Pyrolysis Mass Spectrometry Analysis of Electrochemically Grafted Polyacrylonitrile with Thiophene

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In this work, structural and thermal analyses of a polythiophene/polyacrylonitrile (PTh/PAN) sample, prepared by electrochemical polymerization of thiophene onto a poly(acrylonitrile) coated anode, have been performed by a direct insertion probe pyrolysis mass spectrometry technique. The evolution profiles of PTh based products from PTh/PAN showed nearly identical trends with those recorded during the pyrolysis of pure PTh. However, when PAN based products were considered, contrary to the trends observed for pure PAN, evolution of HCN and the degradation products due to the homolytic cleavages of the polymer backbone continued throughout the pyrolysis indicating a significant increase in their production even at the final stages of pyrolysis. On the other hand, the yield of thermal degradation products associated with decomposition of the unsaturated cyclic imine segments decreased. A careful analysis of the data pointed out the presence of mixed dimers. Yet, because of the possible contributions of various products to the corresponding peaks, a copolymer formation cannot be confirmed.

Introduction

In general, because of the π-electron system along the conducting polymer backbone leading to rigidity and crosslinking, conducting polymers are poorly processable. Among the several ways used for improvement of the mechanical characteristics, usage of thiophene and pyrrole derivatives as modified monomers was widely performed (1–3). Another convenient method is the preparation of blends or block or graft copolymers of conducting polymers with certain insulating polymer matrices having good mechanical characteristics (4, 5). The block and graft copolymers are commonly synthesized by electrochemical polymerization of conducting polymers onto an electrode coated by an insulating polymer. There have been several studies on preparation of composites and copolymers of polythiophene. The composites of polythiophene with styrene, natural rubber and polyamide were discussed in the literature (5–7). Graft and block copolymers of polystyrene and polythiophene were also synthesized (8). The copolymers of thiophene are much more preferential than the composites of

polythiophene due to their homogeneity, well defined structure and good mechanical properties (9).

Of course, a detailed structural analysis is necessary for determination of all the possible routes of modifications. In general, electrochemically prepared conducting polymers are insoluble in common solvents due to their network structure. Furthermore, they contain high concentrations of charge carriers. Therefore, application of common classical spectroscopic techniques for structural analysis is usually limited. Pyrolysis mass spectrometry techniques and their applications to polymer studies have been discussed in a number of studies (10, 11). We have applied pyrolysis mass spectrometry techniques as an alternative way to investigate structural and thermal characteristics of conducting polymers and the results obtained for polypyrrole and polythiophene were discussed in details in our previous studies (12–14).

Polyacrylonitrile (PAN) is one of the versatile polymers having good mechanical characteristics and is widely used for making membranes. It has good solvent resistance property and preserves its morphology upon pyrolysis. In this study, the structural and thermal characterization of BF_4^- doped polythiophene/poly(acrylonitrile) (PTh/PAN) film prepared by electrochemical polymerization of thiophene onto a poly(acrylonitrile) coated anode have been performed by direct insertion probe pyrolysis mass spectrometry technique. The pyrolysis mass spectrometry analyses of both components of the copolymer, PAN and PTh, and their mechanical mixture have also been carried out and compared.

Experimental

Thiophene (Merck) and acetonitrile (Merck) were purified by distillation prior to electrolysis and stored at $4°C$. Tetrabutylammonium tetrafluoraborate (TBATFB) was used after purification by recrystallization. Dimethylsulfoxide (Merck), poly(acrylonitrile) (PAN) (Sigma-Aldrich) were used without further purification. Polyacrylonitrile film was obtained from 4.1% PAN dimethylsulfoxide solution.

Thiophene (0.05 M) was electrochemically polymerized onto a polyacrylonitrile coated anode in a three compartment cell with platinum plates ($1.5\,cm^2$) as working and counter electrodes and Ag/Ag^+ as the reference electrode. A HEKA IEE 488 potenstiostat was used to perform electrolysis at 1.9 V (1.2 V vs Fe/Fe^+) in acetonitrile/ tetrabutylammonium tetraflouroborate, TBATFB (0.2 M) solvent electrolyte system. The solution was purged with dry N_2 before electrolysis to remove O_2. The polymer film, polythiophene/poly(acrylonitrile), (PTh/PAN) produced, was washed with CH_3CN several times to remove unreacted monomer and excess TBATFB and dried in vacuum.

