

Thermal and XPS Studies on Polyaniline Salts Prepared by Inverted Emulsion Polymerization

B. Sreedhar,¹ M. Sairam,² D. K. Chattopadhyay,³ Pragnya Paromita Mitra,¹ D. V. Mohan Rao³

¹*Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad, India*

²*Center of Excellence in Polymer Science, Karnatak University, Dharwad, India*

³*Organic Coatings and Polymers Division, Indian Institute of Chemical Technology, Hyderabad, India*

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ABSTRACT: Conductive polyaniline salts were synthesized by inverted emulsion polymerization method and were characterized by thermogravimetric analysis (TGA), thermogravimetry-mass (TGA-MS) analysis, and X-ray photoelectron spectroscopy (XPS) methods. The various characteristic fragments evolved during the thermal degradation of polyaniline were identified. The weight loss of dopants as well as sodium lauryl sulfate decomposition were identified at different temperatures from TGA-MS analysis. The kinetic analysis of the thermal decomposition processes of polyaniline

in doped state was performed. Broido, Chang, and Friedman methods were used for the evaluation of kinetic parameters in nitrogen atmosphere. High resolution XPS analysis was used to provide a method of differentiating the presence of nitrogen and carbon associated in the different environments in the polyaniline base and doped-samples. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 499–508, 2006

Key words: polyaniline; degradation; XPS

INTRODUCTION

Conducting polymers have attracted significant attention in recent decades because of their potential applications in various fields. Among these polymers, polyaniline (PANI) is unique due to ease of preparation, excellent environmental stability, good room temperature conductivity, and other potential applications. As a result, it has been studied extensively and has emerged as the most promising candidate for commercial applications.^{1–3} The possibility of synthesizing and doping polyaniline with protonic acid dopants containing different types of counter-ions is one of the key factors responsible for the versatility of this class of polymers. The protonation of PANI emeraldine base (PANI-EB) or its derivatives with organic acids can be used for the protonation of electrically conducting polymers with improved processability.⁴ Inverted emulsion polymerization⁵ is one among the various methods^{6–11} reported for the preparation of polyaniline. Inverted emulsion polymerization consists of an aqueous solution of the monomer that is emulsified in a nonpolar organic solvent, for example, chloroform, as in the present study, and the polymerization is initiated with an oil soluble initiator, for

example, benzoyl peroxide and sodium lauryl sulfate was used as surfactant. During the course of the reaction, polyaniline remains as a soluble component in the organic phase.⁵ Therefore, surfactant as well as mineral acid groups are present as dopants on the PANI prepared by inverted emulsion polymerization whereas the PANI prepared by bulk polymerization contains only acid as dopant. Inverted emulsion polymerization technique results in polyaniline soluble in the organic phase whereas bulk polymerization technique results in polyaniline salt in powder form, which is insoluble in common organic solvents.

Several researchers have reported the electrochemical stability and thermal degradation of conducting polyanilines. Wang et al.¹² have shown that the thermal treatment of doped polyaniline could result in reduction in the conductivity due to the crosslinking reaction. Yue et al.¹³ have shown that the sulfonation of polyaniline results in increased thermal stability of the parent polyaniline. Lacroix and Diaz¹⁴ have proposed that thermal decomposition of polyaniline occurs in two stages. The first stage was attributed to the loss of moisture whereas the second stage was associated with the breakdown of polymer backbone. Patil et al.¹⁵ have proposed a three-step sequence for the thermal degradation of doped polyaniline. Neoh et al.¹⁶ have shown that the emeraldine base of polyaniline is stable up to about 500°C. Yang et al.¹⁷ have reported the thermal decomposition of undoped and doped polyaniline. Matveera et al.¹⁸ have reported the occurrence of two kinds of bound water in polyaniline

Correspondence to: B. Sreedhar (sreedharb@iict.res.in).

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line. However, these studies were carried out on the polyaniline prepared by bulk polymerization technique. The thermal degradation studies on the polyaniline prepared by inverted polymerization were confined to polyaniline sulfosalicylic acid salt.⁵ So far in the literature, no detailed studies have been carried out to identify the mass fragments evolved during the thermal decomposition of polyaniline salts prepared either by bulk or inverted emulsion polymerization technique. To our knowledge, the only report is from Gomez et al.,¹⁹ where the authors have studied the pyrolytic decomposition of polyaniline (emeraldine and pernigraniline) at 700°C by using a mass spectrometry detector. In the present study, PANI doped with mineral and dicarboxylic acids and prepared by inverted emulsion polymerization has been characterized by TGA-MS and XPS techniques. Thermal degradation of polyaniline salts doped with inorganic acids and dicarboxylic acids were carried out to study the fragmentation of polyaniline on thermal treatment. XPS technique was used to find out the role of surfactant on the polymerization of aniline by inverted emulsion polymerization. Kinetic study of the thermal decomposition process of polyaniline salts prepared by inverted emulsion polymerization is carried out, and the activation energies and reaction orders are presented. The polyaniline salts were converted to their corresponding bases PANI-base (H_2SO_4), PANI-base (HNO_3), or PANI-base (HCl). The regeneration of PANI salts from the PANI-base was monitored. The polyaniline base [PANI-base (PANI- H_2SO_4)] prepared from polyaniline-sulfuric acid salt was redoped to polyaniline salts such as PANI-RD-HCl, PANI-RD- H_2SO_4 , PANI-RD- HNO_3 . The dedoping and the redoping of polyaniline were also examined using XPS. To the best of our knowledge, this is the first report on the TGA-MS studies of polyaniline degradation prepared by inverted emulsion polymerization.

EXPERIMENTAL

Materials

Aniline (reagent grade) from E. Merck was distilled prior to use. Reagent grade sodium lauryl sulfate (SLS), acids, solvents chloroform (BDH, India) were used without further purification. Maleic acid, maleic anhydride, phthalic anhydride methanol, and acetone were purchased from S.D. fine chemicals (Mumbai, India) and were used as received. Reagent grade benzoyl peroxide (BDH, India) was recrystallized from chloroform/methanol system.

