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Structures and properties of chemically reduced polyanilines

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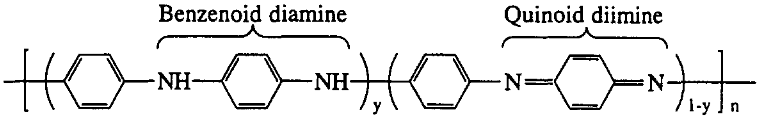
HCl-doped emeraldine form of polyaniline (PANI-H) was synthesized by oxidative polymerization of aniline in aqueous hydrochloric acid solution using potassium dichromate as an oxidant. The undoped form of PANI-H (i.e. PANI) was chemically reduced using hydrazine as the reductant. The structure, doping, conductivity and thermal stability of the reduced polyaniline (PANI-R) were studied by elemental analysis, *FT*-i.r., solid-state ^{13}C-NMR, XPS and TGA. It was found that most of the quinoid structural units in PANI were reduced to benzenoid structural units. PANI-R had been doped with HCl and iodine, but only the iodine-doped product (PANI-RI) showed high electrical conductivity. *FT*-i.r. and XPS results indicated that some of the benzenoid structural units in PANI-R were oxidized to quinoid structural units during the iodine-doping process and a highly conjugated π system might be formed in the PANI-RI molecular chains. TGA results indicated that PANI-R had better thermal stability than PANI. The dopants—HCl and iodine—were almost completely removed from the HCl and iodine-doped polyanilines below 250°C. PANI-R could also be oxidized by potassium dichromate. The thermal stability of the intrinsically oxidized PANI-R (PANI-RO) was unexpectedly poor. The electrical conductivity of HCl-doped PANI-RO was much lower than that of HCl-doped PANI. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: polyaniline; conducting polymer; chemical reduction)

INTRODUCTION

Polyaniline is an environmentally stable conducting polymer with excellent electrical, magnetic and optical properties. It has attracted considerable attention over the past 10 years and is generally regarded as one of the conducting polymers with very high potential in commercial applications. The potential applications of polyaniline include secondary batteries[1], electromagnetic interference shielding[2], molecular sensors[3], non-linear optical devices[4], electrochromic displays[5] and microelectronic devices[6]. However, there are still many unresolved problems concerning the structures, properties such as electrical conductivity, and applications of polyanilines because of the complexities in molecular structures, poor solubility in water and most organic solvents as well as the very different structures obtained by different synthesis conditions and post-synthesis treatments.

Doping and oxidation levels are two of the most important factors affecting the electrical conductivity and other properties of polyanilines[7–9]. Many investigations[9–11] have been carried out on the doping of polyanilines. There are also some published work[12–14] on the preparation, structures and properties of polyanilines with different oxidation levels. In general, the oxidation level of a polyaniline synthesized by either a chemical or electrochemical method can be described by the following molecular formula[7,8]:



Here, $y = 1$, 0.5 and 0, the corresponding polymers are the fully reduced polyaniline (leucoemeraldine), the half oxidized polyaniline (emeraldine), and the fully oxidized polyaniline (pernigraniline), respectively. The emeraldine form of polyaniline showed the highest electrical conductivity after it had been doped with protonic acid[7,15]. The previous research effort was concentrated on employing electrochemical method to change the oxidation levels of polyanilines[10,11,16]. In contrast, very limited research has been done on the utilization of chemical method to modify the polyanilines and some of the results were conflicting[12,14]. In this work, polyaniline was synthesized chemically with potassium dichromate as the oxidant and was then reduced by the chemical method. The structure, doping and properties of the reduced polyanilines were investigated.

EXPERIMENTAL

Synthesis of polyaniline

Polyaniline was synthesized by oxidative polymerization of aniline in aqueous hydrochloric acid solution at room temperature using potassium dichromate as an oxidant. Forty grams of aniline hydrochloride (Aldrich, reagent grade) and 23.0 g of potassium dichromate (Aldrich, reagent grade) were dissolved separately in two 375 ml of 1.5 M hydrochloric acid (Riedel-deHaen, reagent grade) aqueous

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solutions. The potassium dichromate solution was added dropwise to the stirred solution of aniline hydrochloride. After reacting for 60 min, the black precipitate was filtrated, washed with 1.0 M HCl aqueous solution until the filtrate was clear, and then dried under a dynamic vacuum at 80°C for 48 h. The product obtained was HCl-doped polyaniline and was labelled as PANI-H. Afterwards the PANI-H was undoped with an excess amount of 1.0 M $NH_3{\cdot}H_2O$ (Riedel-deHaën, reagent grade) aqueous solution and washed with excess water to obtain the intrinsic form of polyaniline, labelled as PANI.

Reduction of polyaniline

Twenty grams of PANI was added to an Erlenmeyer flask containing 200 ml of hydrazine (Aldrich, 35 wt% aqueous solution). The mixture was stirred for 5 h at room temperature. The product was filtrated, washed with excess water and then dried under a dynamic vacuum at 80°C for 16 h. The intrinsic form of the reduced polyaniline was obtained and labelled as PANI-R. The PANI-R was added into excess 1.5 M HCl aqueous solution. HCl-doped PANI-R was obtained and labelled as PANI-RH.

Eight grams of PANI-R was added to an Erlenmeyer flask containing 100 ml of 1.5 M HCl aqueous solution and 4.0 g potassium dichromate. The mixture was stirred for 5 h at room temperature. The product was filtrated, washed with excess water and then dried under a dynamic vacuum at 80°C for 16 h. HCl-doped oxidized PANI-R was obtained and labelled as PANI-ROH. The PANI-ROH was then added into excess 1.0 M $NH_3{\cdot}H_2O$ aqueous solution. Intrinsically oxidized PANI-R was obtained and labelled as PANI-RO.

Iodine-doping of intrinsically reduced polyaniline (PANI-R)

Five grams of iodine [E. Merck (India) Co., Ltd.; reagent grade] was added to an Erlenmeyer flask containing 100 ml of ethanol (Riedel-deHaën, reagent grade). Then 3.0g of PANI-R was added into this solution. The mixture was stirred for 48 h at room temperature. The product was filtrated, washed with 150 ml ethanol three times and then washed with excess water. Finally the sample was dried under a dynamic vacuum at 70°C for 30 h. Iodine-doped PANI-R was obtained and labelled as PANI-RI. Note that all the reagents were used as received without further purification. All the water used in the experiments was deionized water.

