

The Characterization of Polyaniline and Polypyrrole Composites by 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 structural characteristics of electrochemically prepared polyaniline (PANI), polypyrrole (PPy), and their composites/copolymers synthesized either by electrochemical polymerization of pyrrole on PANI-coated electrode (PANI/PPy) or by coating PANI on PPy (PPy/PANI) in H₂SO₄ solutions. It has been determined that the polymer first coated on the electrode degraded to a certain

extent during the polymerization of the second. The extent of degradation was greater for PPy and increased with the increase in acid concentration. On the other hand, the detection of mixed dimers confirmed copolymer formation. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3130–3136, 2009

Key words: polyaniline; polypyrrole; composites; pyrolysis mass spectrometry

INTRODUCTION

Among various conducting polymers, polyaniline (PANI), polypyrrole (PPy), and their blends and composites are among the most widely studied ones.^{1–15} Electrochemical copolymerization of pyrrole (Py) and aniline (ANI) or electrochemical deposition of PANI and PPy layers on different substrates have been reported.^{9–13} Recently, PANI/PPy composites were prepared and certain interaction between PANI and PPy was confirmed by their morphology, conductivity, X-ray photoelectron spectroscopy, thermal gravimetric analysis (TGA), X-ray diffraction, and contact angle measurement. It has been shown that the different preparation conditions and even the storing time of the dispersions have significant influence on the properties of the resulting composites.¹⁴ Although, the thermal characteristics of PANI and PPy have also been the subject of several studies,^{16–25} there is very little literature on thermal stability of PANI/PPy copolymers and composites.^{26–29}

Upon exposure to elevated temperatures, changes in molecular structure, dedoping, and dopant degradation were proposed for PANI. The undoped PANI (polyemeraldine base form) did not experience significant decomposition below 700 K and the lower thermal stability of the conducting form is mainly attributable to the decomposition of the counterion.^{16–21} Thus, the thermostability of protonated PANI was

the same as the stability of dopants. Stability of PPy, thermal degradation, effect of temperature on conductivity, enhancement of thermal stability, kinetics of degradation of the electrical conductivity of PPy under thermal aging have been investigated.^{22–25}

In our previous studies, we applied direct pyrolysis mass spectrometry to investigate the thermal characteristics of electrochemically prepared PANI and PPy films.^{21,25} It has been determined that the thermal degradation of both samples showed three main thermal degradation stages; the first being due to removal of dopants, the second due to loss of low molecular weight oligomers, and the final due to the degradation of polymer backbone and decomposition of aromatic ring.

In this work, characteristics of electrochemically prepared PANI, and PPy and their composites/copolymers prepared by electrochemical deposition of either PANI on PPy-coated electrode or deposition of PPy on PANI-coated electrode in H₂SO₄ solutions were determined by direct pyrolysis mass spectrometry.

EXPERIMENTAL

Electrochemical polymerization

Electrochemical syntheses were performed in a three compartment cell with a three electrode configuration with the use of a potentiostat (Potentiostat MODEL Entek PS95D, Turkey). Platinum plates (1.5 cm²) were used as working and counter electrodes, and Ag/Ag⁺ was used as the reference electrode.

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Preparation of PANI: 0.1M pure ANI (Merck Chemicals Ltd.) was electrochemically polymerized in 0.25M H₂SO₄ solution at 0.8 V under inert atmosphere for 30 min.

Preparation of PPy: 0.02M Py (Merck) was polymerized in 0.25M H₂SO₄ solution at 1.0 V under inert atmosphere for 30 min.

Preparation of PANI/PPy: 0.1M pure ANI was electrochemically polymerized in 0.25M H₂SO₄ solution at 0.8 V under inert atmosphere for 30 min. The electrode was washed with distilled water and dried at 60°C. The PANI-coated electrode was then used as working electrode for electropolymerization of 0.02M Py monomer in 0.25M H₂SO₄ solution at 1.0 V under inert atmosphere for 30 min.