Procedure for the synthesis of polyaniline salts doped with mineral acids

Polyaniline salts were prepared by inverted emulsion polymerization as reported earlier.⁵ Benzoyl peroxide

(4.85 g) was dissolved in 60 mL chloroform in a 250-mL round bottomed flask. To this solution, 40 mL aqueous solution containing sodium lauryl sulfate (1.5 g) was added slowly while stirring which gave an emulsion. To this emulsion, 90 mL aqueous solution containing 2.4 mL aniline and mineral acid (9 mL H_2SO_4 /17.5 mL HCl /12.6 mL HNO_3) was added drop wise (15–20 min interval) and stirred constantly at 30°C for a period of 24 h. The organic layer that contains polyaniline salt and the aqueous layer were separated from the reaction mixture. Polyaniline salt in solution form (PANI-chloroform solution) was isolated by separating the organic layer, and the organic layer was washed thrice with deionized water and kept on sodium sulfate and finally filtered. Polyaniline salt in the powder form was isolated by pouring the chloroform solution into acetone. Polyaniline salt was obtained by filtration; the obtained polyaniline salt was washed with deionized water, acetone, and finally with methanol. The sample was dried at 100°C till constant weight.

The polyaniline salts were named as PANI-HCl, PANI- H_2SO_4 and PANI- HNO_3 for the hydrochloric, sulfuric, and nitric acid doped polyaniline, respectively.

Synthesis of polyaniline base

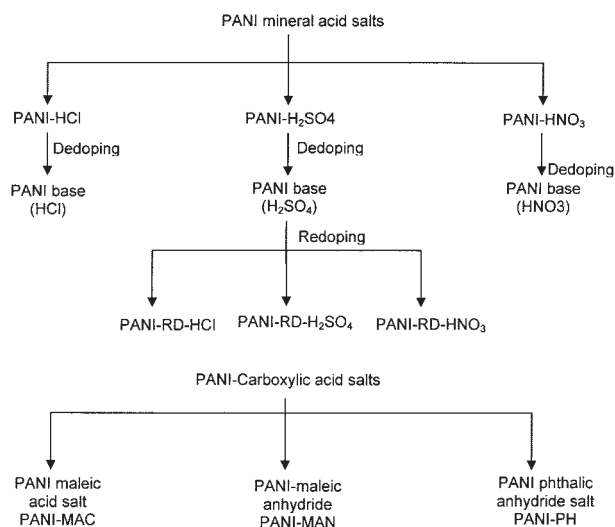
Polyaniline salt synthesized with different acids such as sulfuric, nitric, or hydrochloric acid was dedoped using aqueous sodium hydroxide solution. Polyaniline salt (1.0 g) was stirred in 100 mL of 1N sodium hydroxide solution for 12 h at ambient temperature. The solution was filtered to get the base form of polyaniline, and it is washed with sodium hydroxide solution followed by deionized water and finally with acetone. The powder was dried at 100°C till constant weight.

Synthesis of polyaniline salt from polyaniline base-redoping to salt

Polyaniline base [PANI-BASE (H_2SO_4)] (1.0 g) prepared from polyaniline-sulfuric acid salt was stirred with 1M acids such as hydrochloric acid, sulfuric, or nitric for 12 h. The solution was filtered to recover the redoped polyaniline salt. The obtained polyaniline salt was washed with 1M acid, followed by deionized water and finally with acetone. The powder was dried at 100°C till constant weight. The prepared PANI salts were named as PANI-RD-HCl, PANI-RD-(H_2SO_4), and PANI-RD- HNO_3 , when the base was treated with HCl , H_2SO_4 , or HNO_3 acid, respectively.

Procedure for the preparation of polyaniline with dicarboxylic acids

Sodium lauryl sulfate (1.0 g) was dissolved in 20 mL deionized water and mixed with a solution containing



Scheme 1 Dedoping and redoping steps of different polyaniline salts synthesized.

3.0 g of benzoyl peroxide in 30 mL chloroform. The milky white emulsion thus formed was stirred mechanically at 35°C. Solution containing aniline (1 mL) and maleic acid (2.9 g) or maleic anhydride (2.45 g) or phthalic anhydride (3.33 g) in 50 mL of deionized water was added drop wise to the above mixture over a period of ~20 min. The reaction was allowed to proceed for 8 h at 35°C. The color of emulsion at this time becomes green. The reaction mixture was separated into two layers, the lower oily green phase containing the polyaniline dicarboxylic acid salt and upper aqueous phase. The upper aqueous phase was removed by means of a separating funnel and the oily green phase was added to the 300 mL acetone. The precipitated polyaniline powder (1.2 g) was filtered, washed with 500 mL deionized water, and finally washed with 250 mL acetone.

The polyaniline salts so obtained were named as PANI-MAC, PANI-MAN, and PANI-PH when maleic acid, maleic anhydride, and phthalic anhydride were used, respectively, as dopants. Scheme 1 shows the dedoping and redoping steps of different polyaniline salts synthesized.

Characterization of polyaniline salts

Thermogravimetric analyses (TGA) of different PANI salts were carried out on a Mettler Toledo TGA/SDTA 851^e instrument (Zurich, Switzerland) in nitrogen atmosphere (flow rate, 30 mL/min) at a temperature from 25 to 600°C at a heating rate of 10°C/min. The sample sizes were in the range of 9–10 mg. The TGA instrument was coupled to Balzers Thermostar Quadrapole Mass GSD 300T, which can measure atomic mass of evolved gaseous fragments up to 300 amu. X-ray photoelectron spectroscopic analyses were car-

ried out on KRATOS AXIS 165 X-ray Photoelectron Spectrometer. The X-ray gun was operated at 15 kV and 20 mA. Survey and high-resolution spectra were collected using 40 and 80 eV pass energy, respectively, with Mg K α 1253.6 eV radiation. The analyzer chamber was degasified and the pressure was kept at as low as $\sim 10^{-8}$ Torr. Samples were mounted on double-sided adhesive tape; excess loose powder was shaken off, leaving enough samples for analysis. Spectral analysis was carried out using the standard software for quantification and peak fitting. Quantification was based on peak areas calculated from the high-resolution spectra. All spectra are presented charge-balanced and energy-referenced to C 1s at 284.6 eV. The total acquisition time per sample was 15 min.

