $2\theta = 15.8^\circ$ ,  $16.06^\circ$ , and  $25.32^\circ$ . In our previous work,<sup>27</sup> it has been demonstrated that such high crystallinity of PPY-(1,5-NDSA) was formed by long-range periodic structure of dopant counterion incorporated in PPY chain. Thus, these above results further support our previous assumption that a long-range ordered structure formed by 1,5-NDSA counterion with PPY contributed to the high crystallinity of PPY-(1,5-NDSA). Furthermore, pure phase of 1,5-NDSA does not appear in the aged polymer (Fig. 6).

## CONCLUSIONS

Thermal stability of PPY doped with various naphthalene mono/disulfonic acids has been systematically measured by TG. Generally speaking, as-synthesized PPY loses its weight on three steps. It was found that the position and number of sulfonic acid group on naphthalene had great effect on the three steps. The order of thermal stability of as-resulted PPY was PPY-( $\beta$ -NSA) > PPY-( $\alpha$ -NSA)  $\approx$  PPY-(1,5-NDSA). And only PPY-(1,5-NDSA) had the clear sec-

ond step (e.g.,  $230^\circ C$ ) in its thermogram under nitrogen atmosphere. Its long-range ordered molecular structure would be destroyed seriously and it became amorphous on the second step. On the other hand, its room-temperature conductivity would decrease greatly from about  $10^0$  S/cm to  $10^{-4}$  to  $10^{-6}$  S/cm after aging for 9 h under  $N_2$  and at  $230^\circ C$  due to a partly dedoping process which was confirmed by elemental analysis, FTIR, XPS, and X-ray diffraction.

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