Investigation of the Effect of Dopant on Characteristics of Poly(3-methyl thiophene) via Pyrolysis Mass Spectrometry

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In this work, a direct insertion probe pyrolysis mass spectrometry technique was applied to investigate the thermal and the structural characteristics of electrochemically prepared PF_6^- and BF_4^- doped poly(3-methylthiophene) (PMTh) to explore the effect of dopant on thermal and structural characteristics. It has been determined that the thermal degradation of PMTh occurs in two steps as in the case of polythiophene, (PTh). The first step was assigned to the loss of the dopant, and the second step to the degradation of the polymer backbone producing segments of various conjugation lengths. Generation of some oligomers occurred at lower temperatures for PF_6^- doped films compared to BF_4-PMTh. On the other hand for both PMTh samples products due to the degradation of thiophene ring were detected in the same temperature range. Evolution of dopant based products occurred in a broad temperature range for both PF_6^- and BF_4^- doped poly(3-methylthiophene). Reactions of dopants with H_2O and polymer were very effective, especially for PF_6^- and substitution of thiophene ring was noted for both samples. Decomposition of the polymer and inward diffusion of counter ion during dedoping processes of both polymers pointed out that electrochemical reversibility of the transition between the doped and undoped states is limited for PMTh.

Keywords: poly(3-methylthiophene); conducting polymers; thermal degradation; pyrolysis mass spectrometry

1 Introduction

Conducting polymers, being active materials in microelectronic devices, sensors, catalysts, solid-state batteries, chemically modified electrodes etc., have attracted considerable attention (1–4). Polythiophene (PTh) and poly(3-methylthiophene) (PMTh) have been studied for various applications. PMTh has better conductivity and lower peak potential than that of PTh (5). Furthermore, due to its stereoregularity, PMTh has more regular and homogenous structure than PTh and shows higher stability (6, 7).

Few studies on thermal degradation of poly(3-methylthiophene) have appeared in the literature (6, 8, 9). Thermo gravimetry analysis of TGA of PMTh films electrochemically doped with $SnCl_5^-$ and $SbCl_6^-$ anions indicated that the decomposition of the $SbCl_6^-$ doped PMTh occurs at a temperature lower than that of $SnCl_5^-$ doped PMTh (9). Among the two degradation stages, the first one around $250°C$ was assigned to loss of the dopant, $SbCl_6^-$ and the weight loss in the temperature range of $300–500°C$ was

assigned to the degradation of the polymer. On the other hand, thermo gravimetry analysis of $SnCl_5$ doped PMTh indicated three stages of weight loss, at 150, $300–500$, and $500–700°C$. Weight loss around $150°C$ was assigned to the loss of water and weight loss around $300–500°C$ was assigned to the loss of low molecular weight species and dopant $SnCl_5^-$ and that around $500–700°C$ to the decomposition of PMTh (8). In a recent study, pyrolysis mass spectrometry analysis of BF_4^- doped poly(3-methyl thiophene) indicated that the thermal degradation of PMTh occurs in two steps as in the case of PTh (9). The first step was attributed to evolution of the dopant and the second step to the degradation of the polymer backbone. The similarities in the thermal behavior of PMTh and PTh have been noted indicating that methyl substitution has no significant effect on thermal characteristics of polythiophenes. Dedoping caused not only the removal of the dopant to a certain extent but also inward diffusion of the counter ion $N(C_4H_9)_4^+$ as in the case of polythiophene. Furthermore, degradation of the polymer backbone indicated that the electrochemical reversibility of the transition between the doped and undoped states is limited for PMTh.

In this work, direct insertion probe pyrolysis mass spectrometry technique was applied to investigate the thermal and the structural characteristics of electrochemically prepared PF_6^- and BF_4^- doped poly(3-methylthiophene)

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(PMTh) to explore the effect of dopant on thermal and structural characteristics.