Characterizations of various forms of polyanilines

Samples of the various forms of polyanilines were pressed into disks of 18 mm diameter and *ca.* 2 mm thickness under a pressure of *ca.* 250 MPa. The electrical conductivity was measured by the four-point-probe technique at room temperature. If the conductivity fell below 1.0×10^{-4} S cm^{-1}, silver paste electrical contacts were made on both sides of the sample and the electrical conductivity was measured by a Hewlett Packard 34401A multimeter.

The contents of C, H, N, O, Cl and I in the samples were determined by elemental analysis performed at the Guangzhou Institute of Geochemistry, Academia Sinica. [Cl]/[N] and [I]/[N] molar ratios indicated the doping levels of the HCl- and iodine-doped polyanilines respectively. Fourier transform infrared (*FT*-i.r.) spectroscopy was performed on Perkin Elmer 16PC *FT*-i.r. spectrometer. All *FT*-i.r. spectra with 4 cm^{-1} spectral resolution were obtained from compressed KBr pellets in which the polyaniline powders were evenly dispersed. The pellets were prepared by pressing the mixtures of polyaniline and KBr powders which were ground together in an agate mortar. Thirty scans were used to record each *FT*-i.r. spectrum.

Solid-state C-13 nuclear magnetic resonance (^{13}C-NMR) spectra were obtained from JEOL JNM-EX 400 *FT*-NMR System operating at 400 MHz for ^{1}H. The cross-polarization magic angle spinning (CPMAS) technique was employed to obtain all the spectra. The polyaniline powders were ground with an agate mortar and then placed into the zirconia rotor. All samples were spun between 4.0 and 4.5 kHz at 23°C. The chemical shifts were referenced to tetramethylsilane (TMS) by assigning the upfield peak of adamantane (the external standard) to 29.5 ppm. A sum of 11 000 transients were collected for all CPMAS spectra of the various polyaniline samples.

X-ray photoelectron spectroscopy (XPS) was performed on Physical Electronics PHI 5600 Surface Science Analysis System with its packaged software PHI Access for data acquisition, curve fitting and data analysis. The XPS specimens were prepared by pressing the polyaniline powders into the adhesives of the indium foils (Aldrich, 99.99%, 0.127 mm thickness, 50 mm diameter). Each specimen was examined under an optical microscope to ensure that the polyaniline powders fully covered the surface of the In-foil before it was placed into the XPS sample chamber. The X-ray source was generated with an Al monochromic anode at the K_α-line (i.e. 1486.6 eV) energized at 14 kV and 350 W. Both XPS survey and multiplex spectra were collected at a fixed takeoff angle of 45° with respect to the spherical capacitance analyser. All measurements were performed under a vacuum of 10^{-7} Pa at room temperature. To compensate for surface charging effects, all binding energies were referenced to the C_{1s} graphite carbon peak at 284.6 eV. After a linear background subtraction, curve-fitting for the core line envelopes was carried out by a non-linear least-squares curve-fitting routine in which each parameter describing the several component peaks was varied in turn so as to maximize a 'goodness of fit' parameter. Each component peak was described by its height, position, full-width-at-half-maximum (FWHM), gaussian/lorentzian ratio and asymmetry parameter. For each curve fit the number of component peaks and their approximate positions were decided, based on the chemical functionalities that might be expected for the various forms of polyanilines. Initial component peaks were set up manually and the computer program allowed to iterate so as to produce a physically reasonable fit.

Thermogravimetric analysis (TGA) was carried out on TA Instruments TGA 2950 thermogravimetric analyzer at a heating rate of 10°C min^{-1} in air.

RESULTS AND DISCUSSION

Composition and conductivity measurements

Table 1 presents the composition and conductivity of various forms of polyaniline. The y-values and [Cl]/[N] or [I]/[N] molar ratios, corresponding to oxidation levels and doping levels, respectively, were calculated on the basis of compositions and are also listed in *Table 1*. PANI had about the same composition as the emeraldine base ($y = 0.5$) and that of PANI-R was similar to the leucoemeraldine base ($y = 1$). The y-value for PANI-R was slightly smaller than 1,

Table 1 Composition and conductivity of various forms of polyaniline

Sample	Composition	*y*	[Cl]/[N] or [I]/[N] (molar ratio)	Conductivity (S/cm)
PANI	$C_{24.00}H_{17.78}N_{4.07}\cdot(H_2O)_{0.34}$	0.45	—	4.26×10^{-11}
PANI-R	$C_{24.00}H_{19.57}N_{4.11}\cdot(H_2O)_{0.27}$	0.89	—	1.07×10^{-11}
PANI-RO	$C_{24.00}H_{18.12}N_{3.98}\cdot(H_2O)_{0.71}$	0.53	—	2.26×10^{-10}
PANI-H	$C_{24.00}H_{17.85}N_{4.06}\cdot(HCl)_{1.96}\cdot(H_2O)_{1.63}$	0.46	0.48	13.80
PANI-RH	$C_{24.00}H_{20.07}N_{4.13}\cdot(HCl)_{1.84}\cdot(H_2O)_{1.69}$	1.02	0.45	1.82×10^{-3}
PANI-ROH	$C_{24.00}H_{18.09}N_{3.96}\cdot(HCl)_{1.78}\cdot(H_2O)_{1.92}$	0.52	0.45	0.25
PANI-RI	$C_{24.00}H_{19.63}N_{4.04}\cdot I_{4.16}\cdot(H_2O)_{0.29}$	0.91	1.03	7.94

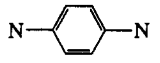
indicating that there were still a small amount of quinoid structural units in the PANI-R molecular chains. The composition of PANI-RO was similar to that of PANI, indicating that the reduced polyaniline was probably chemically oxidized again. The doping levels of PANI, PANI-R and PANI-RO were about 0.5 when using HCl as the dopant.

As shown in *Table 1*, the conductivity of PANI, PANI-R and PANI-RO was very low and they were insulators. However, after doping with HCl, PANI-H, PANI-RH and PANI-ROH all demonstrated much higher conductivity. In particular, PANI-H had the highest conductivity of 13.80 S cm^{-1}. This result was in agreement with many other results[7,15]. Theoretically, HCl-doped leucoemeraldine should be an insulator[9,17], but PANI-RH exhibited a certain conductivity. It might be attributed to the small amount of quinoid structural units in the PANI-R molecular chains. It is of interest that the iodine-doped PANI-R, i.e. PANI-RI, had a conductivity of 7.94 S cm^{-1}, which was much higher than PANI-RH and iodine-doped emeraldine form of polyaniline[12,18].

