

# Pyrolysis mass spectrometry analyses of poly(3-methylthiophene)

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## Abstract

In this work, pyrolysis mass spectrometry techniques were applied to investigate the thermal and the structural characteristics of electrochemically prepared  $\text{BF}_4^-$  doped poly(3-methylthiophene) (PMTh) and to explore the effect of methyl substitution on thermal and structural characteristics of polythiophene (PTh). It has been determined that thermal degradation of  $\text{BF}_4^-$  doped PMTh films occurs in two steps as in the case of polythiophene. 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. Detection of  $\text{H}_2\text{S}$ ,  $\text{C}_3\text{H}_4$ , and  $\text{C}_2\text{H}_2$  in the final stage of pyrolysis was again associated with a network structure. Significant decrease in the relative intensities of dopant-based products indicated decrease in extent of doping. However, as dopant-based products of PMTh appeared at slightly higher temperatures, a stronger interaction between the dopant and the host polymer PMTh may be proposed. Decomposition of polymer during dedoping pointed out that electrochemical reversibility of the transition between the doped and undoped states is limited for PMTh.

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## 1. Introduction

Substituted polymers of the five membered heterocycles are either more or less conducting than their parent polymers [1]. Among these, poly(3-methylthiophene) (PMTh) has better conductivity and lower peak potential than that of polythiophene (PTh) [2]. PMTh appears to be more regular and homogeneous material than PTh and shows higher stability due to its stereoregularity [3]. The analysis of stability of conductivity has shown that doping level and conductivity of  $\text{SO}_3\text{CF}_3^-$  doped PMTh were not changed when stored in air. The undoped PMTh behaved in the same manner [2]. Similarly, no change in the colour and absorption spectra have been detected for  $\text{BF}_3$  ethlyether doped PMTh exposed to air at room temperature for 80 days indicating stability of the PMTh films [4].

Although several studies on thermal degradation of polythiophene appeared in the literature [5–9], there are only few studies on thermal stability of PMTh [2,10]. The thermal stability of PMTh films electrochemically doped with  $\text{SnCl}_5^-$

and  $\text{SbCl}_6^-$  anions was studied by thermogravimetric analysis, TGA. It has been determined that the decomposition of the  $\text{SbCl}_6^-$  doped PMTh occurs at a temperature lower than that of  $\text{SnCl}_5^-$  doped PMTh [10]. The weight loss at 250 °C was assigned to loss of the dopant,  $\text{SbCl}_6^-$  and the weight loss in the temperature range of 300–500 °C was assigned to the degradation of the polymer. Thermogravimetric analysis of  $\text{SnCl}_5^-$  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  $\text{SnCl}_5^-$  and that around 500–700 °C to the decomposition of PMTh [10]. However, the applied technique was not suitable for characterization of degradation products. A more detailed study on thermal degradation of PMTh was still missing in the literature.

Application of common spectroscopic techniques in elucidation of the structure of conducting polymers is still limited as the samples prepared are insoluble and contain high concentrations of charge carriers. Application of pyrolysis mass spectrometry techniques for the structural analysis of polymers have been discussed in the literature in detail [11,12]. We have applied pyrolysis mass spectrometry

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technique for structural and thermal characterization of polythiophene, one of the most common conducting polymers, recently [7–9].

In this work, pyrolysis mass spectrometry techniques were applied to investigate the thermal and the structural characteristics of electrochemically prepared  $\text{BF}_4^-$  doped poly(3-methylthiophene) (PMTh) and to explore the effect of methyl substitution on thermal and structural characteristics polythiophene (PTh).

## 2. Experimental

3-Methylthiophene (MTh) (Merck) and acetonitrile (Merck) were purified by distillation prior to electrolysis and stored at 4 °C. Tetrabutylammonium tetrafluoroborate (TBATFB) was used after purification by recrystallization. 3-Methylthiophene (0.05 M) was electrochemically polymerized in a three-compartment cell with three electrode configuration in acetonitrile/tetrabutylammonium tetrafluoroborate (TBATFB) (0.2 M) solvent electrolyte system. 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 HEKA IEE 488 potentiostat 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,  $\text{BF}_4^-$  doped PMTh and dedoped PMTh were washed with  $\text{CH}_3\text{CN}$  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 analyzes consists of a 5973 HP quadruple mass spectrometer coupled to a JHP SIS direct insertion probe pyrolysis system. 0.01 mg samples