Preparation of PPy/PANI: 0.02M Py was polymerized in 0.25M H₂SO₄ solution at 1.0 V under inert atmosphere for 30 min. The electrode was washed with distilled water and dried at 60°C. A total of 0.1M pure ANI was then electrochemically polymerized in 0.25M H₂SO₄ solution at 0.8 V using PPy-coated electrode as working electrode under inert atmosphere for 30 min.

The polymer films obtained were washed with distilled water several times to remove unreacted monomer as well as excess electrolyte and subsequently dried in vacuum. Electrochemical polymerizations were repeated in 0.5M and 1.0M H₂SO₄ solutions.

Pyrolysis mass spectrometry analyses

The direct insertion probe pyrolysis mass spectrometry system used for the thermal analyses consists 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. A total of 0.01 mg samples 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 films and films obtained from parallel electrochemical polymerization processes.

RESULTS AND DISCUSSIONS

The total ion current (variation of total ion yield as a function of temperature) curves of PANI, PPy, PANI/PPY, and PPy/PANI samples electrochemically prepared in 0.25M H₂SO₄ were almost identical (Fig. 1). The pyrolysis mass spectra recorded around 270°C, the maximum of the broad peak present in the TIC curves, were dominated with peaks diagnostic to dopant and those recorded above 400°C showed peaks due to thermal decomposition of polymers. For all the samples under investigation, dopant-based peaks were the most intense. SO₂ was by far the major product. Products diagnostic to dopant

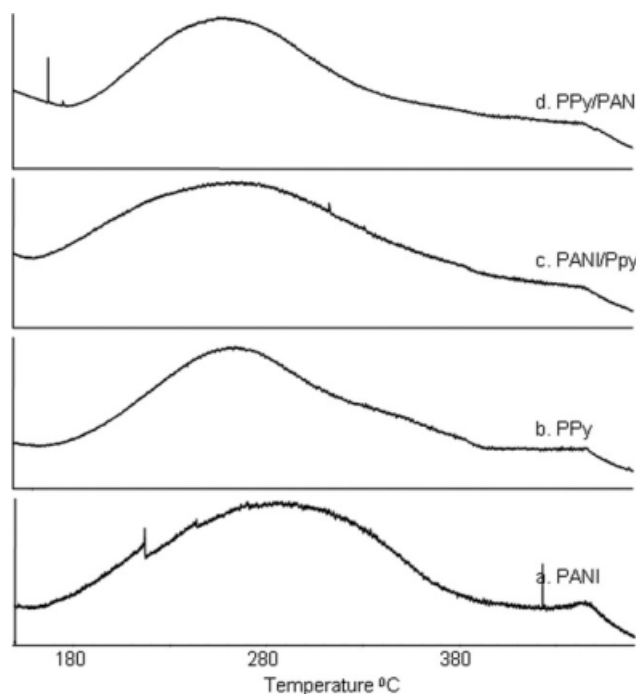


Figure 1 Total ion current curves for (a) PANI, (b) PPy, (c) PANI/PPy, and (d) PPy/PANI.

were recorded in a broad temperature range, and for PPy, this range was slightly narrower. Although the TIC curves of PANI/PPy, PPy/PANI, and homopolymers exhibit similar features, significant differences in the relative intensities of polymer-based peaks were observed in the pyrolysis mass spectra recorded at elevated temperatures.

In Figure 2 single ion pyrograms, the evolution profiles, of dopant and polymer-based products, namely SO₂ ($m/z = 64$ Da), monomers Py ($m/z = 67$ Da), and ANI ($m/z = 93$ Da) and their dimers (Py dimer, $m/z = 132$ Da and ANI dimer, $m/z = 184$ Da) detected during the pyrolysis of PANI, PPy, PANI/PPY, and PPy/PANI are shown. Detection of mixed dimer peak ($m/z = 160$ Da), though quite weak during the pyrolysis of PANI/PPy and PPy/PANI films confirmed growth of the second polymer on the one coated on the electrode. Products that can be attributed to degradation of ANI and Py rings were detected around 400°C (not shown in the figure). Evolution of CO₂ in a broad temperature range indicated the oxidation of the polymer samples under investigation during syntheses and/or storage conditions.

