

# Characterization of Polyaniline via Pyrolysis Mass Spectrometry

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**ABSTRACT:** In this work, direct insertion probe pyrolysis mass spectrometry technique was applied to investigate the thermal and the structural characteristics of electrochemically prepared HCl and HNO<sub>3</sub>-doped polyaniline (PANI) films. It has been determined that the thermal degradation of both samples showed three main thermal degradation stages. The first stage around 50–60°C was associated with evolution of solvent and low-molecular-weight species adsorbed on the polymer, the second stage just above 150°C was attributed to evolution of dopant-based products, and the final degradation stage at moderate and elevated temper-

atures was associated with evolution of degradation products of the polymer. Chlorination and nitrolysis of aniline during the electrochemical polymerization were detected. Extent of substitution increased as the electrolysis period was increased. Furthermore, for the HNO<sub>3</sub>-doped PANI, the evolution of CO<sub>2</sub> at elevated temperatures confirmed oxidation of the polymer film during electrolysis. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 400–405, 2008

**Key words:** polyaniline; pyrolysis; thermal degradation; mass spectrometry

## INTRODUCTION

Among various conducting polymers, polyaniline (PANI) is one of the most investigated and promising candidate for applications such as energy storage, sensors, electronic devices, electromagnetic interference shielding, and inhibition of corrosion, because of its high stability toward air and moisture. It also possesses electrical conductivity for use in microelectronics and optoelectronics devices.<sup>1–6</sup> In any of the applications, the knowledge of the stability and degradation is of primary importance, and several studies have appeared in previous literature on the stability of polyaniline. Thermal stability of PANI was mainly investigated by means of thermogravimetric analyses.<sup>7–21</sup> In some of these studies, data from other characterization techniques such as elemental analysis, differential scanning calorimetry, X-ray photoelectron spectroscopy, infrared spectroscopy, UV–Visible spectroscopy, and conductivity measurements have been reported. The conductivity was clearly shown to decrease with time, at a rate depending on the nature of the dopant as well as on the morphology of the material.

Numerous studies were devoted to the thermal studies of polyaniline, and they showed that undoped

polyaniline (polyemeraldine base form) did not experience significant decomposition below 700 K.<sup>16,17</sup> The lower thermal stability of the conducting form is mainly attributable to the decomposition of the counterion. In general, three stages of thermal degradation, the first being due to removal of dopants, the second due to loss of low-molecular-weight oligomers or side products, and the final due to the degradation of backbone units of PANI were detected. It has been noticed that the thermostability of protonated PANI was the same as the stability of dopants.<sup>12</sup> Among the several studies on thermal degradation of PANI, only a few concentrated on identification of thermal degradation products. Gomez and Folch determined that benzene, aniline, phenylenediamine, and diphenylamine, and other greater oligomers and compounds derived from the cyclization reactions were the main thermal degradation products by pyrolysis-HRGC-MS.<sup>19</sup> In a more recent study, the weight loss of dopants during the thermal degradation of PANI was identified at different temperatures by TGA-MS analysis.<sup>20</sup> In this study, it was claimed that the first stage of degradation was due to the loss of superficial water molecules in the form of moisture associated with the doped PANI and the second step of degradation was due to release of chemisorbed water and decomposition of dopants. Evolution of water has also been studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).<sup>21</sup> It has been shown that the matrix of PANI contained water molecules participating in both reversible and irreversible

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adsorption. The obtained data were interpreted in terms of chemical interaction of water molecules with PANI chains through hydrolysis of imine bond of the polymer.<sup>21</sup>

Although there have been several studies on thermal stability of PANI, a detailed study for *in situ* characterization of degradation products is still missing in the literature. In the few studies involving the investigation of thermal degradation products, the techniques applied were limited to detection of stable degradation products only as the thermal degradation processes were carried outside the mass spectrometer. This study is a detailed investigation of thermal degradation behavior of PANI doped with HCl and HNO<sub>3</sub> via direct pyrolysis mass spectrometry that favors vaporization and, thus, allows the analysis of higher molecular mass and/or unstable pyrolyzates. In this technique, as the high vacuum system causes the removal of degradation products from the heating zone, secondary reactions and condensation reactions are avoided.<sup>22-24</sup>