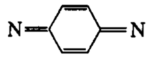
FT-i.r. spectra

The *FT*-i.r. spectra of PANI, PANI-R and PANI-RO are shown in *Figure 1*. PANI had strong absorption peaks at 832, 1164, 1308, 1498, and 1590 cm^{-1} These peaks are attributed to the out-of-plane bending vibration of C–H on *para*-disubstituted rings, characteristic vibrational mode of

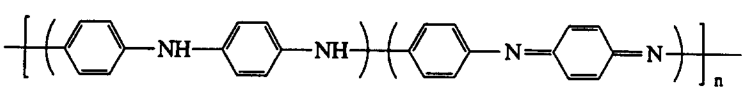
stretching vibration of C–N, stretching vibration of



ring and stretching vibration of



rings, respectively[8,9,16,19]. The *FT*-i.r. spectrum of PANI is very similar to those of the electrochemically synthesized polyaniline [16] or chemically synthesized polyaniline using ammonium persulfate as the oxidant[19]. In combination with the elemental analysis result in *Table 1*, the authors believe that PANI was composed of the emeraldine base structure (i.e. $y = 0.5$):



After reducing PANI with hydrazine, the intensities of absorption peaks at 1164 and 1590 cm^{-1}, which are attributed to the quinoid units, decrease remarkably. Nevertheless, these two peaks (i.e. 1166 and 1596 cm^{-1}) do not disappear completely in the *FT*-i.r. spectrum of the reduced polyaniline (PANI-R). These results suggest that a large portion of the quinoid structural units in PANI molecular chains were reduced to benzenoid structural units, in agreement with the elemental analysis result. The oxidized product of PANI-R (i.e. PANI-RO), which was oxidized by potassium dichromate, displays much higher peak intensities at 1166 and 1592 cm^{-1} than PANI-R. This suggests that some benzenoid units in PANI-R were oxidized into quinoid units by potassium dichromate.

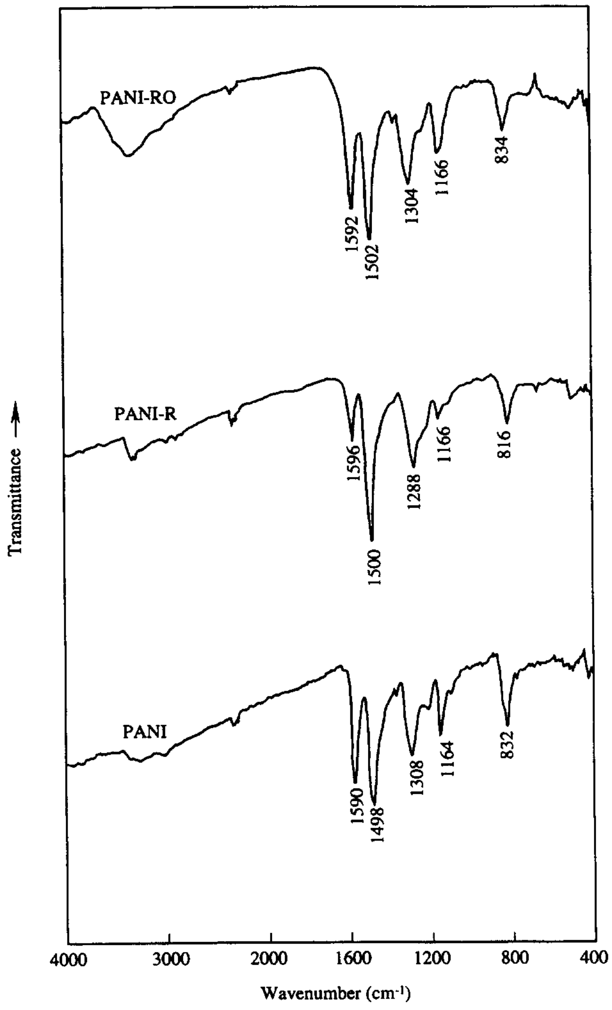


Figure 1 *FT*-i.r. spectra of PANI, PANI-R and PANI-RO.

Figure 2 shows the *FT*-i.r. spectra of PANI-H, PANI-RH, PANI-ROH and PANI-RI. When comparing with PANI, the major peaks in all of these spectra obtained from HCl- and iodine-doped polyanilines are shifted to lower wavenumbers with more uniform intensities. It is due to the Christiansen filter effect arising from the high refractive index dispersion and scattering of the large sizes of the analytes. In some situations, a shift of greater than 50 cm^{-1} in the apparent maximum of an absorption band may occur [20]. Nevertheless, since all the spectra in *Figure 2* are similarly affected, valid comparisons can still be made within *Figure 2*. In the PANI-H spectrum, shifting of the peaks attributed to the quinoid units appears to be particularly significant, which is in agreement with some published work[19]. The changes in the spectrum of PANI-ROH are very similar to those of PANI-H. However, there are some significant differences for the HCl-doped PANI-R (i.e. PANI-RH). The absorption peak of PANI-R at 1166 cm^{-1}, which is considered as a characteristic peak for the electron delocalization in polyaniline[19], is only shifted down to 1 150 cm^{-1} in PANI-RH. In contrast, this characteristic peak is shifted to 1120 and 1137 cm^{-1} for PANI-H and PANI-ROH, respectively. It reveals that the extent of electron delocalization in PANI-RH is smaller than both PANI-H and PANI-ROH. This probably resulted from the smaller amount of quinoid units present in the PANI-R molecular chains, which may also be the major reason for the lower electrical conductivity in PANI-RH.