The direct insertion probe pyrolysis mass spectrometry (DP-MS) system consists of a 5973 HP quadruple mass spectrometer coupled to JHP SIS direct insertion probe pyrolysis system. 0.01 mg samples were pyrolyzed in flared glass sample vials. The temperature was increased at a rate of $10°C/min$ and the scan rate was 2 scans/s. To investigate the effect of dissociative ionization inside the mass spectrometry on pyrolysis products, pyrolysis mass spectra were obtained using electron energies of 70 and 20 eV.

Results and Discussion

It is known that pyrolysis mass spectrometry analyses of samples involving multi-components are usually quite difficult. Thus, in order to investigate the structural and thermal characteristics of electrochemically prepared BF_4^- doped PTh/PAN film,

pyrolysis mass spectrometry analyses of polyacrylonitrile powder, polyacrylonitrile films treated under the electrolysis conditions in the absence of thiophene, polythiophene and the mechanical mixture of thiophene and poly(acrylonitrile) have also been carried out.

Several studies appeared in the literature on thermal degradation of polyacrylonitrile (15–18). The chemical changes occurring in the thermal degradation of PAN was determined to be essentially a twin process, involving structure stabilization leading to the formation of cyclic product (residue) as a result of oligomerization of nitrile groups and homolytic cleavage of the backbone yielding gaseous and volatile products. The thermal degradation of polyacrylonitrile by thermal volatilization analysis (TVA) showed that ammonia and hydrogen cyanide were the main products of degradation. It has been observed that during the pyrolysis of polyacrylonitrile at 200–300°C, a single conjugated structure of imine moieties is formed by polymerization of pending CN groups. This stage was reported to occur, also in the presence of air (17). It is known that the double conjugated ladder structure would be achieved by heating in vacuum or under N_2 at elevated temperatures, above 300°C, as shown in Scheme 1. Upon further heating, denitrogenation occurred yielding carbon structure or skeleton.

Direct pyrolysis of PAN showed the evolution of HCN, monomer, low molecular weight oligomers and products stabilized by cyclization reactions around 300°C. Products confirming dehydrogenation were detected in the final stages of pyrolysis around 400°C in accordance with results in the literature (15–18). When polyacrylonitrile films treated under electrolysis conditions in the absence of thiophene were pyrolyzed, decrease in the yields of monomer and oligomers, and increase in the amount of products stabilized by cyclization reactions were detected.

It has been shown that the thermal decomposition of BF_4^- doped polythiophene mainly occurs in two steps; the first being the loss of the dopant, and the second being the degradation of the polymer backbone (12–14). Evolution of dopant based products around 240°C was followed by the decomposition of the polymer around 400°C. Though, thiophene monomer and low molecular weight oligomers were detected, the relative intensities of fragments indicating the decomposition of the thiophene ring such as H_2S and C_2H_2 were more intense. This behavior was associated with a network structure in our previous studies (12–14).