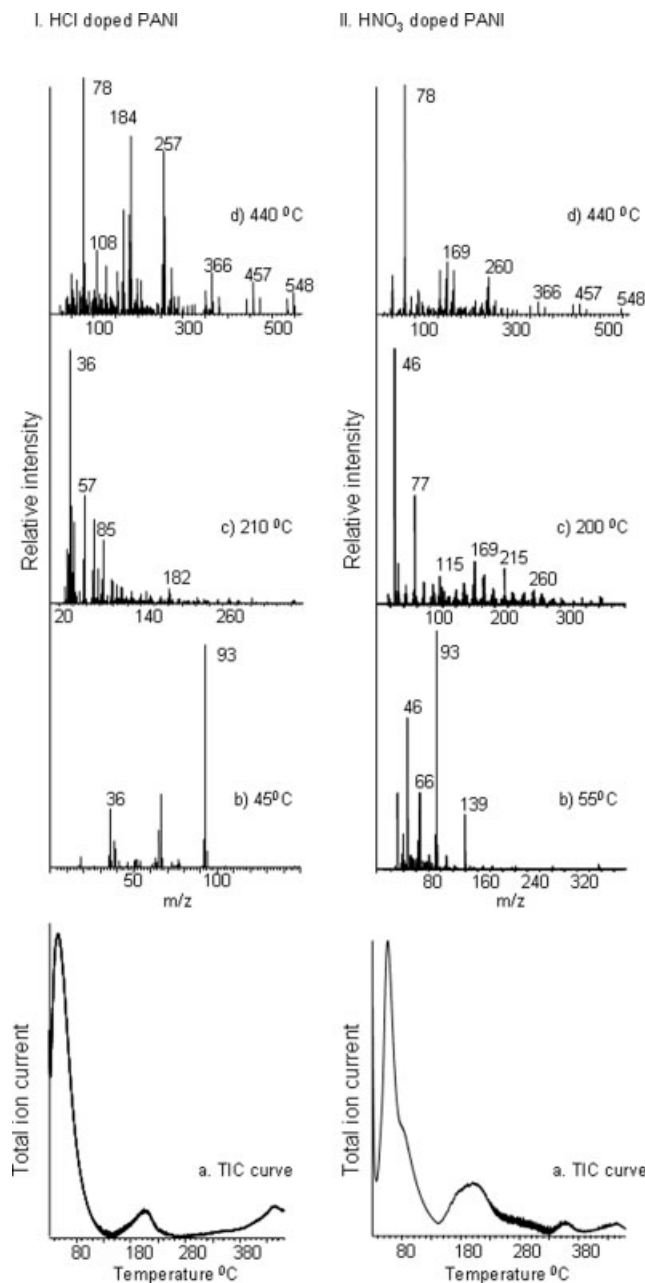
### EXPERIMENTAL

Pure aniline (0.5M) was electrochemically polymerized in a three compartment cell with a three-electrode configuration in 2.0M HCl or HNO<sub>3</sub> solution. Platinum plates (1.5 cm<sup>2</sup>) were used as working and counter electrodes, and Ag/Ag<sup>+</sup> was used as the reference electrode. A potentiostat (Potentiostat MODEL PS95D, Turkey) was used to perform electrolysis at 0.7 V. The polymer films were washed with distilled water several times to remove unreacted monomer as well as excess electrolyte and subsequently dried in vacuum.

The direct insertion probe pyrolysis mass spectrometry (DP-MS) system used for the thermal analyses consisted of a 5973 HP quadrupole mass spectrometer coupled to a JHP SIS direct insertion probe pyrolysis system with a maximum attainable temperature of 450°C. Samples (0.01 mg) were pyrolyzed in the flared glass sample vials. The temperature was increased at a rate of 10°C/min, the scan rate was 2 scans/s, and the mass range was 10–800 Da. Pyrolysis experiments were repeated using samples of the same PANI films and films obtained from parallel electrochemical polymerization processes.