As shown in *Figures 1* and *2*, there are great differences in the *FT*-i.r. spectra of PANI-RI and PANI-R. In the PANI-RI spectrum, the intensity of the peak at 1578 cm^{-1} due to the quinoid units is greater than that of the peak at 1480 cm^{-1} due to the benzenoid units. It indicates that some of the benzenoid units in PANI-R molecular chains were oxidized to quinoid units when PANI-R was doped with iodine. The authors have previously[18] found that major changes occurred only at the absorption peaks of the quinoid units when the emeraldine base form of polyaniline was doped with iodine; and, that iodine-doped polyaniline had only a low conductivity of 10^{-3} S cm^{-1}. Therefore, the authors believe that a highly conjugated π system, which is similar to the structure of HCl-doped emeraldine form of

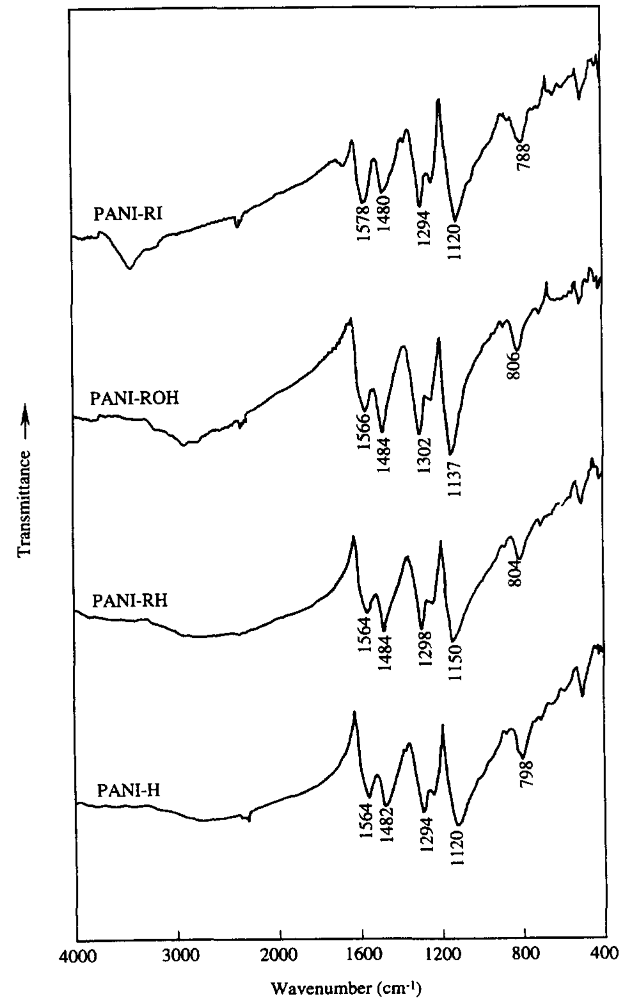


Figure 2 *FT*-i.r. spectra of PANI-H, PANI-RH, PANI-ROH and PANI-RI

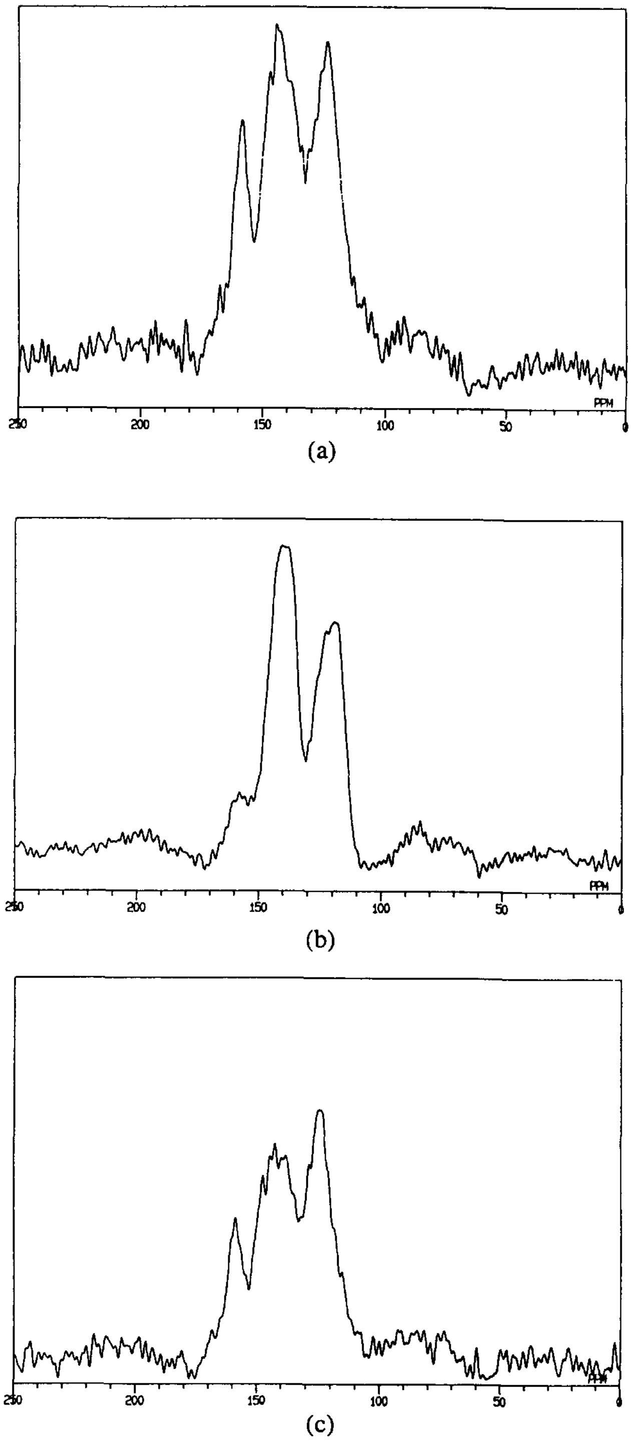
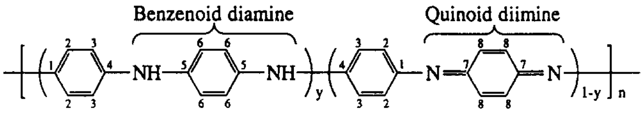


Figure 3 Solid-state ^{13}C-NMR spectra: (a)PANI; (b) PANI-R; (c) PANI-RO

Table 2 Assignment of the peaks in the ^{13}C-NMR spectrum of PANI



Peak (ppm)	Assignment (carbon number)
123.9	2, 3, 6
138.3	8
144.3	4, 5
147.0	1
158.5	7