The total ion current (TIC) curve recorded during the pyrolysis of electrochemically prepared PTh/PAN film is shown in Figure 1, together with the TIC curves for the mechanical mixture and the corresponding homopolymers PAN and PTh. It is clear that the TIC curve of PTh/PAN is significantly different than all of the others, whereas that of the mechanical mixture is quiet similar to that of PAN. Actually, the mechanical mixture has been prepared using equal amounts of both components, because of the physical characteristics of PTh film, it was not possible to obtain a homogeneous mixture. Nevertheless, pyrolysis mass spectra of various mechanical mixture samples showed diagnostic peaks of both PTh and PAN with quite similar trends with the corresponding
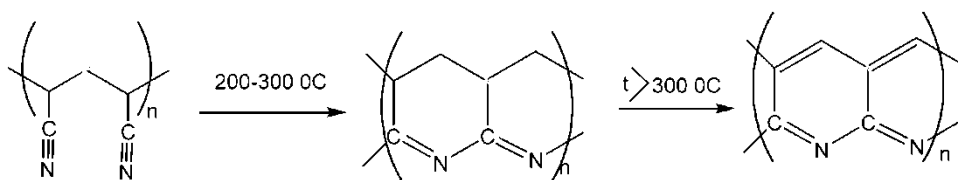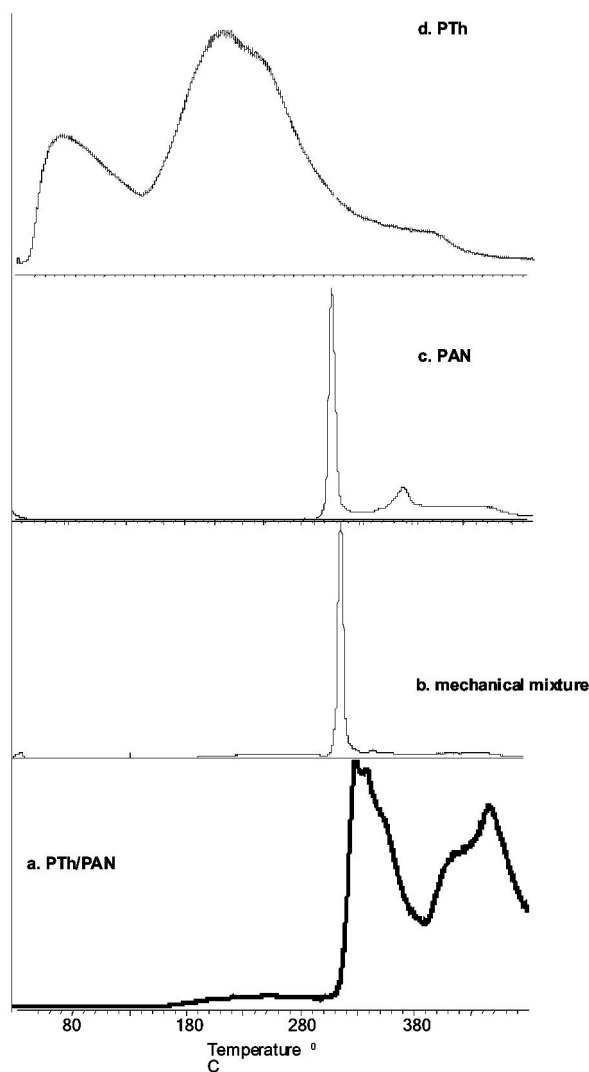

Scheme 1.

Figure 1. The TIC curves for a) PTh/PAN, b) Mechanical mixture of PAN and PTh, c) PAN and, d) PTh.

homopolymers indicating that thermal degradation of each components occurred independently. The pyrolysis mass spectra of PTh/PAN and were also dominated with diagnostic peaks of PTh and PAN. Thus, presence of both components in both mechanical mixture and PTh/PAN samples was confirmed. However for the electrochemically grafted sample significant changes in the relative intensities of product peaks were noted. The pyrolysis mass spectra recorded at the maxima of the TIC curves of the mechanical mixture and PAN/PTh are shown in Figures 2 and 3 respectively.