### RESULTS AND DISCUSSIONS

Although both of the samples under investigation namely HCl and HNO<sub>3</sub>-doped PANI films showed comparable three main degradation stages, the trends above 100°C observed from the TIC curves where total ion yield varied as a function of temperature were significantly different. In Figure 1, the



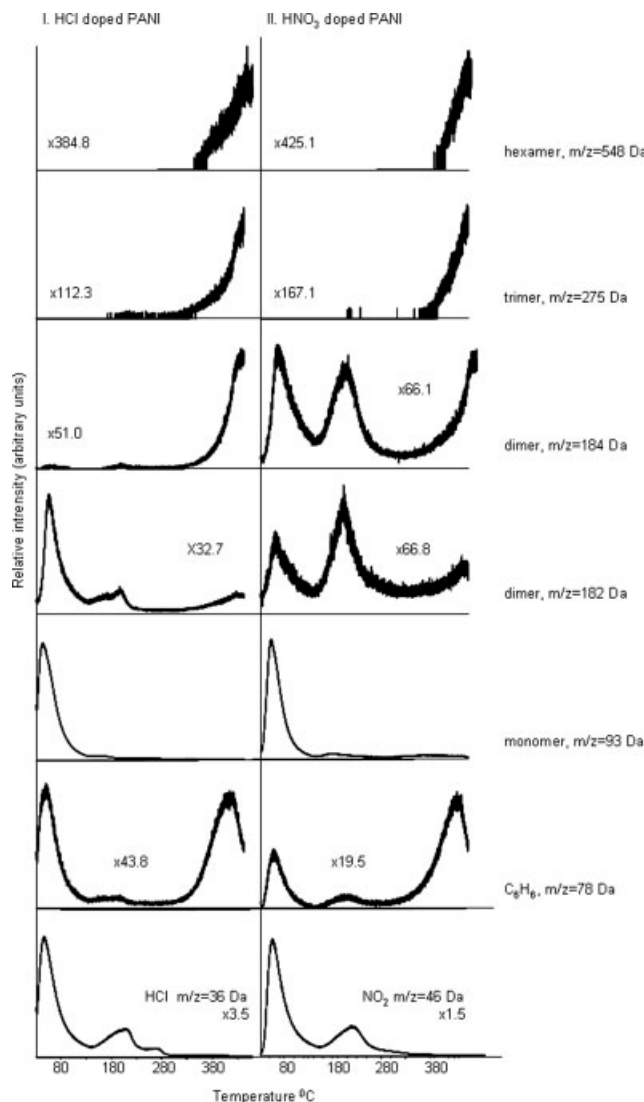
**Figure 1** Total ion current curve of (I) HCl and (II) HNO<sub>3</sub>-doped PANI and the mass spectra recorded at the TIC maxima.

total ion current, (TIC) curves and the pyrolysis mass spectra recorded at the maxima determined in the respective TIC curves of HCl, and HNO<sub>3</sub>-doped PANI are given. For the HNO<sub>3</sub>-doped PANI, the pyrolysis mass spectra recorded around 320 and 440°C were quite similar and thus only the mass spectra recorded at 440°C is shown in Figure 1. In general, peaks due to evolution of solvent and low-molecular-weight species adsorbed by the polymer, and those due to dopant-based products were detected in the pyrolysis mass spectra recorded around 50–60°C and just above 150°C, respectively. In the final

degradation stage at moderate and elevated temperatures, peaks due to degradation products of the polymer were recorded. For HNO<sub>3</sub>-doped PANI, decomposition of polymer in two regions around 320 and 440°C was attributed to presence of polymer chains with different molecular weights.