Table 3 Deconvolution results of N_{1s} XPS spectra of PANI, PANI-R and PANI-RO

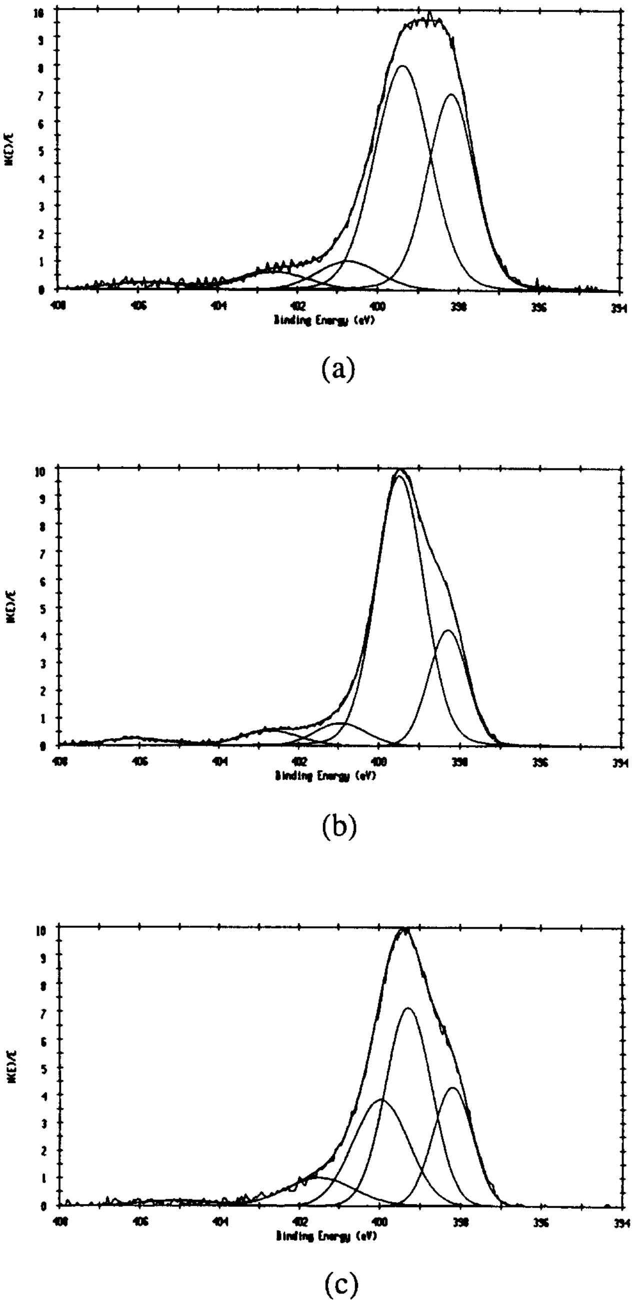
Sample	Binding energy (eV)	Percentage of total area (%)
PANI	398.20	37.17
	399.39	48.97
	400.72	7.01
	402.57	4.81
	405.80	2.04
PANI-R	398.30	21.58
	399.48	65.68
	400.95	5.74
	402.70	4.52
	406.10	2.48
PANI-RO	398.21	21.09
	399.30	41.43
	399.98	26.58
	401.48	9.06
	405.08	1.84

polyaniline[21], was formed in the current PANI-RI molecular chains, resulting in the highly conductive PANI-RI.

NMR spectra

Figure 3(a)–(c) are the solid-state ^{13}C-NMR spectra of PANI, PANI-R and PANI-RO. As shown in *Figure 3*(a), PANI has well-defined resonance peaks at 123.9, 138.3, 144.3, 147.0 and 158.5 ppm. With reference to previous related works[7,17], the assignments of these peaks are listed in *Table 2*. The peak centred at 123.9 ppm is broad and probably consists of several resonances, indicating that there are differences in the chemical enviromnents of carbon 2, 3 and 6. The assignments of this resonance band are currently being studied by the authors and will be reported in a future paper.

Only two strong and broad resonance peaks are observed at about 121.0 and 142.0 ppm in the PANI-R spectrum [*Figure 3*(b)]. The intensity of the peak centred at about 157.7 ppm is very low, indicating that the concentration of quinoid structural units in PANI-R is very low. However, the spectrum of PANI-RO [*Figure 3*(c)] shows reappearance of the peak at 159.0 ppm after oxidation by potassium dichromate. Hence the NMR results correlate with the *FT*-i.r. results very well. One additional observation of the PANI-RO ^{13}C-NMR spectrum is that the relative intensity of the peak at 142.6 ppm is much more reduced than the other peaks as compared to those of PANI spectrum.



(a)

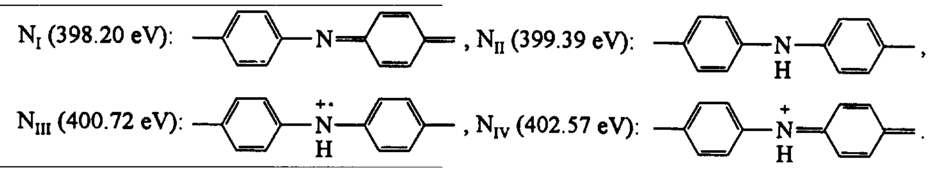
(b)

(c)