2 Experimental

3-Methylthiophene (MTh) (Merck) and acetonitrile (Merck) were purified by distillation prior to electrolysis and stored at 4°C. Tetrabutylammonium tetrafluoraborate (TBATFB) and tetrabutylammonium hexafluoraphosphate were used after purification by recrystallization. 3-Methylthiophene (0.20 M) was electrochemically polymerized in a three compartment cell with a three electrode configuration in acetonitrile/electrolyte (tetrabutylammonium tetraflouroborate, TBATFB (0.05 M) or tetrabutylammonium hexafluoro-phosphate, TBAHFP (0.05 M)) systems. Platinum plates (1.5 cm^2) were used as working and counter electrodes, and Ag/Ag$^+$ was used as the reference electrode. A HEKA IEE 488 potenstiostat was used to perform electrolysis at 1.7 V. Dedoped samples were obtained by reduction of poly(3-methylthiophene), PMTh at -1.7 V. The polymer films, BF$_4^-$ doped PMTh and dedoped PMTh were washed with CH$_3$CN several times to remove unreacted monomer and excess TBATFB and dried in vacuum.

The direct insertion probe pyrolysis mass spectrometry (DP-MS) system used for the thermal analyses consists of a 5973 HP quadruple mass spectrometer coupled to a JHP SIS direct insertion probe pyrolysis system. 0.01 mg samples were pyrolyzed in the flared glass sample vials. The temperature was increased at a rate of 10°C/min and the scan rate was 2 scans/s. Pyrolysis mass spectra were recorded using 70 eV and 19 eV electrons to differentiate the extent of dissociative ionization in the ion source in the mass range of 10–800 Da. Pyrolysis experiments were repeated using samples of the same PMTh films and films obtained from parallel electrochemical polymerization processes.

3 Results and Discussions

The total ion current (TIC) (the variation of total ion yield as a function of temperature) curves for both BF$_4^-$ and PF$_6^-$ doped PMTh show three peaks; the first at around 60°C was due to the evolution of adsorbed solvent, monomer, the second at around 260°C was due to the evolution of dopant-based products and the last at around 440°C was attributed to the evolution of degradation products of the polymer. The TIC curves and the pyrolysis mass spectra recorded at the maxima in the TIC curves of PF$_6^-$ and BF$_4^-$ doped PMTh are given in Figure 1, a and b, respectively.

For both polymers, oligomers up to heptamer were recorded. However, for the BF$_4^-$ doped PMTh the oligomer yields were quite low, while the products indicating dissociation of the thiophene ring were significantly enhanced. Strong evidence indicating reactions of dopant with the
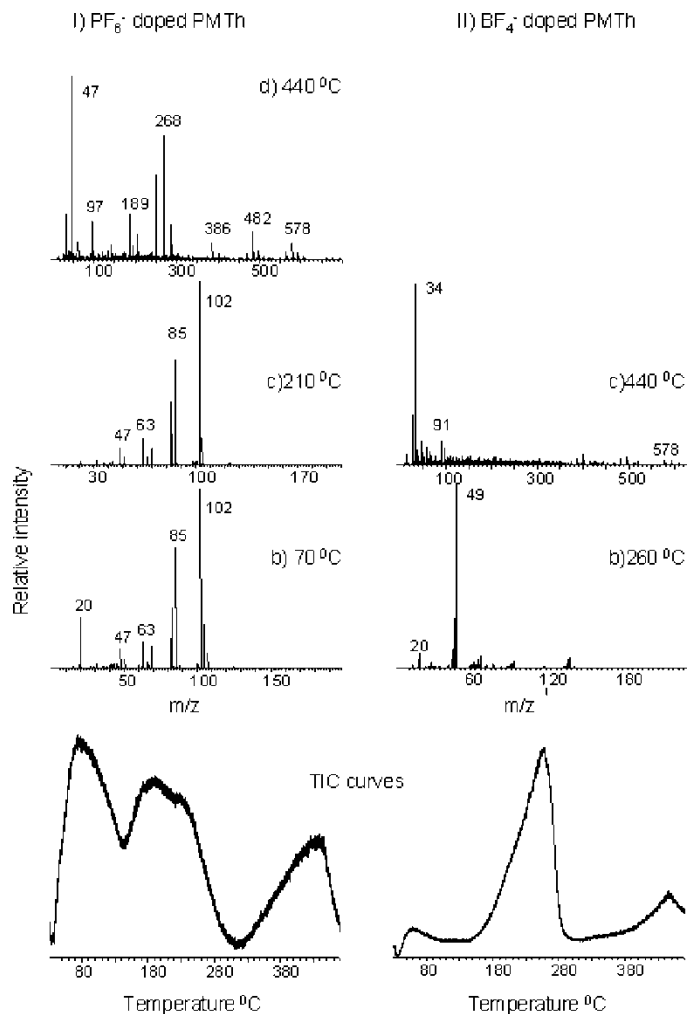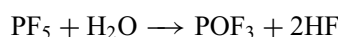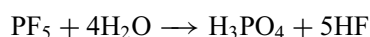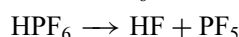