The low temperature evolutions were mainly due to the adsorbed dopant HCl yielding isotopic peaks at  $m/z = 36$  and  $38$  Da due to H<sup>35</sup>Cl and H<sup>37</sup>Cl respectively, NO<sub>2</sub> ( $m/z = 46$  Da) and unreacted monomer ( $m/z = 93, 77, 66,$  and  $39$  Da due to C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>, C<sub>5</sub>H<sub>6</sub>, or C<sub>4</sub>H<sub>3</sub>NH, and C<sub>3</sub>H<sub>3</sub>, respectively). Around 200°C, the yield of dopant-based products increased significantly for both samples. Furthermore, in the pyrolysis mass spectra of both samples recorded around this temperature, the relative intensity of the peak at  $m/z = 77$  Da due to C<sub>6</sub>H<sub>5</sub> increased about threefolds while that of the monomer decreased significantly indicating that it was not only due to aniline but also due to some other substances (such as oligomers) yielding C<sub>6</sub>H<sub>5</sub> fragment during thermal degradation and/or ionization inside the mass spectrometer. Thus, the data may strongly suggest that either low-molecular-weight oligomers or substituted benzenes also decomposed around this temperature range. In the final stage of pyrolysis, the presence of oligomer peaks (dimer, trimer, tetramer, and pentamer peaks at  $m/z = 184, 275, 366,$  and  $457$  Da, respectively) pointed out decomposition of the polymer itself. Detection of peak at 128 Da due to chloroaniline for the HCl-doped PANI and peak at 139 Da due to nitro aniline for the HNO<sub>3</sub>-doped PANI indicated substitution of aniline during electrolysis or/and thermal degradation processes. Another point that should be noted was the intense CO<sub>2</sub> peaks (CO<sub>2</sub> and CO at  $m/z = 44$  and  $28$  Da, respectively) in the pyrolysis mass spectra of the HNO<sub>3</sub>-doped PANI. These observations were slightly unexpected because actually in the case of direct pyrolysis mass spectrometry analysis, as the high vacuum system would rapidly remove the degradation products from the heating zone, secondary reactions and condensation reactions should be almost completely eliminated. To investigate when and how substitution and oxidation of the PANI films took place, pyrolysis experiments were repeated using samples prepared by electrolysis for 30 and 75 min. The results will be discussed later.

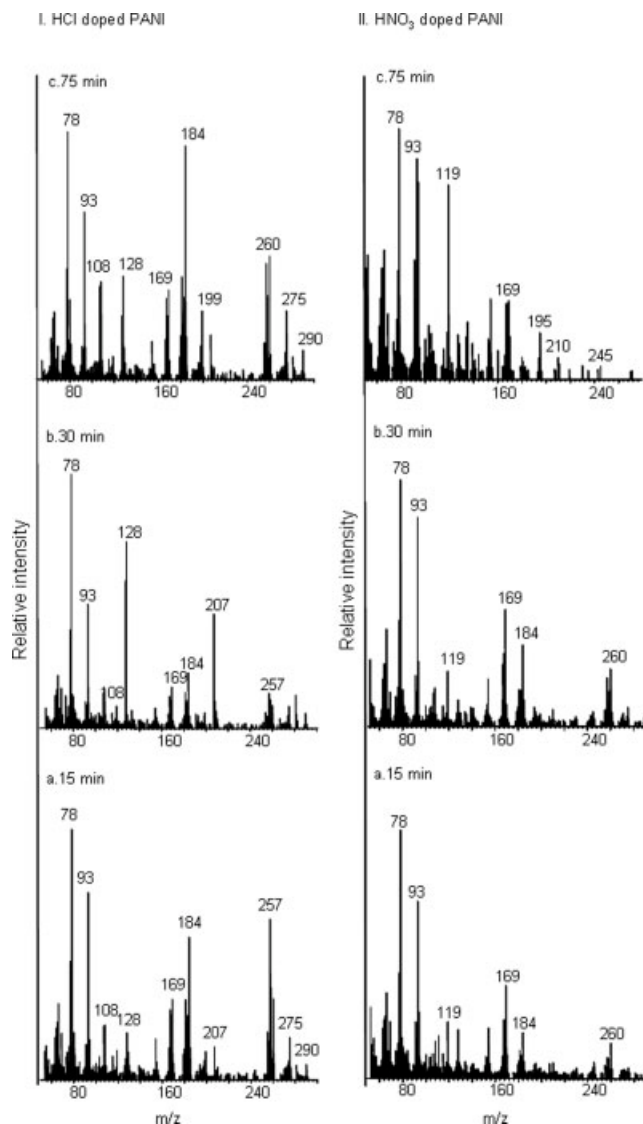
In Figure 2, the single ion pyrograms (evolution profiles) of some selected degradation products namely dopant-based products H<sup>35</sup>Cl ( $m/z = 36$  Da) and NO<sub>2</sub>, as well as PANI-based products C<sub>6</sub>H<sub>6</sub> ( $m/z = 78$  Da), aniline monomer ( $m/z = 93$  Da), aniline dimers ( $m/z = 182$  and  $184$  Da), trimer C<sub>6</sub>H<sub>5</sub>NC<sub>6</sub>H<sub>4</sub>NC<sub>6</sub>H<sub>4</sub> ( $m/z = 257$  Da), and hexamer ( $m/z = 548$  Da) are shown. The very low temperature evolution