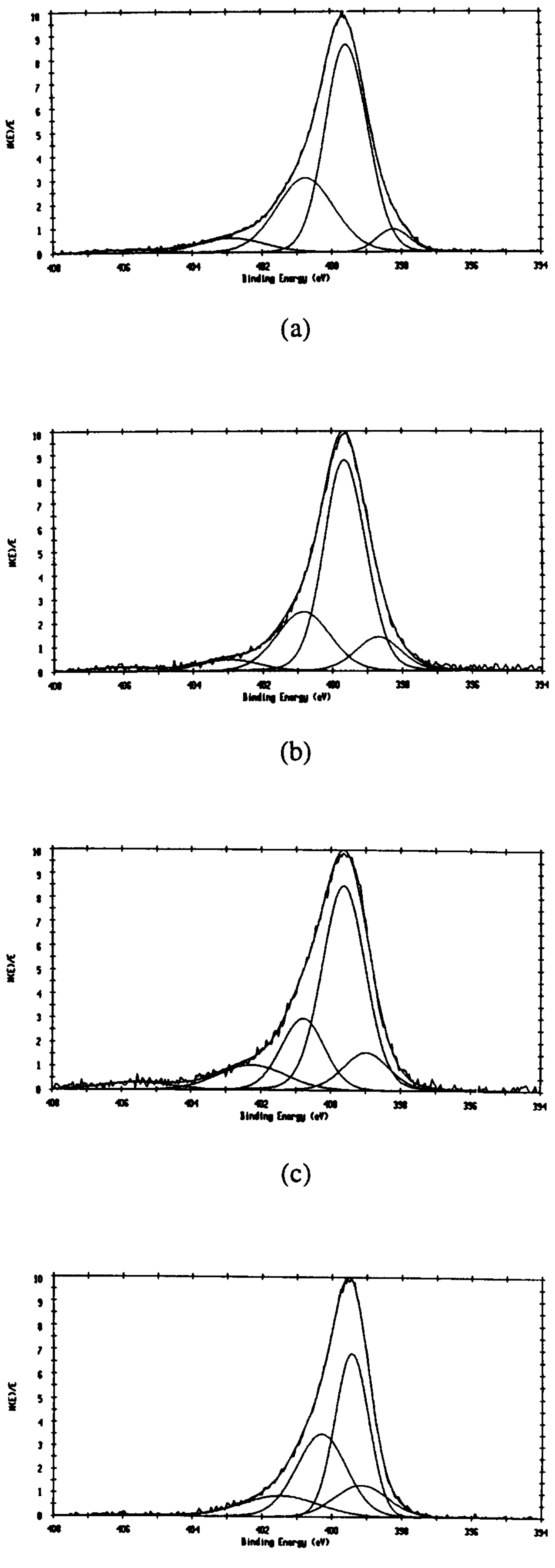
Figure 4 N_{1s} XPS spectra: (a) PANI; (b) PANI-R; (c) PANI-RO

XPS spectra

Figure 4(a)–(c) are the N_{1s} XPS spectra of PANI, PANI-R and PANI-RO. *Table 3* contains the deconvolution results. The N_{1s} spectrum of PANI can be resolved into five peaks at 398.20, 399.39, 400.72, 402.57 and 405.80 eV. According to results previously reported[11,13,22], the former four peaks are attributed to the four different kinds of nitrogen atoms in the following structural units:



The intensities of the peaks at 400.72 and 402.57 eV are very small, indicating that the concentrations of positively charged nitrogen atoms are very low in PANI. The last peak



(a)

(b)

(c)

(d)

Figure 5 N_{1s} XPS spectra: (a) PANI-H; (b) PANI-RH; (c) PANI-ROH; (d) PANI-RI

Table 4 Deconvolution results of N_{1s} XPS spectra of PANI-H, PANI-RH, PANI-ROH and PANI-RI

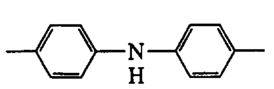
Sample	Binding energy (eV)	Percentage of total area (%)
PANI-H	398.23	4.76
	399.56	58.55
	400.75	28.89
	402.86	6.31
	405.76	1.49
PANI-RH	398.69	10.82
	399.64	60.83
	400.84	21.71
	402.95	4.68
	405.97	1.96
PANI-ROH	398.99	11.20
	399.64	55.59
	400.81	19.32
	402.25	10.59
	405.57	3.30
PANI-RI	399.17	12.72
	399.44	41.69
	400.31	32.65
	401.48	12.05
	405.52	0.89

at 405.80 eV is very weak and is the N_{1s} shake-up satellite of the ionized nitrogen atoms in the PANI molecular chains[23].

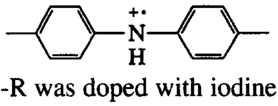
Comparing the N_{1s} spectra of PANI-R and PANI, the PANI-R spectrum is composed of a lower N_I (398.30 eV) peak intensity and a higher N_{II} (399.48 eV) peak intensity than PANI. It indicates that some of the quinoid structural units in PANI were reduced to benzenoid structural units, confirming the *FT*-i.r. and NMR results. As shown in *Figure 4*(c) and *Table 3*, the relative intensity of the peak due to N_{II} (399.30 eV) is much lower in the PANI-RO spectrum than in the PANI-R spectrum. It indicates that the concentration of the benzenoid structural units was decreased for the oxidized PANI-R. Moreover, the intensities of the peaks at higher binding energy are greater in the N_{1s} spectrum of PANI-RO.

Figure 5(a)–(d) are the N_{1s} XPS spectra of PANI-H, PANI-RH, PANI-ROH and PANI-RI. The deconvolution results are listed in *Table 4*. The PANI-H spectrum is composed of a weaker N_I peak (398.23 eV) but a stronger N_{III} peak (400.75 eV) than the PANI spectrum. It shows that protonation took place in the quinoid diimine nitrogen atoms and a large number of radical cations were formed. As a result, PANI-H had a high conductivity. Similar changes are also observed in the N_{1s} spectra of PANI-RH and PANI-ROH.

The N_{1s} and $I_{3d5/2}$ XPS spectra of the iodine-doped PANI-R (i.e. PANI-RI) are shown in *Figures 5 and 6*, and the corresponding deconvolution results are listed in *Tables 4 and 5*, respectively. In the N_{1s} XPS spectrum of PANI-RI, the intensity of the N_{II} peak (399.44 eV) is much lower while the intensity of the N_{III} peak (400.31 eV) is higher than those in the PANI-R and PANI-RH spectra. It means that some



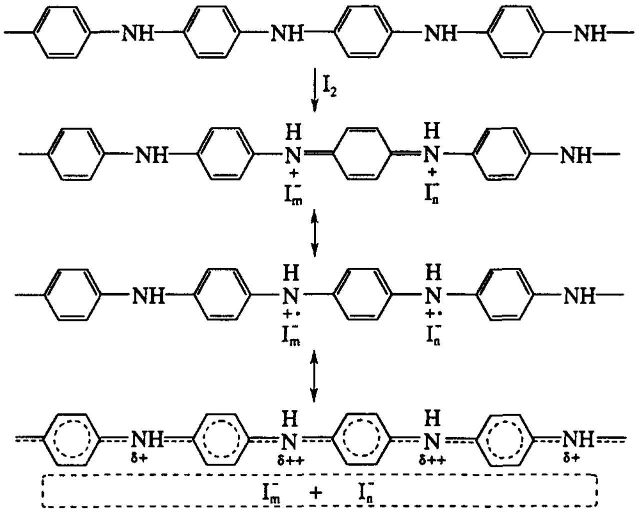
units in PANI-R were changed to



units when PANI-R was doped with iodine. The $I_{3d5/2}$ XPS spectrum of PANI-RI can be resolved into two peaks at 618.53 and 619.98 eV. They are attributed to the I_3^- and

I_5^- anions, respectively, according to the work of Slaneck *et al.*[24] and Kang *et al.*[25] on iodine-doped polyacetylene and polypyrrole.