RESULTS AND DISCUSSION

PANI-HCl, PANI-H₂SO₄, and PANI-HNO₃ samples were prepared with inverted emulsion polymerization pathway using benzoyl peroxide oxidizing agent. PANI-HCl, PANI-H₂SO₄, and PANI-HNO₃ samples were dedoped using aqueous sodium hydroxide solution. The amount of dopant present in the polymer chain was calculated based on the amount of polyaniline salt and polyaniline base.

The value of dopant per aniline unit (0.27) and yield (69.7%) of the polyaniline-sulfate and polyaniline-nitrate salts were found to be nearly the same. However, lower yield (49.7%) was obtained for polyaniline-hydrochloride salt. The dedoped polyaniline base [PANI-BASE (H₂SO₄)] was redoped to polyaniline salt using 1M sulfuric acid, nitric acid, or hydrochloric acid.

Thermal degradation of polyaniline salts

The relative thermal stability of the synthesized PANI-salts was evaluated from TGA data. The values of T_{2ON} (initial decomposition temperature for the second step of decomposition), T_{3ON} (initial decomposition temperature for the third step of decomposition), T_{2MAX} (temperature of maximum rate of weight loss for the second step), T_{3MAX} (temperature of maximum rate of weight loss for the third step), T_{EN} (final decomposition temperature), % weight loss at 210°C, % weight loss at 370°C, and char yield at 460°C are tabulated in Table I. The corresponding thermogravimetric curves are shown in Figures 1–3 along with TGA-MS for PANI-H₂SO₄, PANI-HNO₃, and PANI-MAC, respectively. From these figures it is observed that the thermograms reveal a common feature in all the acids and undergoes a three-step decomposition profile irrespective of the counter-ion used. The first step of degradation is small and occurring between 80 and 120°C with 4–8% weight loss, which is attributed to the desorption of superficial water molecules asso-

TABLE I
Thermal Stability Data of Polyaniline Salts

Sample	T_{2ON}	T_{2MAX}	T_{2EN}	T_{3ON}	T_{3MAX}	T_{3EN}	wt % at 210°C	wt % at 370°C	wt % at 460°C
PANI-HCl	200.7	253.6	268.0	469.8	500.9	525.7	89.0	68.8	65.0
PANI-H ₂ SO ₄	234.7	251.3	270.2	—	—	—	91.8	61.8	52.1
PANI-HNO ₃	199.8	267.8	280.6	457.4	491.2	522.6	91.8	73.2	65.0
PANI-MAC	236.2	264.0	284.3	457.0	482.2	518.1	94.1	61.8	57.2
PANI-MAN	231.5	255.8	268.7	—	—	—	91.4	72.3	47.5
PANI-PH	220.8	262.6	288.7	456.6	488.2	520.9	92.8	59.4	54.9

ciated with the doped PANI.^{4,20} The second stage of decomposition, followed by the first step corresponds to the loss of dopants (dedoping) and low molecular weight fragments of the polymer that starts above 200°C with an ending temperature more than 268.0°C.²¹ The third step of degradation was due to the decomposition of the polymer chain, which starts above 456°C and ends above 518°C.²² The nature of the DTG curves showed the complexity of the degradation following two to three steps of which two major steps are involved. The second decomposition step of different inorganic acid doped PANI salts corresponds to 17, 22, and 29% weight loss for PANI-HCl, PANI-HNO₃ and PANI-H₂SO₄, respectively. The sec-

ond step decomposition of different carboxylic acid-doped PANI salts corresponds to 32.5%, 30.4%, and 16.0% weight loss for PANI-MAC, PANI-MAN, and PANI-PH, respectively. In the third step, the weight loss that corresponds to 21, 25, 13, and 15.2% for PANI-HCl, PANI-HNO₃, PANI-MAC, and PANI-PH, respectively, was associated with the chain degradation. From the TGA curve of the investigated samples shown in Figure 4, it is observed that the doped polymers are significantly less thermally stable than those of their base [PANI-base (H₂SO₄)] because the dopants decompose at an early stage. After the initial weight

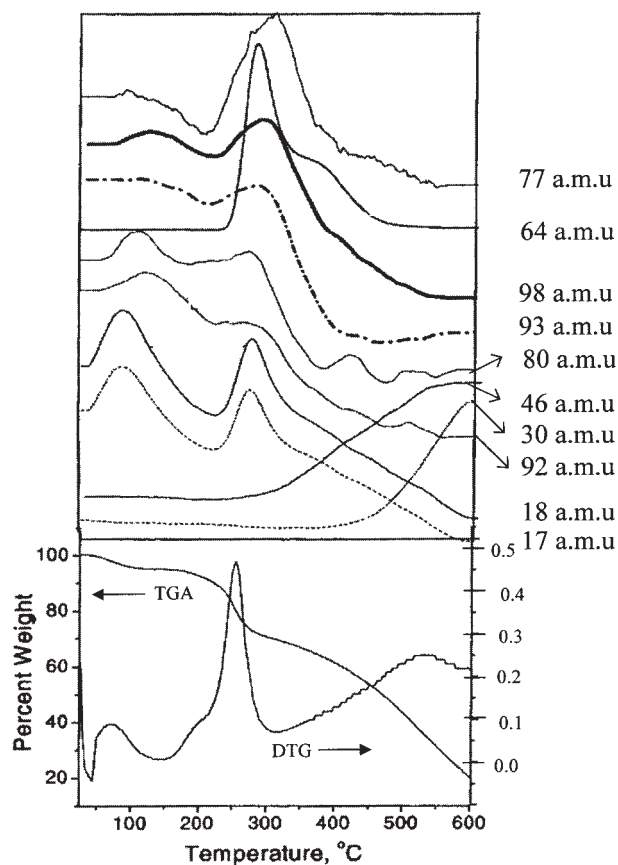


Figure 1 The TGA and TGA-MS curves of PANI-H₂SO₄.