In case of PPy/PANI, prepared by coating PANI on PPy, the relative intensities of the peaks due to Py and its dimer with respect to the base peak due to SO₂, (SO₂/monomer and SO₂/dimer ratios) decreased about 4.9- and 4.0-folds compared with what were detected for PPy. On the other hand, the relative intensities of aniline and its dimer peaks with respect

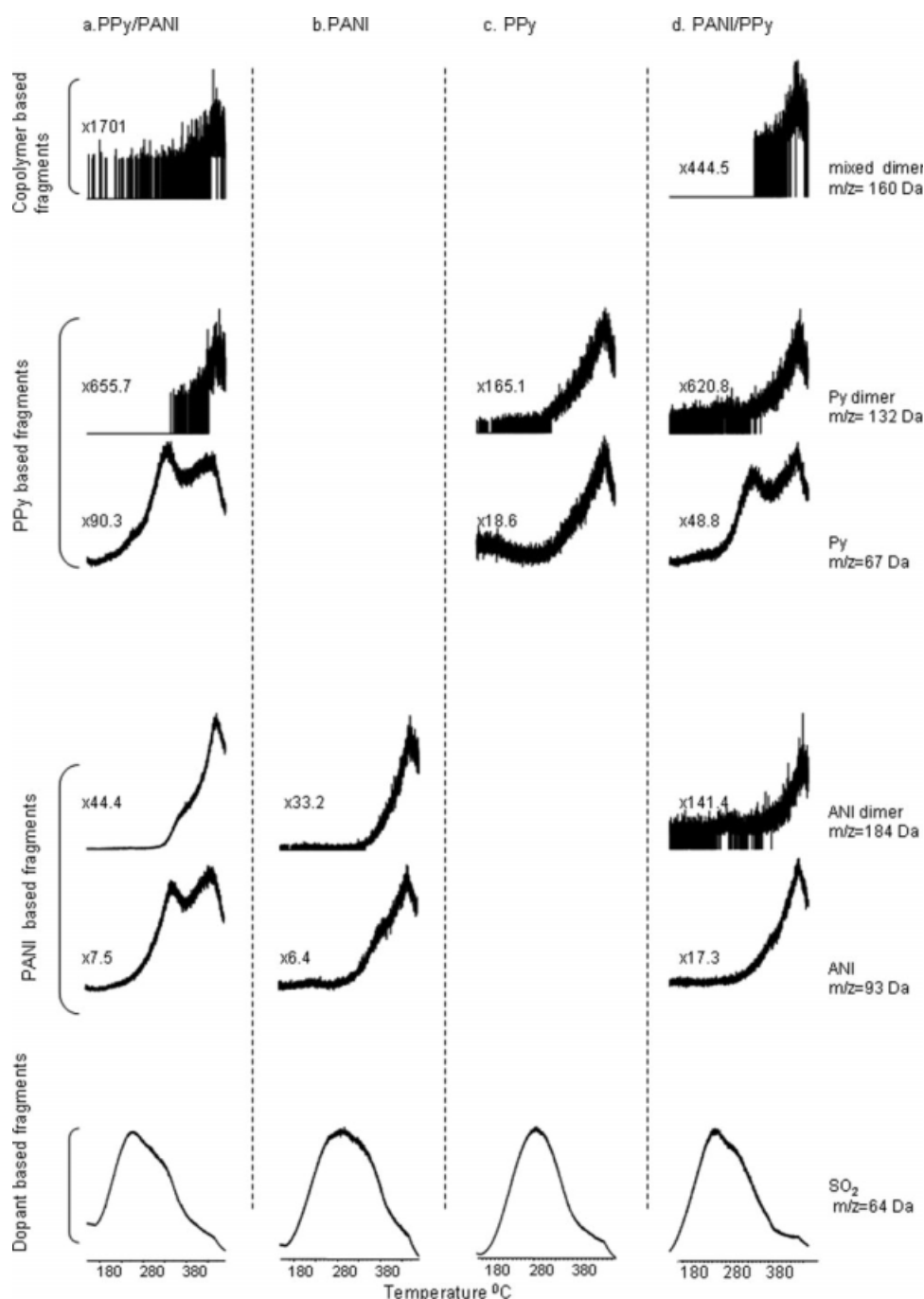


Figure 2 Evolution profiles of SO_2 , aniline, aniline dimer, pyrrole, pyrrole dimer, and mixed dimer detected during the pyrolysis of (a) PPy/PANI, (b) PANI, (c) PPy and (d) PANI/PPy.