In combination with the *FT*-i.r. results, the reaction mechanism in the iodine-doping of PANI-R can be depicted as follows:



where I_m^- and I_n^- are mainly I_3^- or I_5^- anions. When PANI-R was treated with iodine, an oxidative doping reaction would take place. As a result, a highly conjugated π system, which is similar to the HCl-doped emeraldine form of polyaniline[21], was formed in the PANI-RI molecular chains. Consequently, PANI-RI exhibited high conductivity.

TGA thermograms

Figures 7 and *8* are the TGA results for the instrinsic and doped polyanilines, respectively. The analytical results are shown in *Table 6*. The small fractions of weight loss before 120°C are attributed to the loss of moisture in the polyaniline sample[26,27]. The amounts of weight loss due to evaporation of moisture are greater for PANI-H, PANI-RH and PANI-ROH than PANI, PANI-R and PANI-RO, indicating that the HCl-doped polyanilines absorbed water readily. The TGA results agree with the elemental analysis results shown in *Table 1*. Matveeva *et al.*[26] reported that it was very difficult to remove the bound water completely by drying. On the other hand, the weight loss for PANI-RLI is very small up to 120°C.

Table 5 Deconvolution results of $I_{3d5/2}$ XPS spectrum of PANI-RI

Sample	Binding energy (eV)	Percentage of total area (%)
PANI-RI	618.53	61.85
	619.98	38.15

As shown in *Figure 7* and *Table 6*, there is very little weight loss for PANI up to 365°C, indicating that PANI had very good thermal stability. However, a very significant weight loss begins to occur at 365°C due to thermal decomposition of the molecular main chains. For PANI-R, although the onset decomposition temperature (T_d) is almost the same as that of PANI, the temperature at 50% weight loss ($T_{50\%}$) is much higher than that of PANI, revealing a better thermal stability of PANI-R. The authors believe that the main reason is that PANI-R molecular chains consisted mainly of the benzenoid structural units which have better thermal stability than the quinoid structural units. When PANI-R was oxidized to PANI-RO, its T_d and $T_{50\%}$ were much lower than those of PANI and PANI-R, meaning that the thermal stability was degraded drastically.

When PANI, PANI-R and PANI-RO were doped with HCl to form PANI-H, PANI-RH and PANI-ROH, respectively, there were not great changes in the T_d and $T_{50\%}$ except PANI-H. However, the HCl-doped polyanilines showed much greater weight loss before T_d than the undoped polyanilines. The weight loss between 120 and 250°C was mainly due to the evolution of the dopant HCl[28]. As shown in *Figure 8* and *Table 6*, the thermal stability of PANI-RI was worse than that of PANI-RH and PANI-R. It was probably because some of the benzenoid structural units in PANI-R were oxidized into the quinoid structural units during the iodine-doping process. The weight loss for PANI-RI between 120 and 250°C was mainly due to the evolution of the dopant iodine.

CONCLUSIONS

When the emeraldine base form of polyaniline (PANI) was treated with hydrazine, most of the quinoid structural units in PANI molecular chains would be reduced to benzenoid structural units. The hydrazine-reduced polyaniline (PANI-R) was doped with HCl or iodine. However, the conductivity of HCl-doped PANI-R (i.e. PANI-RH) was