Fig. 1. Total ion current curves and the pyrolysis mass spectra of I) PF$_6^-$ and, II) BF$_4^-$ doped PMTh.

H$_2$O and polymer were noted. For the PF$_6^-$ doped PMTh, peaks that may be attributed to POF$_3$ (POF$_3$ at m/z = 104 Da, POF$_2$ at m/z = 85 Da, PF$_2$ at m/z = 69 Da and PO at m/z = 47 Da), and to H$_3$PO$_4$ (H$_3$PO$_4$ at m/z = 98 Da, H$_2$PO$_3$ at m/z = 81 Da, PO$_2$ at m/z = 63 Da and PO at m/z = 47 Da) were recorded. It is known that PF$_x$ compounds, when interacted with water, produce POF$_3$, H$_3$PO$_3$ and H$_3$PO$_4$ according to the following equations:

$$6H_2O \longrightarrow 4H_3O^+ + 4e^- + O_2$$
$$PTh^+ - PF_6^- + H_3O^+ + e^- \longrightarrow PTh + HPF_6 + H_2O$$
$$HPF_6 \longrightarrow HF + PF_5$$
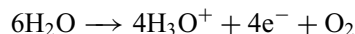$$PF_5 + 4H_2O \longrightarrow H_3PO_4 + 5HF$$
$$PF_5 + H_2O \longrightarrow POF_3 + 2HF$$
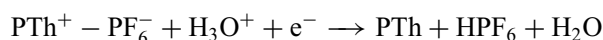
On the other hand, the presence of intense HF in the pyrolysis mass spectra of BF$_4^-$ doped PMTh also pointed

out hydrolysis of BF_4^- with water adsorbed on the polymer according to the following equations:

$$6H_2O \longrightarrow 4H_3O^+ + 4e^- + O_2$$

$$PTh^+ - BF_4^- + H_3O^+ + e^- \longrightarrow PTh + HBF_4 + H_2O$$

$$HBF_4 \longrightarrow HF + BF_3$$
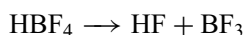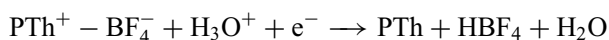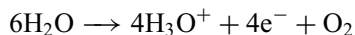
Under the direct pyrolysis conditions, secondary reactions were almost completely eliminated. Thus, it is thought that phosphorous-fluorine, phosphorous-oxygen compounds and HF were most probably generated either during the electrochemical synthesis process or during the storage. However, as electrochemical polymerizations have been carried out in dry CH_3CN and electrolytic solutions were purged with N_2 before electrolysis, their production during the synthesis process was not likely. Thus, it can be concluded that reactions of dopants with water during storage were very effective.

Furthermore, for the PF_6^- doped PMTh, the presence of strong peaks at $m/z = 102$ 189, 252, and 268 Da may be attributed to reactions of methyl thiophene with HF and H_3PO_4 (10−12).