to SO_2 peak were comparable with those detected for pure PANI; aniline peak intensity decreased about 1.3-folds and the dimer peak intensity decreased only about 1.2-folds. It may be thought that as the total time for the electrolysis doubled during the coating of the second polymer, the extent of doping or absorption of dopant ions should also be increased. Consequently, the relative intensities of dopant-based product peaks should also be increased with respect to those of polymer-based products. Yet, the experi-

mental results revealed that the decreases in the relative intensities of PPy-based product peaks were significantly greater, whereas the corresponding values for PANI-based product peaks were less than that could be expected. Another point that should be noted was the evolution of Py and aniline around 300°C indicating presence of chains with significantly low thermal stabilities.

During the pyrolysis of PANI/PPy, the sample prepared by polymerization of Py on PANI-coated

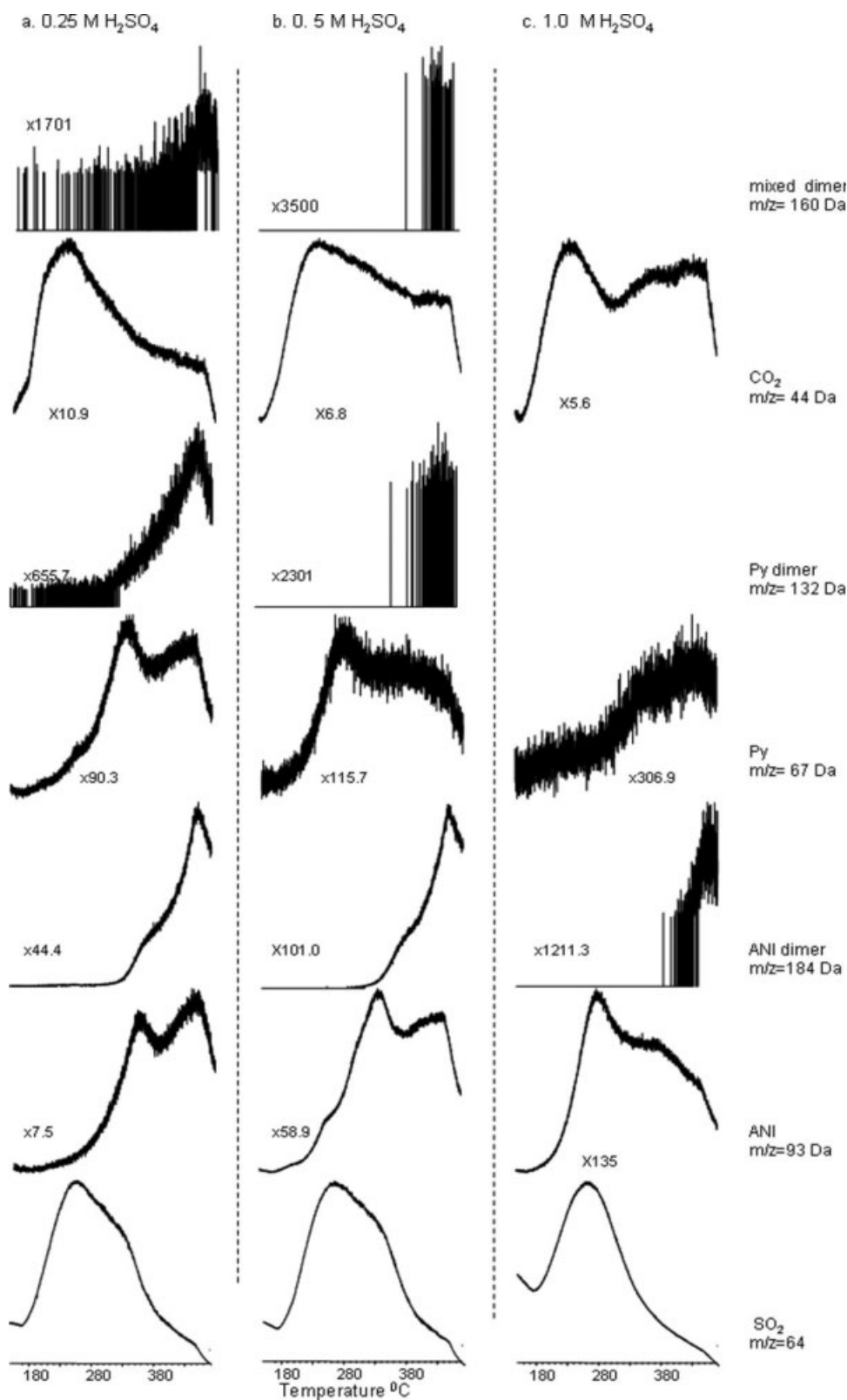


Figure 3 Evolution profiles of SO₂, aniline, aniline dimer, pyrrole, pyrrole dimer, CO₂, and mixed dimer detected during the pyrolysis of PPY/PANI films electrochemically prepared in (a) 0.25, (b) 0.50, and (c) 1.0M H₂SO₄ solution.

electrode, the decrease in the relative intensities of aniline peak was about 2.7-folds and that of aniline dimer peak was 4.3-folds compared with PANI. For

this sample, the corresponding decreases for Py and its dimer peaks were about 2.6- and 3.8-folds, respectively. Again, Py evolution was detected at moderate