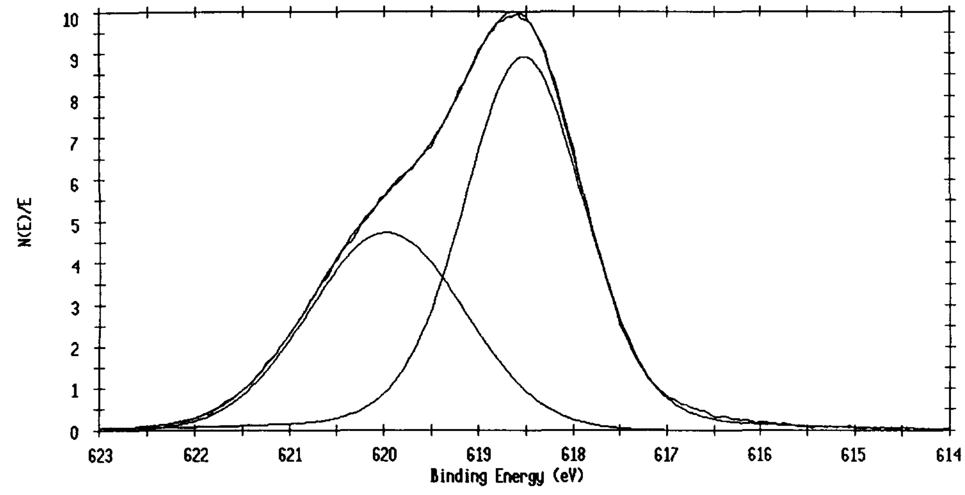


Figure 6 $I_{3d5/2}$ XPS spectrum of PANI-RI

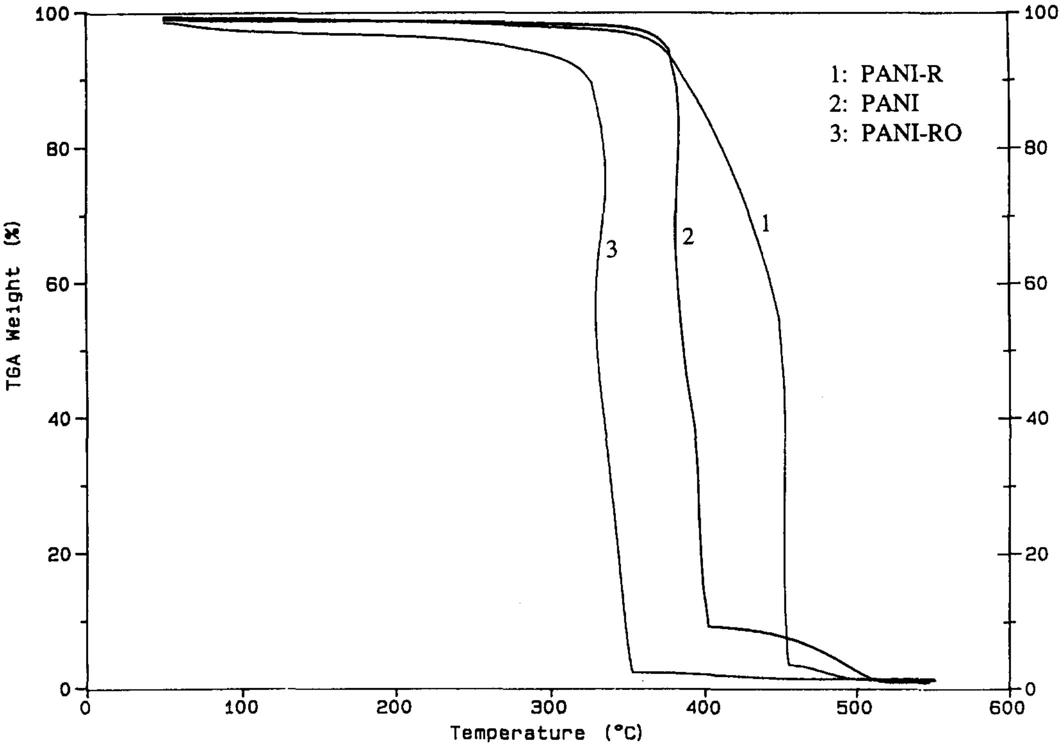


Figure 7 TGA curves of PANI, PANI-R and PANI-RO (note: the abnormality in temperature at the precipitous points of the curves is due to insufficient heat supply by the furnace during the thermal decomposition of molecular main chains)

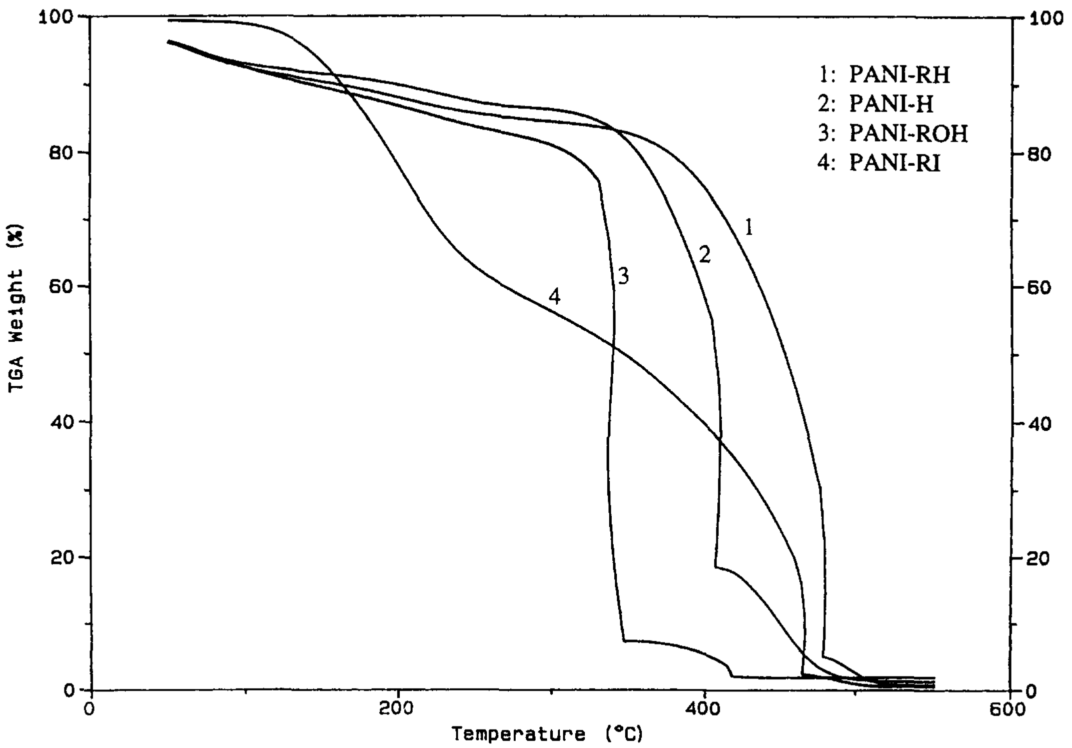


Figure 8 TGA curves of PANI-H, PANI-RH, PANI-ROH and PANI-RI (note: the abnormality in temperature at the precipitous points of the curves is due to insufficient heat supply by the furnace during the thermal decomposition of molecular main chains)

much lower than that of HCl-doped PANI (i.e. PANI-H). On the other hand, iodine-doped PANI-R (i.e. PANI-RI) showed very high electrical conductivity. *FT*-i.r. and XPS results indicated that some benzenoid structural units in PANI-R were oxidized to quinoid structural units during the iodine-doping process. As a result, a highly conjugated π system might be formed in the PANI-RI molecular chains. These results reveal that quinoid stuctural units play an important role in the electrical conductivity of polyaniline. Since the benzenoid structural units have better thermal stability than the quinoid structural units, the thermal stability of PANI-R was better than that of PANI. The TGA results showed that the dopants, both HCl and iodine, were almost completely removed from the HCl- and iodine-doped polyanilines below 250°C. In addition, PANI-R was oxidized again by potassium dichromate. The thermal

Table 6 TGA results of various forms of polyaniline

Sample	Weight loss at 120°C (%)	Onset decomposition temperature T_d (°C)	Weight loss at T_d (%)	Temperature at 50% weight loss $T_{50\%}$ (°C)	Temperature at 90% weight loss $T_{90\%}$ (°C)
PANI	1.5	364.8	3.4	385.9	401.6
PANI-R	0.8	368.0	4.5	450.0	451.6
PANI-RO	3.2	322.7	9.4	329.7	346.9
PANI-H	7.7	339.6	16.5	406.3	448.2
PANI-RH	7.9	365.4	18.4	451.3	478.1
PANI-ROH	9.1	323.5	22.4	338.8	344.2
PANI-RI	1.9	357.3	51.9	346.9	464.7

stability of the oxidized PANI-R (i.e. PANI-RO) was poor and the conductivity of HCl-doped PANI-RO was much lower than that of HCl-doped PANI.

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