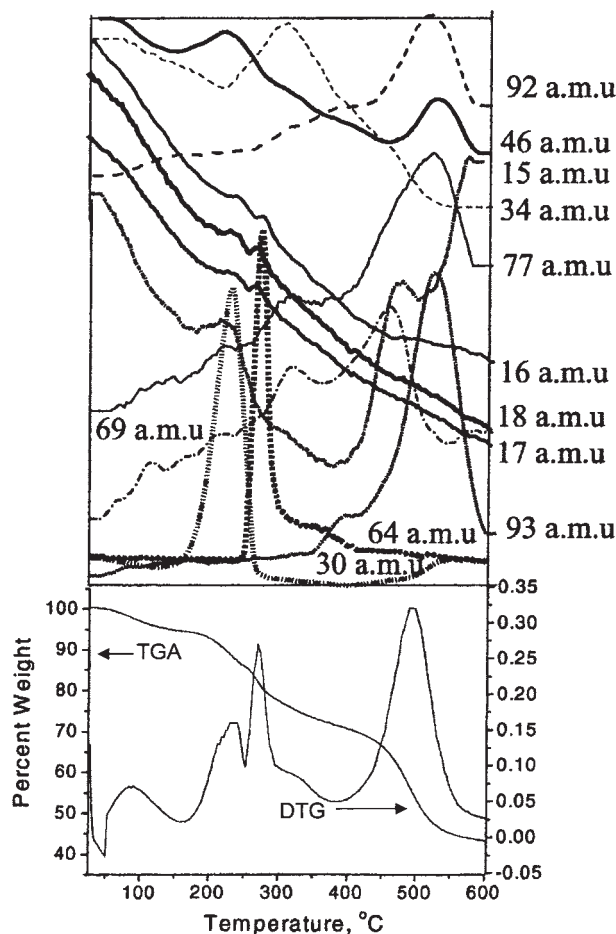


Figure 2 The TGA and TGA-MS curves of PANI-HNO₃.

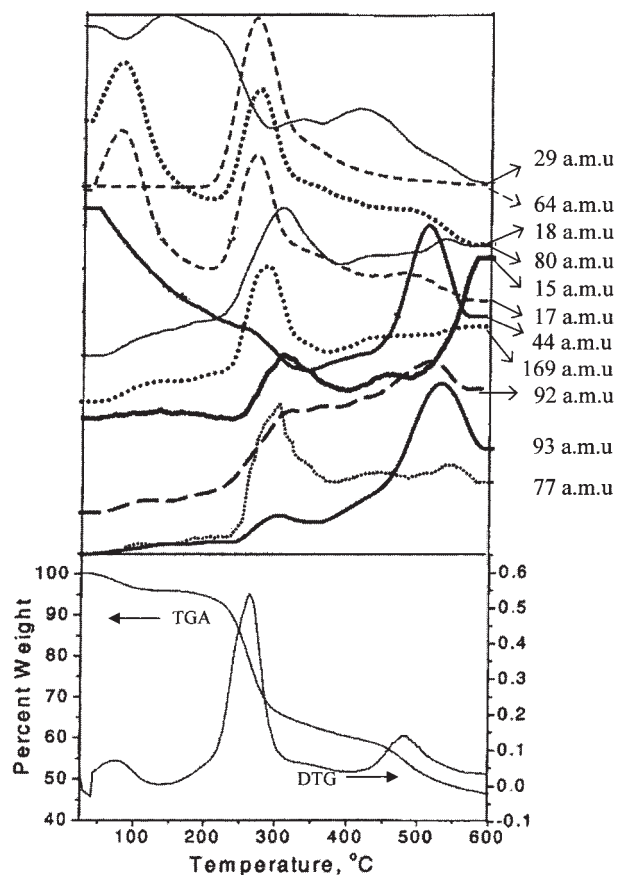


Figure 3 The TGA and TGA-MS curves of PANI-MAC.

loss, for example, PANI-base shows a slow weight loss, which may be assigned to the loss of low molecular-weight oligomer, and does not show significant weight loss until 450 °C, where PANI chains begin to decompose. PANI-H₂SO₄ shows lower stability at higher temperature, when compared to the other inorganic acid doped polyaniline salts. Similarly for the dicarboxylic acid doped polyaniline, PANI-MAN has lower stability and higher temperature than the other dicarboxylic acid doped polyaniline, PANI-MAC, and PANI-PH. These studies reveal that the type of dopant anion employed affects the thermal properties of the resulting PANI.²³⁻²⁵

TGA-MS studies

The mass fragments observed for the polyaniline doped with inorganic acid and dicarboxylic acids are shown in Figures 1 to 3 for PANI-H₂SO₄, PANI-HNO₃, and PANI-MAC, respectively. The mass fragments observed for the inorganic acid doped PANI were *m/z* of 15 (NH), 16 (NH₂), 17 (OH), 18 (H₂O), 30 (NO— from HNO₃ doped PANI), 34 (H₂S), 36 (Cl— from HCl doped PANI), 37 (HCl— from HCl doped PANI), 46 (NO₂— from HNO₃ doped PANI), 64 (SO₂— from H₂SO₄ doped PANI as well as from the surfactant), 69

(HNO₃— from HNO₃ doped PANI), 77 (C₆H₅), 80 (SO₃— from H₂SO₄ doped PANI), 92 (C₆H₅NH), 93 (C₆H₅NH₂) and 98 (H₂SO₄— from H₂SO₄ doped PANI). The mass fragments observed for the carboxylic acid doped PANI were *m/z* of 15 (NH), 17 (OH), 18 (H₂O), 29 (C₂H₅— from maleic acid and maleic anhydride), 44 (CO₂), 64 (SO₂— from the surfactant), 77 (C₆H₅), 80 (SO₃— from surfactant), 92 (C₆H₅NH), 93 (C₆H₅NH₂) and 169 (C₆H₅—NH—C₆H₅ arises from the main chain).

The mass fragments, *m/z* of 17 and 18 were observed for all the analyzed samples between the temperature of 80 and 120 °C, which suggests that the first step was due to the loss of superficial water molecules present as moisture associated with the doped PANI. In the second step of degradation, *m/z* values corresponding to the fragments evolved were due to the loss of both the dopant and the degradation of the dopant. Figure 2 shows the peak corresponding to *m/z* 15, 16, 17, 18, 30, 34, 46, 64, and 69 between 135 and 350 °C. The presence of *m/z*, 17 and 18 correspond to OH and H₂O evolved in the second step of decomposition, which corresponds to the release of molecularly bound water (chemisorbed water) and also from the decomposition of dopants such as H₂SO₄ or HNO₃ in PANI salts. Scheme 2 shows the structure of PANI-base and PANI-salts derived from mineral acids as well as from the dicarboxylic acid and acid anhydride. The *m/z* corresponding to 30 (NO) and 64 (SO₂) in the second decomposition zone of PANI-HNO₃ clearly indicates that both HNO₃ and surfactant were present as dopants and were released at two different temperature ranges namely 140–275 °C and 260–425 °C. Since the surfactant SLS contains —O—SO₃[−]Na⁺ group at the end of the chain, which can be converted to —O—SO₃H upon protonation. Therefore, in this study the surfactant also acts as the dopant. In the third step of degradation, *m/z* corresponding to 15, 46, 69, 77, and 92 were observed, which suggests that third step of decomposition was attributed to the main chain degradation. As can be seen from Figure 1 and