**Figure 2** Single ion pyrograms of some selected ions recorded during the pyrolysis of (I) HCl and (II) HNO<sub>3</sub>-doped PANI.

of the monomer and dopant (below 80°C) can directly be associated with the loss of adsorbed unreacted monomer. Dopant-based products were also detected above 150°C. Though weak, peaks due to oligomers up to hexamer were detectable in the pyrolysis mass spectra recorded in the final stage of pyrolysis. In addition, the monomer yield was found to be relatively low in this region. These observations may be attributed to the crosslinked structure of the polymer where depolymerization reactions yielding mainly monomer are not likely.

The raw data of the samples prepared by electrolysis for 30 and 75 min are not presented here. However, the analysis of collected measurements was carried out, and it was found that both sets showed quite similar thermal behavior as well as three degradation stages. The main difference was noted in significant variations of the product distribution. The

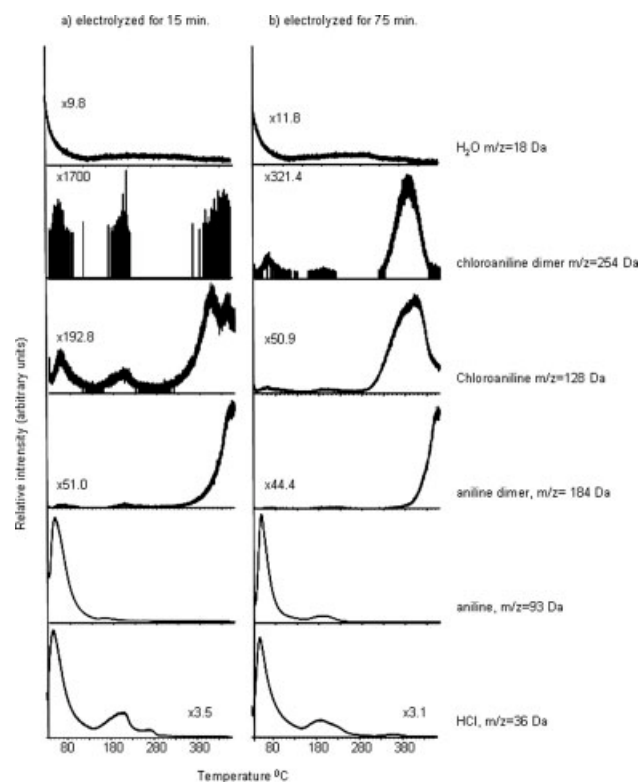


**Figure 3** Pyrolysis mass spectra of (I) HCl and (II)  $\text{HNO}_3$ -doped PANI prepared by electrolysis for (a) 15, (b) 30, and (c) 75 min at  $440^\circ\text{C}$ .