In general, evolution of the dopant, BF_4^-, based products were recorded around 240–250°C for both PTh/PAN and the mechanical mixture. Above 300°C diagnostic peaks of PAN appeared in the spectra, and in the final stages of pyrolysis, peaks not only due to the decomposition products of polythiophene but also due to the fragments
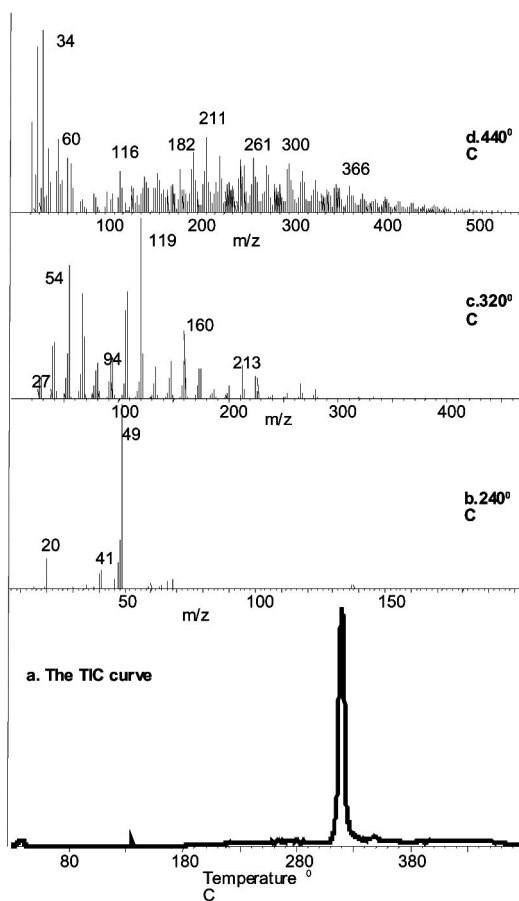
Figure 2. a) The TIC curve and the mass spectra recorded at b) 240°C, c) 320°C, and d) 430°C during the pyrolysis of mechanical mixture PAN/PTh.

with cyclic and unsaturated structures associated with the thermal degradation of PAN were detected. Although similar peaks were present in both of the pyrolysis mass spectra of PTh/PAN and the mechanical mixture the relative intensities of the product peaks showed drastic variations.

The intense and/or characteristics peaks recorded in the pyrolysis mass spectra recorded at the maxima of the TIC curves of PTh/PAN are summarized in Table 1.

Actually, the analyses of pyrolysis data were quite complicated as degradation of both PAN and BF_4^- doped PTh yielded several products over a wide temperature range. What is more important for pyrolysis mass spectrometry analysis is not the presence of a product peak, but the variation of its intensity as a function of temperature, that is its evolution profile. Thus, the evolution profiles of all characteristic thermal decomposition products generated during the pyrolysis of PTh/PAN and the mechanical mixture were studied and compared with those recorded for the corresponding homopolymers. Among the several PAN based products, HCN (m/z = 27 Da), $(C_2H_3CN)H$, (m/z = 54 Da), $(C_2H_3CN)_2CH$ (m/z = 119 Da), $(C_2H_3CN)_4H$ (m/z = 211 Da) generated by the homolytic cleavages and $(CH_2CN)(C_2HCN)_2$ $(C_2H_3CN)_2$ (m/z = 248 Da) and
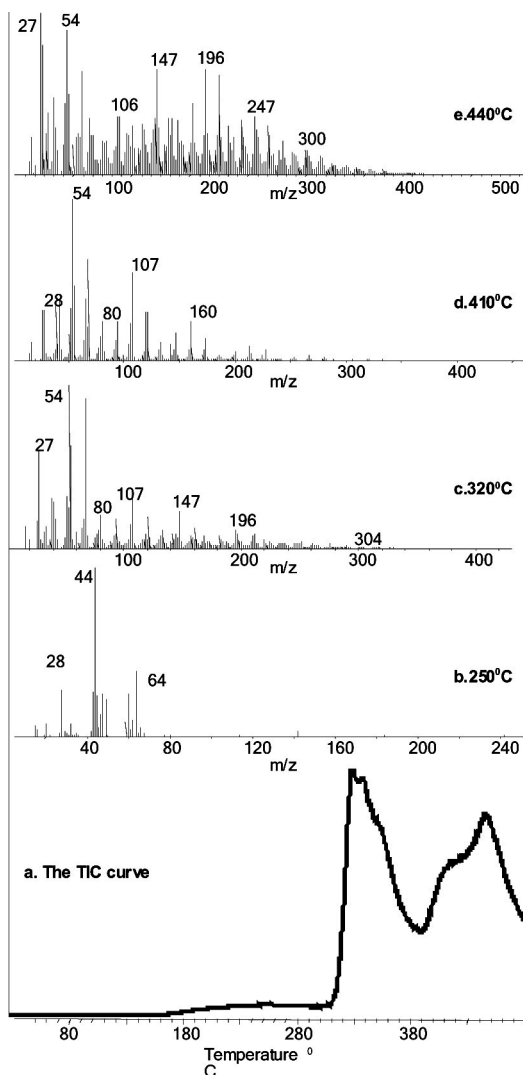
Figure 3. a) The TIC curve and the mass spectra recorded at b) 250°C, c) 320°C, d) 410°C and, e) 440°C during the pyrolysis of PAN/PTh.