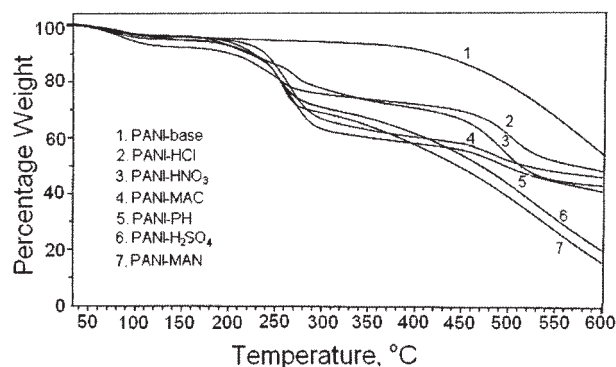
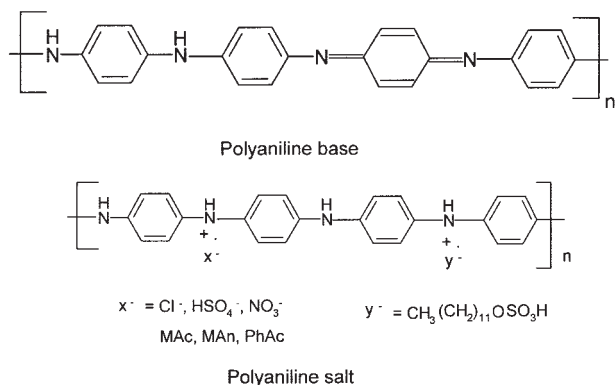


Figure 4 TGA curves of the various PANI salts doped with inorganic acids and dicarboxylic acids.



Scheme 2 The structure of PANI-base and PANI-salts derived from mineral acids as well as from dicarboxylic acid and acid anhydride.

Figure 2 the mass fragments m/z 77, 92, 93 corresponding to the backbone decomposition of the PANI doped with H_2SO_4 were observed in the second decomposition step whereas in PANI- HNO_3 and PANI- HCl it was observed in the third decomposition step and suggests lower thermal stability of PANI- H_2SO_4 in comparison to PANI- HNO_3 and PANI- HCl .

In the case of PANI doped with dicarboxylic acids (PANI-MAC, Fig. 3), m/z values 17, 18 were observed in the first step of decomposition and are attributed to the loss of physisorbed moisture. The evolution of CO_2 (m/z , 44) starts in the second stage at 260°C and continued upto 600°C . The origin of m/z , 64 and 80 suggests that the surfactant is also acting as a dopant and its loss starts from 250°C and continues up to 475°C . The fragments m/z 92, 93, and 169 were observed in the third stage of decomposition and was due to the main chain decomposition. Similar observations were made for PANI-PH also. In the PANI-MAN sample, the mass fragments m/z 77, 92, 93 corresponding to the backbone decomposition of the PANI appeared mainly in the second decomposition step and gradually continued up to the third decomposition step. These observations suggest lower stability of PANI-MAN than PANI-MAC and PANI-PH.

Thermal stability and degradation kinetics

In TGA, reaction rate is defined as the derivative of conversion with respect to time. The normalized TG curves were used for the percentage conversion evaluation.

In the case of polymer degradation, kinetic analysis of thermogravimetric data from a weight loss curve is based on the formal kinetic equation

$$d\alpha/dt = k(1 - \alpha)^n \quad (1)$$

where α is the fraction of material decomposed at time t , n is the reaction order, and k the rate constant.

In TGA, conversion is defined as the ratio of percentage mass loss of the sample after a certain period of time (t) to the total mass in percentage at the beginning of the experiment (100), i.e.,

$\alpha = (100 - w_t)/100$; where w_t is the sample mass in percentage at time t .

The combination of eq. (1) and the empirical Arrhenius expression gives the following expression:

$$d\alpha/dt = Z \exp(-E/RT)(1 - \alpha)^n \quad (2)$$

where Z is the preexponential factor, E is the activation energy of thermal decomposition, and R the gas constant. Introducing the heating rate, β ,

$$d\alpha/dt = Z/\beta \exp(-E/RT)(1 - \alpha)^n \quad (3)$$

Equation (3) is the fundamental expression of analytical methods to calculate kinetic parameters on the basis of TGA data.^{26–29} Based on this expression, a considerable number of methods to derive kinetic triplets E , n , and Z from thermogravimetric curves have been developed. Since the value of kinetic triplets depends upon atmosphere, sample mass, sample shape, flow rate, heating rate, and the mathematical treatment used to evaluate the data, a lot of controversy exists in the literature about the use of different kinetic models for calculation of kinetic triplets. But still researchers used such kind of models for a comparison of stability.^{26–29} In the present investigation, we have used the Broido,³⁰ Friedman³¹ and Chang³² methods for the calculation of kinetic triplets.

Broido equation³⁰ has the form:

$$\ln \ln(1/Y) = E/R(1/T) + \text{Constant} \quad (4)$$

where $Y = (w_0 - w_t)/(w_0 - w_\infty)$ is the fraction of the number of initial molecules not yet decomposed; and $w_t, w_\infty (= 0)$, and w_0 are the weight at time t , the weight at infinite time, and the initial weight, respectively. The slope of the plot of $\ln(\ln(1/Y))$ versus $1/T$ is related to the activation energy.

Friedman method³¹ utilizes the following equation:

$$\ln(d\alpha/dt) = \ln Z + n \ln(1 - \alpha) - E/RT \quad (5)$$

The E value can be determined from the slope of the plot of $\ln(d\alpha/dt)$ versus $1/T$ from a single nonisothermal TGA and single DTG curves, using eq. (5). The plot of $\ln(1 - \alpha)$ against $1/T$ will give the n value from the maximum slope of the line.