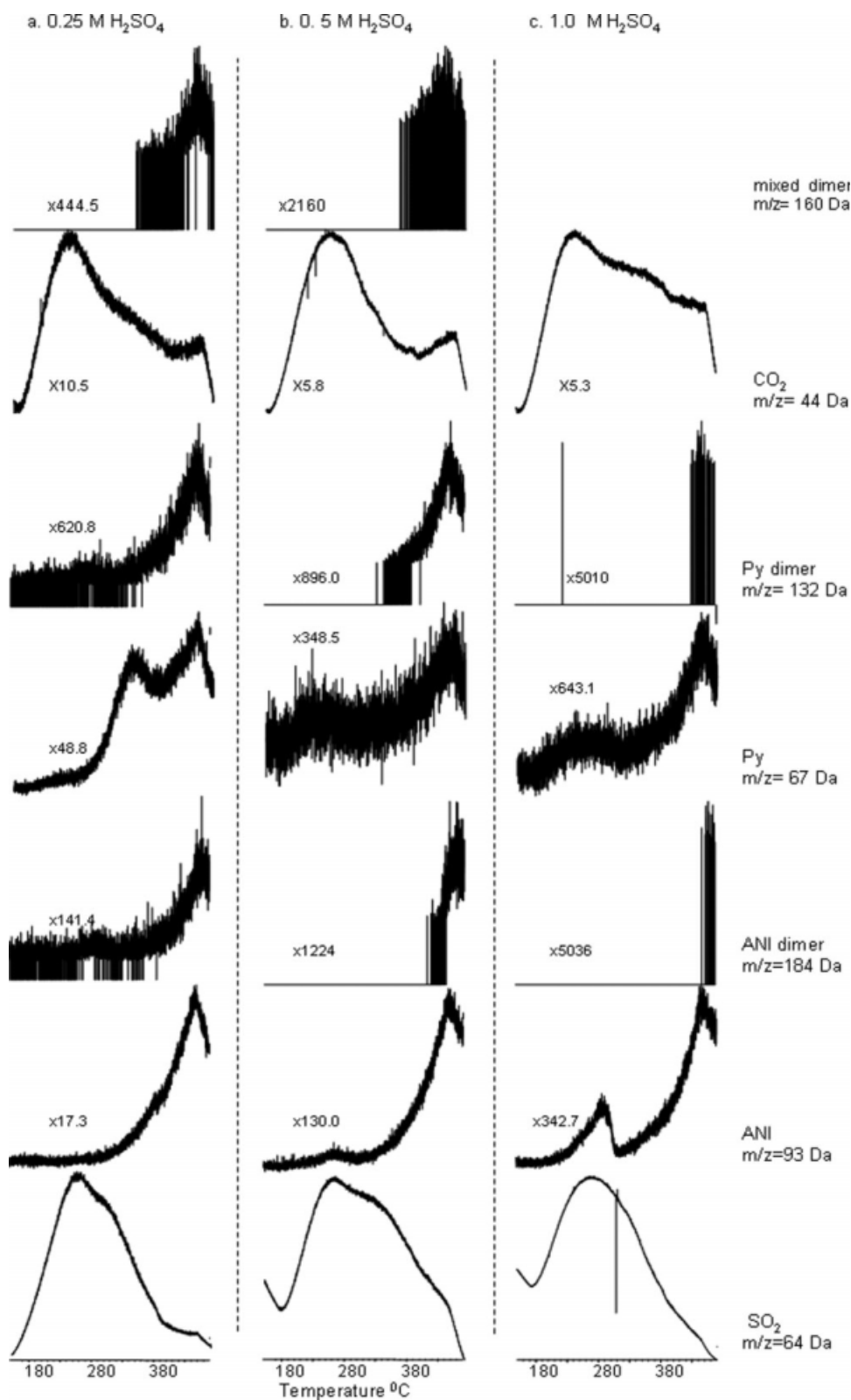


Figure 4 Evolution profiles of SO_2 , aniline, aniline dimer, pyrrole, pyrrole dimer, CO_2 , and mixed dimer detected during the pyrolysis of PANI/PPy films electrochemically prepared in (a) 0.25, (b) 0.50, and (c) 1.0M H_2SO_4 solution.

temperatures. Yet, contrary to our expectations, the evolution of all PANI-based products were only detected at elevated temperatures.

In Figure 3(a–c), evolution profiles of SO_2 , ANI, ANI dimer, Py, Py dimer, CO_2 and mixed dimer generated during the pyrolysis of PPy/PANI composite/

copolymer electrochemically prepared in 0.25, 0.50, and 1.0M H₂SO₄ solutions are shown respectively. For all the samples under investigation, evolution of PANI- and PPy-based products were also detected at moderate temperatures around 300°C. Furthermore, the yield of PPy and PANI-based products progressively diminished with increasing the concentration of the acid. Yet, the decrease in the yields of PPy-based products was noticeably greater than what was observed for PANI-based products. Mixed dimer was not detected for the samples prepared in 1.0M H₂SO₄ solution. CO₂ evolution was detected over a broad temperature range. The maximum CO₂ yield was detected around 250°C, slightly lower than the region where polymer-based products were recorded. Thus, it may be thought that the oxidized polymer chains were thermally less