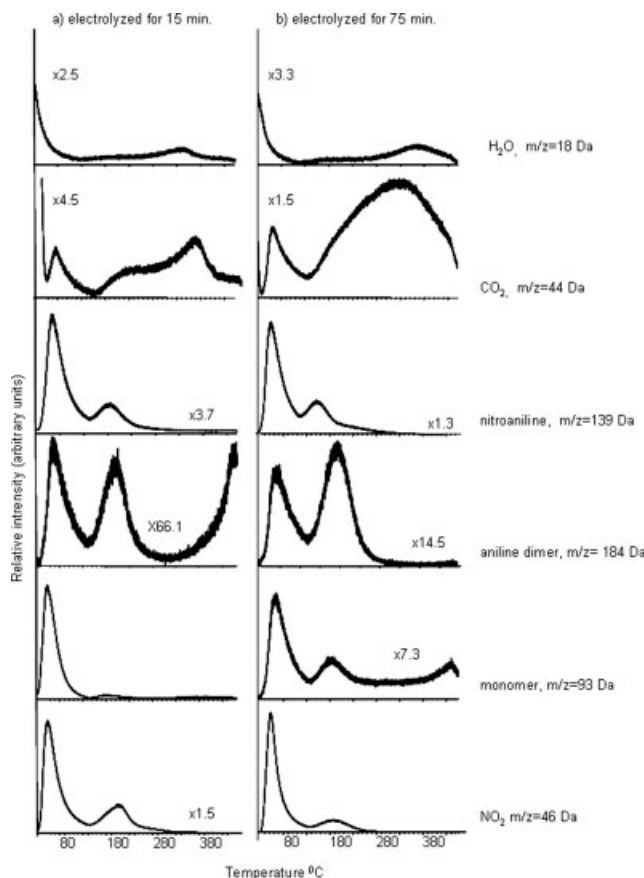
monomer to dopant ratio was almost independent of electrolysis period for the HCl-doped PANI, whereas significant decrease in the monomer to dopant ratio was noticed for the  $\text{HNO}_3$ -doped PANI. For the HCl-doped PANI, the yield of oligomers in the final stages of pyrolysis increased as the electrolysis period was increased from 15 to 75 min. On the other hand, an opposite trend for the  $\text{HNO}_3$ -doped PANI was noted; the relative intensity of oligomer peaks diminished as the electrolysis period increased. Above  $250^\circ\text{C}$ , it was considerably undetectable for the samples prepared by electrolysis for 75 min. In Figure 3, the pyrolysis mass spectra of the HCl and  $\text{HNO}_3$ -doped PANI films prepared by electrolysis for 15 to 75 min recorded at  $440^\circ\text{C}$  are given for comparison. The peaks representing the substitution of aniline ring by dopant, chloroaniline and nitroani-

line peaks in the pyrolysis mass spectra of the HCl and  $\text{HNO}_3$ -doped samples respectively become more abundant as the electrolysis period lengthened. Furthermore, during the pyrolysis of the  $\text{HNO}_3$ -doped PANI,  $\text{CO}_2$  evolution at elevated temperatures increased significantly indicating oxidation of the PANI.

In Figure 4(a,b) the evolution profiles of HCl ( $m/z = 36$  Da) aniline monomer ( $m/z = 93$  Da), aniline dimer ( $m/z = 184$  Da), chloroaniline ( $m/z = 128$  Da), dimer of chloroaniline ( $m/z = 254$  Da), and water ( $m/z = 18$  Da) detected during the pyrolysis of the HCl-doped PANI electrolyzed for 15 and 75 min are shown. Figure 5(a,b) shows the evolution profiles of NO ( $m/z = 30$  Da),  $\text{NO}_2$  ( $m/z = 46$  Da) monomer ( $m/z = 93$  Da), dimer ( $m/z = 184$  Da), nitroaniline ( $m/z = 139$  Da),  $\text{CO}_2$  ( $m/z = 44$  Da), and water ( $m/z = 18$  Da) detected during the pyrolysis of the  $\text{HNO}_3$ -doped PANI electrolyzed for 15 and 75 min. The relative intensities of chloroaniline and nitroaniline increased about three and fourfolds, respectively, as the electrolysis period increased from 15 to 75 min (Figs. 2, 4, and 5). Thus, it can be concluded that substitution reactions mainly took place during the electrochemical synthesis due to the reactions of dopant with aniline and/or polyaniline. In the pyrolysis mass spectra of the HCl-doped



**Figure 4** Single ion pyrograms of some selected ions recorded during the pyrolysis of HCl-doped PANI prepared by electrolysis of (a) 15, (b) 75 min.