Chang method³² uses the following equation:

$$\ln[(d\alpha/dt)/(1 - \alpha)^n] = \ln Z - E/RT \quad (6)$$

The plot of $\ln[(d\alpha/dt)/(1 - \alpha)^n]$ versus $1/T$ will give straight line for the accurate value of n in the linear

TABLE II
Kinetic Parameters for the Thermal Degradation of Polyaniline Salts

Sample	Broido method		Friedman method				Chang method			
	E (kJ mol ⁻¹)	R^2	E (kJ mol ⁻¹)	R^2	$\ln Z$ (min ⁻¹)	n	E (kJ mol ⁻¹)	R^2	$\ln Z$ (min ⁻¹)	n
PANI-HCl										
Second step	23.6	0.982	41.2	0.985	12.5	2.0	43.3	0.984	10.9	2.0
Third step	26.9	0.98	43.3	0.985	16.5	2.0	43.3	0.98	16.5	2.0
PANI-HNO ₃										
Second step	23.4	0.98	42.6	0.987	17.8	2.0	41.6	0.978	14.1	1.8
Third step	31.6	0.975	34.4	0.985	16.0	2.1	37.1	0.99	14.0	2.1
PANI-H ₂ SO ₄										
Second step	28.1	0.99	40.2	0.98	10.1	2.0	43.8	0.985	18.3	2.0
PANI-MAC										
Second step	49.4	0.98	46.9	0.98	18.9	2.1	47.3	0.982	21.7	2.3
Third step	14.3	0.99	17.1	0.98	14.6	2.0	20.2	0.98	17.7	2.0
PANI-MAN										
Second step	42.0	0.98	45.3	0.99	15.7	1.9	45.4	0.983	23.5	1.8
PANI-PH										
Second step	42.0	0.994	46.9	0.982	14.5	2.0	44.3	0.991	16.5	2.0
Third step	16.9	0.99	22.0	0.983	16.0	2.0	28.0	0.99	17.2	2.0

regression analysis. Thus, E and $\ln Z$ values can be obtained from the slope and intercept of the straight line, respectively.

The E_2 values of PANI-HCl, PANI-H₂SO₄, and PANI-HNO₃ were 23.6, 23.4, and 28.1 kJ mol⁻¹, respectively, as calculated from Broido method, which suggests that the dopant loss followed almost the same activation energy for the second step of decomposition (Table II). The E_2 values of all the dicarboxylic acid-doped samples were found to be little higher than the corresponding mineral acid doped samples. The order of decomposition (n) in both the second and third step was found to be near 2¹⁶ as determined by the Friedman and Chang methods. The correlation coefficients (R^2) values in the regression analysis for all the used methods were more than 0.975. The pre-exponential factor $\ln Z$ was between 10 and 22 for all the analyzed samples, as calculated by Friedman and Chang methods. The E_3 values for PANI-MAC and PANI-PH were less than the corresponding E_2 values calculated using all the mentioned equations. For example, E_2 and E_3 values calculated using Broido equation of PANI-MAC and PANI-PH were 49.4, 14.3 kJ mol⁻¹, and 42.0, 16.9 kJ mol⁻¹, respectively.

X-ray photoelectron spectroscopy analysis

XPS analysis constitutes a powerful tool that allows one to characterize the doping degree of conducting polyaniline. From the characteristic binding energies of the photoelectron, the elements involved can be identified and the peak intensity can be related to the atomic concentration in the sample surface. In addition, the various intrinsic redox states of PANI as well as the different neutral and positive nitrogen species can be quantified from the properly curve-fitted N 1s

core-level spectrum.³³ The XPS survey scan of PANI-HCl shows the presence of oxygen (535 eV), nitrogen (400 eV), carbon (285 eV), chlorine (199 eV) and sulfur (168 eV). The elements carbon and nitrogen originated from the PANI backbone whereas the element chlorine is from the hydrochloric acid that was used during the preparation of polyaniline. The element sulfur was due to the surfactant (SLS) that was used as surfactant in the inverted emulsion polymerization of aniline. The survey spectrum of polyaniline base shows the presence of oxygen, nitrogen, and carbon. The absence of sulfur in the PANI-base spectrum indicates the complete dedoping of PANI-H₂SO₄. The presence of sulfur in the survey scan spectrum of PANI-RD-H₂SO₄ indicates the redoping of PANI base to PANI salt form.

Figures 5 and 6 represent the deconvoluted N 1s XPS spectra of all the PANI salts examined in the present study. The N 1s spectrum of PANI-base [Fig. 5(a)] could be resolved into three peaks centered at 398.5, 399.6, and 402.0 eV. These peaks were attributed to the quinine–diimine units, benzene–diamine units, and N-atoms of the semiquinone cationic radicals. In comparison with the former two peaks, the latter peak showed much lower intensity. The N 1s deconvoluted results of the PANI-BASE shows that the imine to amine ratio is 1 : 1, indicating the idealized emeraldine base structure.^{34,35} The decrease in concentration of imine units as evidenced by Figure 5 and the simultaneous appearance of peaks around 401.0–402.7 eV in the redoped PANI-RD-HCl, PANI-RD-H₂SO₄, and PANI-RD-HNO₃ indicate that substantial quantity of imine units are protonated. The presence of a small peak around 398.2 eV in the PANI salts spectra prepared by inverted emulsion polymerization indicates that