stable and started to degrade by evolution of CO₂. During the pyrolysis of the composites/copolymers, CO₂ evolution at elevated temperatures was enhanced as the acidity of the solutions in which electrolysis carried out was increased. Thus, it could be concluded that the oxidation of the polymer matrix mainly occurred during the synthesis process.

When PANI/PPy samples are considered, again a steady increase in the SO₂/Py and SO₂/ANI peak ratios was noted with the increase in acidity of the polymerization medium. In Figure 4(a–c), evolution profiles of SO₂, ANI, ANI dimer, Py, Py dimer, CO₂, and mixed dimer generated during the pyrolysis of PANI/PPy composite/copolymer electrochemically prepared in 0.25, 0.50, and 1.0M H₂SO₄ solutions are shown respectively. PPy-based products were affected more than PANI-based products and the decrease in the yields of PPy-based products was greater. PPy-based products were detected over a very wide temperature range above 250°C, during the pyrolysis of all the PANI/PPy samples. Low temperature evolutions of PANI-based products were only observed during the pyrolysis of the sample film prepared in 1.0M H₂SO₄ solution. Again mixed dimer was not detected for the samples prepared in 1.0M H₂SO₄ solution. Evolution of CO₂ was detected throughout the pyrolysis as in the case of PPy/PANI samples. But, high temperature evolutions were less pronounced.