In Figure 2 (a and b), evolution profiles of characteristic products generated during the pyrolysis of PF_6^- and BF_4^- doped PMTh are shown, respectively. Evolution profiles of monomer ($m/z = 98$ and 97 Da) and hexamer ($m/z = 578$ Da) showed nearly identical trends with each other and with those recorded for PTh. Yet, for PF_6^- doped PMTh the relative intensities of oligomer peaks were higher compared to those of the products generated by decomposition of the thiophene ring. Recent pyrolysis studies on electrochemically prepared polypyrroles and polythiophenes showed that thermal decomposition products due to cleavage of the aromatic ring were more abundant contrary to the chemically prepared samples (10−13). It is known that, in general, a network polymer is produced when electrochemical polymerization is applied. For a network polythiophene, polymerization is initiated from 2 and 5 positions and proceeds from 3 and 4 positions. Thus, during the thermal degradation, cleavage of the aromatic ring will be preferential only if the polymer has a network structure. Thus, H_2S evolution becomes one of the main degradation routes during the thermal degradation of a network PTh. For PMTh, due the methyl substitution growth of polymer from the 3 position is not possible. Therefore, the extent of network structure should be limited for PMTh compared to PTh. Evolution of oligomers from PF_6^- doped polymer occurs slightly at lower temperatures than the products attributed to degradation of thiophene ring (Figure 2). Thus, it may be concluded that blocks involving network structure degraded at higher temperatures as expected. On the other hand, for the BF_4^- doped PMTh, all the products due to the decomposition of the polymer, followed almost in the same temperature regions. Thus, it may be thought that methyl substitution and the dopant used have no significant effect on thermal stability of polythiophene.
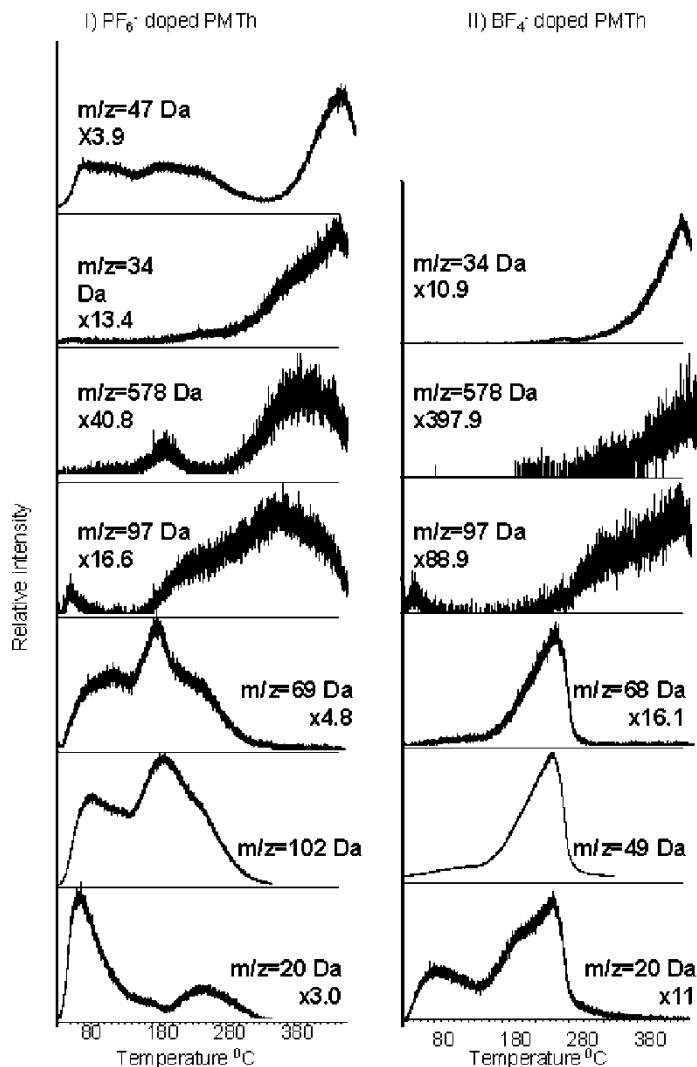
Fig. 2. Evolution profiles of some characteristic degradation products recorded during pyrolysis of I) PF_6^- and, II) BF_4^- doped PMTh.