**Figure 5** Single ion pyrograms of some selected ions recorded during the pyrolysis of  $\text{HNO}_3$ -doped PANI prepared by electrolysis of (a) 15, (b) 75 min.

PANI (Fig. 4), peaks due to chloroaniline ( $m/z = 128$  Da) and its dimer ( $m/z = 254$  Da) were recorded at elevated temperatures above  $350^\circ\text{C}$ . Thus, it can further be suggested that either the substituted monomer has been polymerized or PANI formed during the electrolysis has been chlorinated. On the other hand for the  $\text{HNO}_3$ -doped sample (Fig. 5), nitroaniline evolution mainly occurred at initial stages of pyrolysis and no related dimer or any other oligomer evolution could be detected throughout the pyrolysis process, hence confirming that only the monomer reacted with  $\text{HNO}_3$ .

Another point that should be noted was the increase in  $\text{CO}_2$  yield for the  $\text{HNO}_3$ -doped films with the increase in electrolysis period.  $\text{CO}_2$  evolution was almost negligible for the HCl-doped PANI samples. As all the samples were prepared and stored under the same conditions, it can be concluded that the oxidation of the  $\text{HNO}_3$ -doped PANI films was mainly due to reactions with  $\text{HNO}_3$  during the electrochemical synthesis process. Thus, it may further be concluded that oxidation and nitrolysis of aniline were very effective when  $\text{HNO}_3$  was used as dopant, and these reactions inhibited the electrochemical polymerization of polyaniline. The

decrease in oligomer yield at elevated temperatures for the  $\text{HNO}_3$ -doped PANI may be a result of this inhibition. During the evolution of water, a similar trend was observed. In general, there was a higher rate of releasing water for the  $\text{HNO}_3$ -doped PANI than in the case of the HCl-doped PANI samples. The evolution of absorbed water within the pyrolyzer, the vacuum system, and on the sample exponentially decrease for all the investigations up to  $100^\circ\text{C}$  and remained at a constant value thereafter, which was expected for the HCl-doped PANI. Actually, without baking the whole system for a long period of time during continuous pumping, it was almost impossible to eliminate all the adsorbed water from the surfaces. The same trend was also detected in the background pyrolysis mass spectra recorded with the same system under the same experimental conditions in the absence of sample. On the other hand, for the  $\text{HNO}_3$ -doped PANI evolution of water was detected in the final stages of pyrolysis, above the temperatures where dopant evolution has already completed and thus attributed to the degradation of oxidized polymer. This is contrary to Sreedhar et al.'s recent work<sup>20</sup> in which no explanation about the desorption of water that was adsorbed on the metallic parts of the system was given.

## CONCLUSION

Thermal degradation of the HCl and  $\text{HNO}_3$ -doped PANI films occurred in three main stages. Evolution of solvent and low-molecular-weight species adsorbed by the polymer was detected around  $50$ – $60^\circ\text{C}$ , and just above  $150^\circ\text{C}$ , dopant-based products were evolved. In the final degradation stage, at moderate and elevated temperatures, degradation of the polymer took place. Pyrolysis mass spectrometry analyses of the samples prepared by electrolysis for 15, 30, and 75 min indicated that the extent of substitution and oxidation reactions yielding chloroaniline, nitroaniline, and  $\text{CO}_2$  that were mainly due to the reactions of dopant ions with aniline during the electrochemical polymerization processes increased as the electrolysis period lengthened.

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