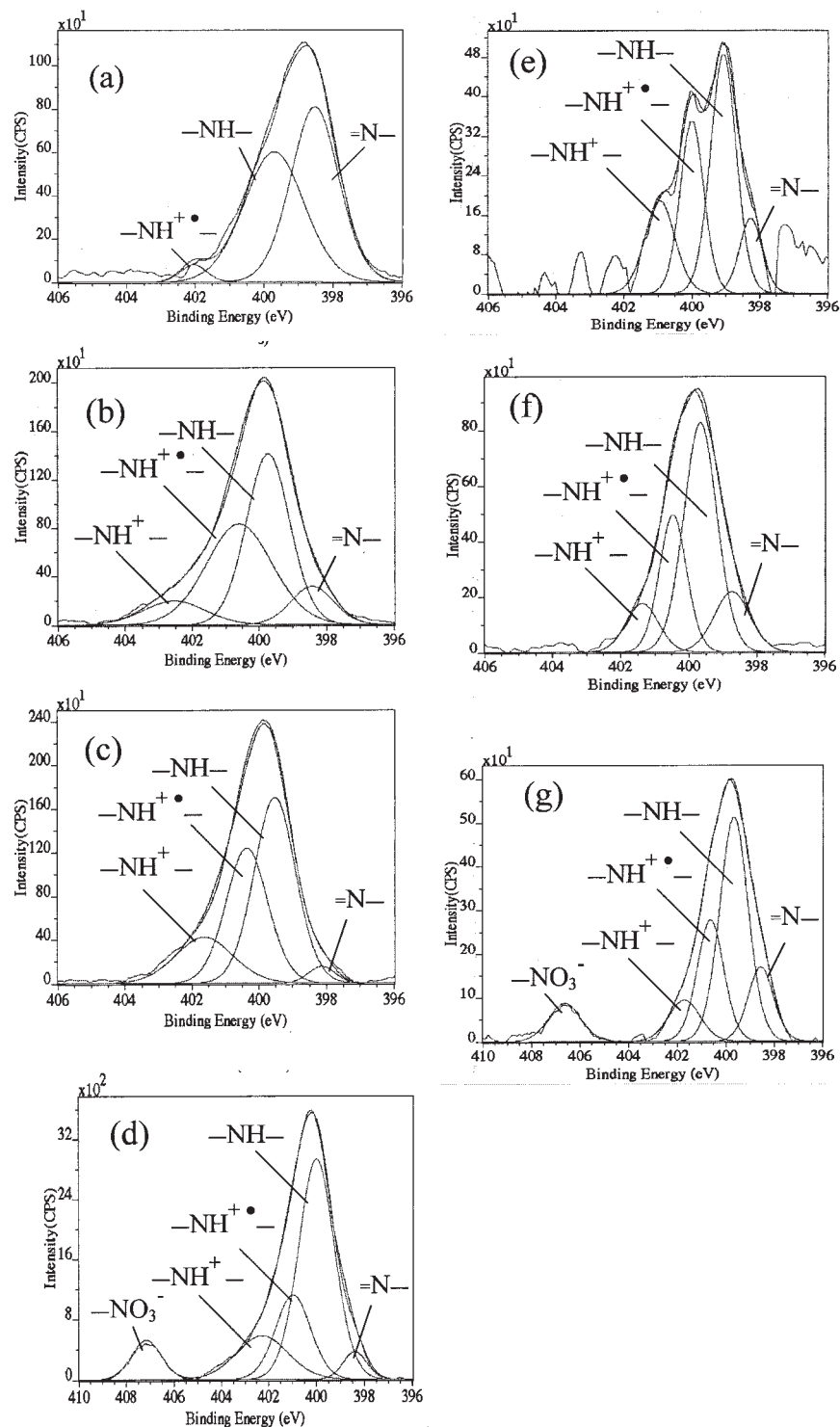


Figure 5 The N 1s deconvoluted spectra of (a) PANI-HCl, (b) PANI-H₂SO₄, (c) PANI-HNO₃, (d) PANI-RD-HCl, (e) PANI-RD-H₂SO₄, and (f) PANI-RD-HNO₃.

most of the imine units of the PANI backbone were protonated. The peak located at higher binding energy of ~ 401.9 eV was assigned to the generated iminium ions ($-\text{N}^+\text{H}-$) while the one at lower energy centered at ~ 400.5 eV indicates the presence of the radical cation ($-\text{N}^{\bullet+\text{H}}-$). For PANI-HNO₃

[see Fig. 5(d)] the peak due to the dopant NO_3^- was observed at 407.1 eV. The N 1s spectra of PANI-carboxylic acid salts [Fig. (6)] can be deconvoluted into four peaks. The imine peak around 398.6 and 398.7 eV was observed in the deconvoluted N 1s spectra indicating incomplete protonation.

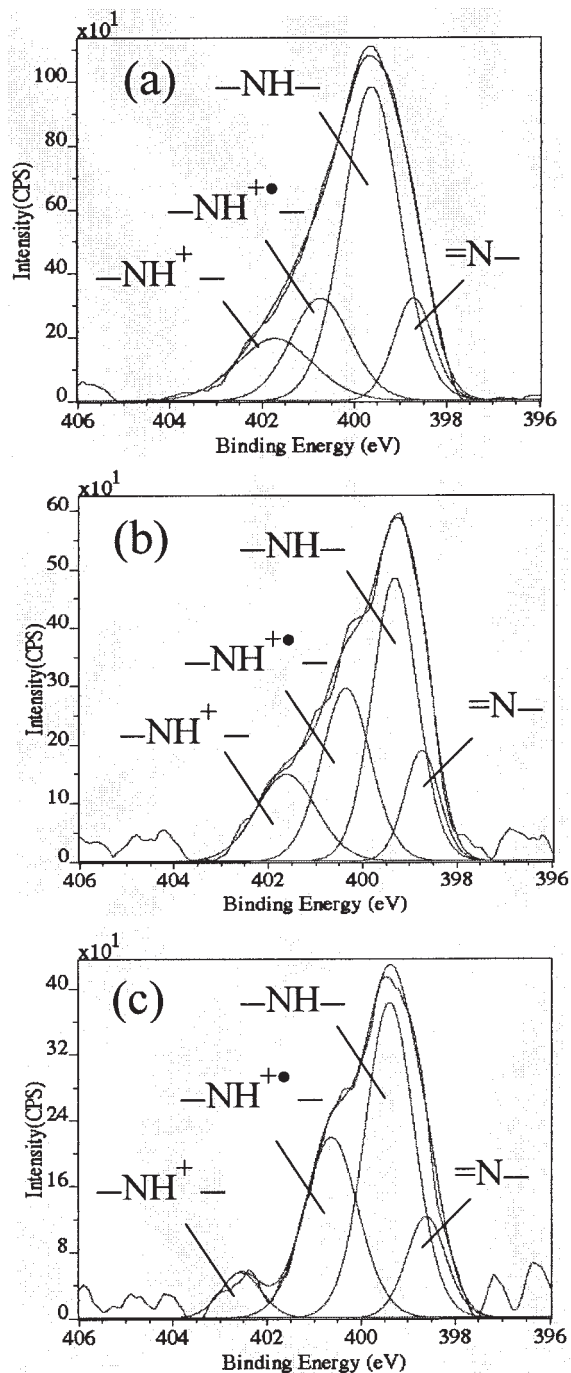


Figure 6 The Ni 1s deconvoluted spectra of (a) PANI-MAC, (b) PANI-MAN, and (c) PANI-PH.