In a previous study, in order to investigate the extent of doping, the intensity of most intense dopant based product peak, BF_2 peak, was compared with that of the most intense polymer based product peak, H_2S peak, for BF_4^- doped PMTh and PTh films (13). It has been determined that the intensity ratio of BF_2/H_2S peaks was 11 and 35 for PMTh and PTh respectively, pointing out a significant decrease in extent of doping for PMTh. For PF_6^- doped PMTh and PTh samples, the intensity ratio of PF_2/H_2S peaks was 2.7 and 0.35 respectively. However, for the PMTh sample oligomer yields were significantly high. However, for both PF_6^- doped PTh and PMTh samples pyrolysis mass spectra were dominated with peaks that can be attributed to products due to the reactions of dopant with H_2O and thiophene. Thus, for both samples doping was mainly affected by these reactions.

In Figure 3, the TIC curves and the pyrolysis mass spectra recorded at the maxima in the TIC curves of dedoped PF_6^- and BF_4^- doped PMTh are given. For both samples, the base

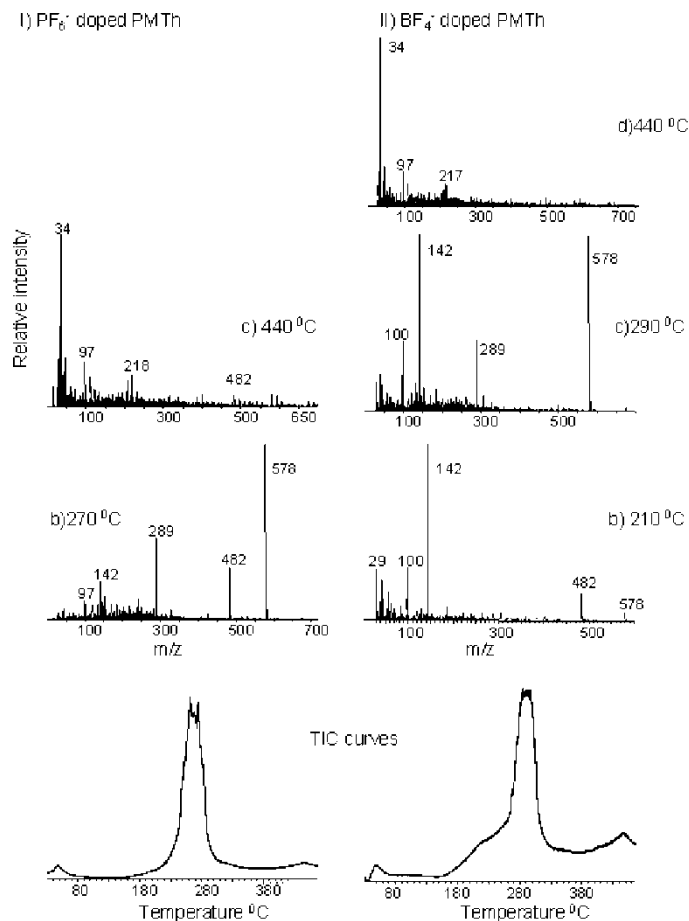**Fig. 3.** Total ion current curves and the pyrolysis mass spectra of dedoped; I) PF_6^- and II) BF_4^- doped PMTh.

peak was due to hexamer at $m/z = 578$ Da. However, the evolution of oligomers occurred just above 250°C, indicating that degradation of the samples occurred during the dedoping process. Furthermore, for both samples the presence of intense 142 and 100 Da peaks pointed out inward diffusion of counter ion during the dedoping process. Yet, no intense peak that can directly be attributed to dopant or dopant based product could be detected for both samples. Peaks that were attributed to reactions of dopant with H_2O and thiophene almost totally disappeared indicating that, although fresh samples were used, these reactions mainly took place during the storage and sampling.