These results revealed that the polymer first coated on the electrode oxidized and decomposed during the electrochemical polymerization of the second. It is clear that the oxidation of PPy was more efficient. Detection of PANI chains with lower thermal stability for all PPy/PANI samples may be related to growth of PANI on low molecular weight PPy chains already decomposed. The decrease in mixed dimer yield with the increase in acidity of the polymerization medium can also be associated with oxidation and/or decomposition of the polymer first coated on the electrode. It has been shown that the

change of medium during electrolysis has a significant effect on the structure and properties of the resulting homopolymers and bilayers.⁹ Changing the order of coating was observed to affect the structure and properties of samples, either partially or fully, based on the synthesis medium. Sari and Talu⁹ observed that coating PANI over PPy in H₂SO₄ solution yielded composite samples, whereas coating PPy over PANI in the same medium yielded copolymer samples. In our case, as mixed dimer peaks were detected for both PPy/PANI and PANI/PPy samples though the yield was lower for PPy/PANI, copolymer formation was confirmed also for PANI coated on PPy. Actually, Sari and Talu used FTIR and TGA data to confirm polymerization.⁹ As, both techniques are less sensitive and precise than MS technique, most probably they were not able to detect copolymer formation.

As a summary, in Figure 5 SO₂/Py and SO₂/ANI peak ratios detected in the pyrolysis mass spectra of the samples as a function of concentration of H₂SO₄ are shown. It is clear that the yield of the products due to the polymer coated first on the electrode diminished to a greater extent. This may be due to the degradation of the polymer coated on the electrode during the polymerization of the other polymer most probably due to the longer period the coated polymer stayed in the acid solution. Yet, as the effect was greater for PPy it can also be concluded that PPy was less stable in H₂SO₄ solution.

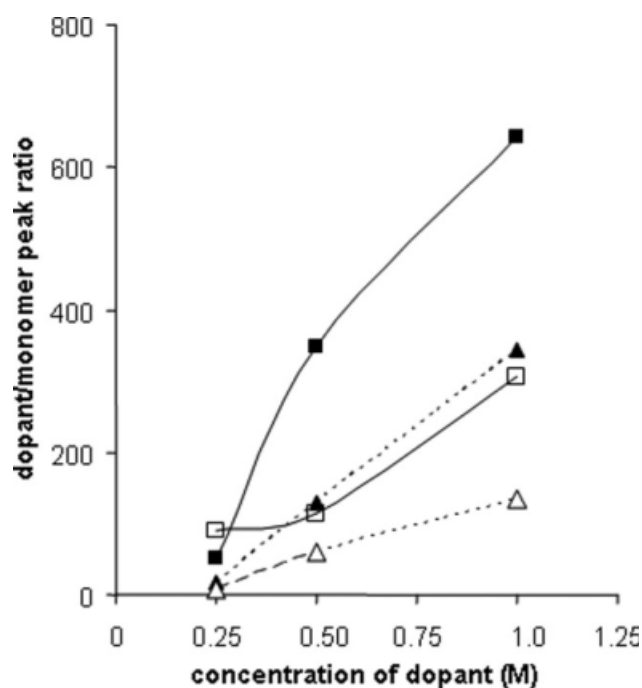


Figure 5 Variation of SO₂/Py (□ and ■) and SO₂/ANI (▲ and △) ratios as a function of concentration of acid detected during the pyrolysis of PPy/PANI (□ and △) and PANI/PPy (■ and ▲) composites/copolymers.

CONCLUSION

Pyrolysis mass spectrometry analysis confirmed copolymer formation while coating PPy over PANI or PANI over PPy in H₂SO₄ solutions. The degradation of the polymer coated first was detected for both PANI/PPy and PPy/PANI samples. The extent of degradation was more for PPy and increased with the acidity of the medium used during electrochemical polymerization.

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