The deconvoluted C 1s XPS spectra of PANI-carboxylic acid salts are shown in Figure 7 and could be resolved into four peaks at different binding energies. The first one at 284.6 eV corresponds to C—C or C—H bonds. The second one at 285.4 eV was assigned to C—N or C=N bonds and the third one at 286.4 eV was due to the C—O bonds. These two peaks had relatively large intensities. The fourth one (C4) at 287.4 eV corresponds to C—N⁺, C=N⁺, or C=O bonds.

When comparing the C 1s deconvolution results of the PANI-base and doped polyanilines, we have observed that the chemical environment of C-atoms was almost unchanged after doping, indicating that the doping reactions did not occur directly at the C-atoms. How-

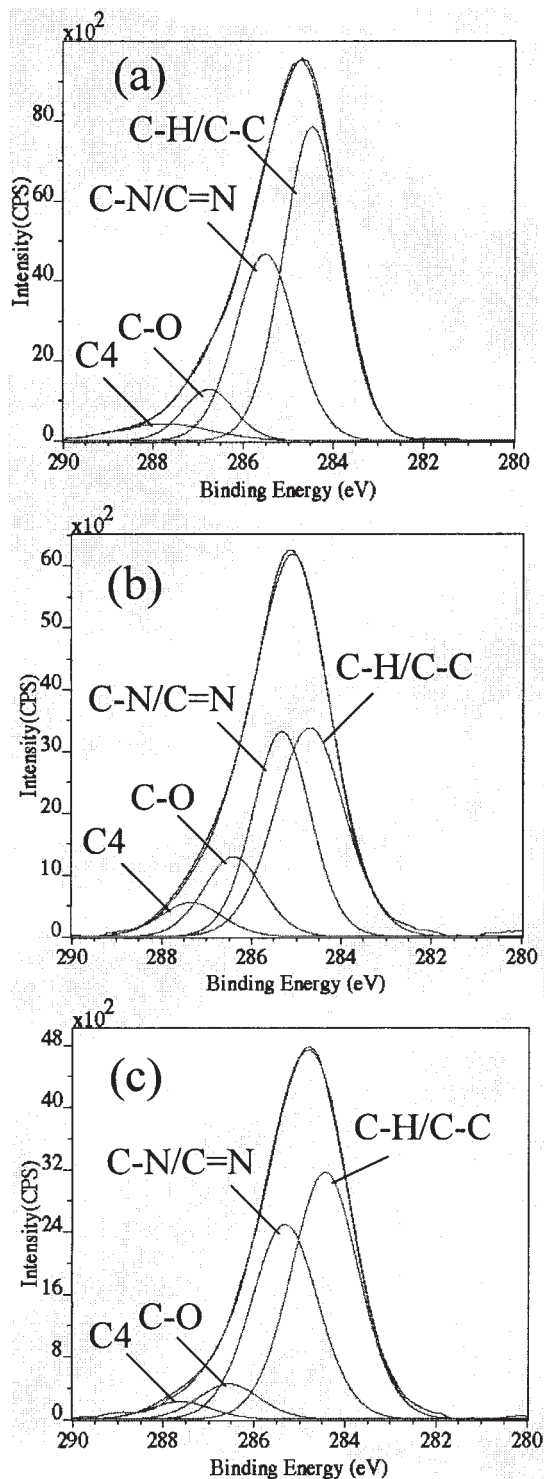


Figure 7 The C 1s deconvoluted spectra of (a) PANI-MAC, (b) PANI-MAN, and (c) PANI-PH. (C4 is due to C—W⁺, C=N⁺, or C=O).

ever, the situation was different for PANI-HCl and the C 1s deconvolution results showed that there were higher concentrations of C-atoms at the high binding energies. There were much greater changes in the chemical environment of the C atoms after HCl doping, which is the cause for its higher conductivity, as suggested by Zeng et al.³⁴ These studies demonstrate that the polyanilines when doped with protonic acids, protonation takes place preferentially at the N-atoms of the quinoid units. The C 1s deconvoluted results are consistent with the earlier results by Han et al.³⁵ on polyaniline/polyimide blends.

The element sulfur is found in all the polyaniline salts (PANI-HCl, PANI-H₂SO₄, PANI-HNO₃, PANI-MAC, PANI-MAN, PANI-PH) prepared by inverted emulsion polymerization, which comes from the surfactant (sodium lauryl sulfate) used in the synthesis of polyaniline salts. From the XPS analysis of polyaniline salts prepared by inverted emulsion polymerization, both the acids as well as the surfactant are found to act as dopants. The element sulfur was not observed in the case of redoped salts (PANI-RD-HCl and PANI-RD-HNO₃) indicating the complete dedoping of the polyaniline salt. The Cl 2p spectra of PANI-HCl and PANI-RD-HCl salts can be split into two peaks (Figure not shown). In PANI-HCl, the Cl 2p_{3/2} was observed at 198.6 eV and Cl 2p_{1/2} at 199.7 eV whereas for PANI-RD-HCl, Cl 2p_{3/2} of 197.1 eV and another at Cl 2p_{1/2} at 200.4 eV with an intensity ratio of 2:1 was observed.

CONCLUSIONS

Inorganic and dicarboxylic acid-doped polyaniline salts were prepared by inverted emulsion polymerization technique. The synthesized salts were studied for their thermal decomposition behavior and the observation suggests that the nature of dopant has a significant influence on the thermal stability. The thermogravimetric profiles and the evolved gas fragments correlate remarkably indicating a typical degradation scheme with water loss, dopant loss for protonated PANI, and polymer degradation. The kinetic triplets (E , $\ln Z$, and n) in the thermal decomposition were calculated. The second and third thermal decomposition of the investigated samples were found to follow second order as determined by the Friedman and Chang methods. High-resolution XPS analyses were used to provide a method of differentiating the pres-

ence of various nitrogen and carbons associated with different environment in the samples.

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