In Figure 4 (a and b), evolution profiles of characteristic products generated during the pyrolysis of dedoped PF_6^- and BF_4^- doped PMTh are shown respectively. For both samples, evolution of monomer and oligomers occurred around 250°C and showed nearly identical trends. However, H_2S evolution took place at significantly high temperatures indicating that the blocks having network structure retained their thermal characteristics.

It may be thought that methyl substitution and the dopant used have no significant effect on thermal stability of polythiophene. Yet, evolution of oligomers from PF_6^- doped
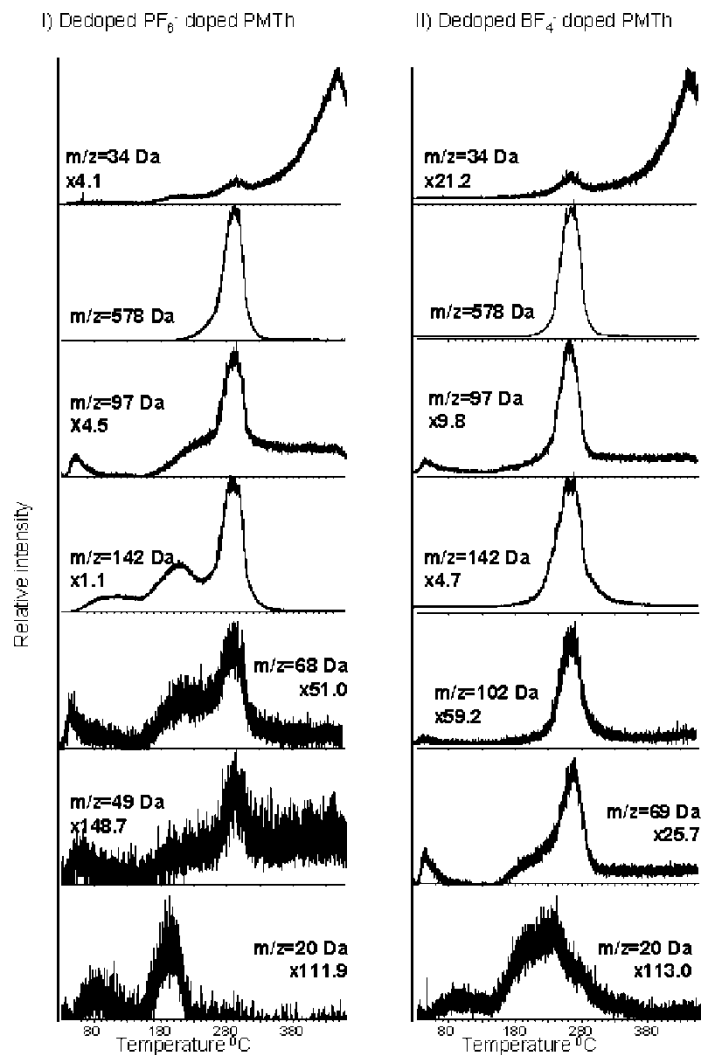

Fig. 4. Evolution profiles of some characteristic degradation products recorded during pyrolysis of dedoped I) PF_6^- and II) BF_4^- doped PMTh films.

polymer occurs slightly at lower temperatures than the products due to decomposition of the thiophene ring indicating a lower extent of network structure.

4 Conclusions

Direct insertion probe pyrolysis mass spectrometry analyses of PF_6^- and BF_4^- doped PMTh indicated that thermal degradation of PMTh occurs in two steps, as in the case of PTh. In the first step, evolution of dopant based products occurred in a broad temperature range for both samples, whereas decomposition of PMTh occurred in the second step. Reactions of dopants both with H_2O and polymer were very effective, especially for PF_6^-, indicating that PF_6^- as a dopant is not very appropriate. Decomposition of the polymer and inward diffusion of counter ion during dedoping processes of both polymers pointed out that

electrochemical reversibility of the transition between the doped and undoped states is limited for PMTh. However, no significant decrease was noted in product yields due to the degradation of blocks having network structure.

5   Acknowledgements

6   References

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