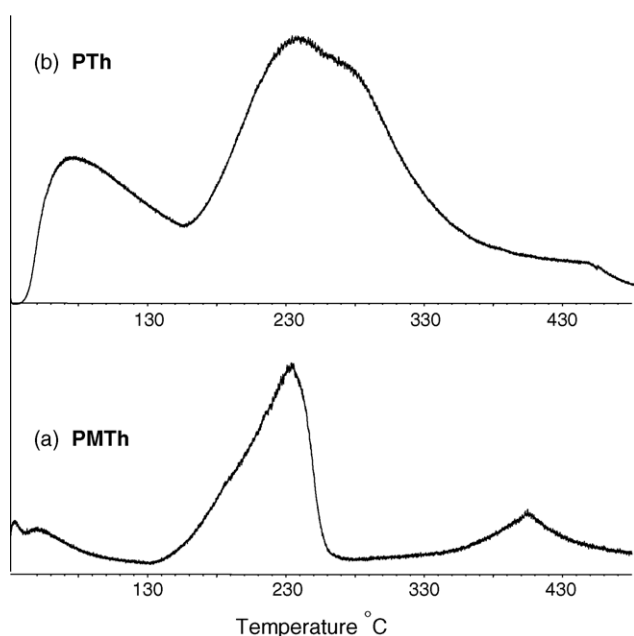


Fig. 1. The TIC curves of PMTh and PTh.

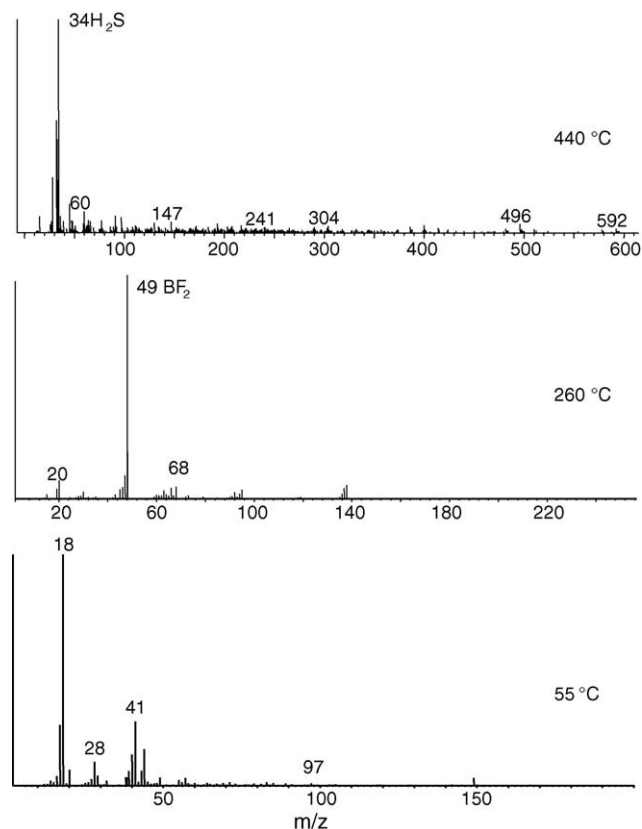


Fig. 2. Pyrolysis mass spectra at the temperatures of three peak maxima of the TIC curve for PMTh.

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

Table 1

The relative intensities of characteristic and/or intense peaks recorded during the pyrolysis of PMTh at 260 and 445 °C

<i>m/z</i>	260 °C	445 °C	Assignments
20	878	261	HF
34	2	1000	H <sub>2</sub> S
30	32	7	BF
49	1000	9	BF <sub>2</sub>
68	55	13	BF <sub>3</sub>
83	2	18	C <sub>4</sub> H <sub>3</sub> S
95	45	7	C <sub>5</sub> H <sub>3</sub> S
97	2	58	CH <sub>3</sub> C <sub>4</sub> H <sub>3</sub> S
121		20	C <sub>4</sub> H <sub>2</sub> SC <sub>3</sub> H <sub>5</sub>
124	1	18	CH <sub>3</sub> C <sub>4</sub> H <sub>2</sub> SC <sub>2</sub> H <sub>3</sub>
138	67	8	CH <sub>3</sub> C <sub>4</sub> H <sub>2</sub> SC <sub>3</sub> H <sub>5</sub>
142	5	0	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> N=CH <sub>2</sub>
155	1	21	CH <sub>3</sub> C <sub>4</sub> H <sub>2</sub> SC <sub>2</sub> H <sub>3</sub> S
185	1	13	(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N
194		19	Dimer
207		36	(CH <sub>3</sub> C <sub>4</sub> H <sub>2</sub> S) <sub>2</sub> CH
217		47	(CH <sub>3</sub> C <sub>4</sub> H <sub>2</sub> S)C <sub>4</sub> H <sub>2</sub> SC <sub>3</sub> H <sub>2</sub>
242		13	(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N
245		14	(CH <sub>3</sub> C <sub>4</sub> H <sub>2</sub> S) <sub>2</sub> C <sub>4</sub> H <sub>4</sub>
290		33	Trimer
386		30	Tetramer
482		20	Pentamer
578		20	Hexamer

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