$(C_2HCN)_3(C_2H_3CN)_5$ (m/z = 418 Da) due to the degradation of dehydrogenated cyclic fragments were selected for comparison. On the other hand, for BF_4^- doped PTh component and HF and BF_2 (m/z = 20 and 49 Da respectively) due to evolution of dopant, the thiophene trimer (m/z = 248 Da) and H_2S (m/z = 34 Da) associated with the cleavage of the thiophene ring were chosen as reference degradation products. The single ion pyrograms of these products recorded during the pyrolysis of mechanical mixture and electrochemically prepared BF_4^- doped PAN/PTh samples are given in Figure 4. The fragment with m/z = 248 Da was diagnostic for both PTh and PAN, thus for convenience, the evolution profile of this fragment is given twice. Furthermore, the evolution profiles of the same products from PAN and PTh are also included in the figure for comparison.

Table 1

The characteristic and/or intense peaks in the pyrolysis mass spectra recorded during pyrolysis of PTh/PAN film

	250°C	320°C	410°C	440°C	Assignment
20	164	28	102	156	HF
26	10	122	188	273	C_2H_2, CN
27	21	314	592	1000	C_2H_3, HCN
28	240	328	595	876	C_2H_4, N_2
34	21	16	139	368	H_2S
41	215	655	923	953	C_4H_5
44	1000	138	227	367	CS
49	186	34	33	43	BF_2
54		1000	1000	873	$(C_2H_3CN)H$, $(C_2H_3)_2$
64	150	127	135	238	S_2, $(C_2H_3)_2CHCH$
80	3	236	204	235	$(C_2H_3)_2CHCH$
83		7	20	43	C_4H_3S
84		10	32	84	C_4H_4S
107		535	303	356	$(C_2H_3CN)_2H$
116		32	60	251	$(C_2H_2S)_2$
119		298	83	171	$(C_2H_3CN)_2CH$
135		18	32	95	$C_2H_3CN-C_4H_2S$, $(C_2H_3)_5$
160		239	51	148	$(C_2H_3CN)_3H$
166		2	16	93	$(C_4H_3S)_2$
182		2	80	436	(C_2HCN) $(C_2H_3CN)_2H$
188		8	31	103	$(C_2H_3CN)_2-C_4H_2S$, $(C_2H_3CN)(C_2H_3)_5$
196		11	115	643	$C_3H_4(C_2H_3CN)_3$
210		5	76	612	$(C_2HCN)(C_2H_3CN)_3$
217		1	11	62	$C_2H_3CN-(C_4H_2S)_2$, $(C_2HCN)_4CH$
234		2	29	342	$C_3H_4(C_2H_3CN)_3$
248		2	22	286	$C_4H_3SC_4H_2SC_4H_3S$, $CH_2CN(C_2HCN)_2(C_2H_3CN)_2$
266		31	17	125	$(C_2H_3CN)_5H$
270			4	54	$(C_2H_3CN)_2-(C_4H_2S)_2$, $(C_2HCN)_4(C_2H_3CN)$
314			8	101	$(C_2HCN)_2(C_2H_3CN)_4$
365			2	40	$(C_2HCN)_3(C_2H_3CN)_4$
418				5	$(C_2HCN)_3(C_2H_3CN)_5$

The similarities in the evolution profiles of degradation products of the mechanical mixture and those of the corresponding homopolymers were quite significant. When the thermal decomposition products of PTh considered, the only difference detected was the decrease in the intensity of the low temperature evolution peak of dopant based products that were attributed to the physically adsorbed dopant and HF generated by reactions of dopant with adsorbed water (12, 13). The evolution profiles of PAN based products
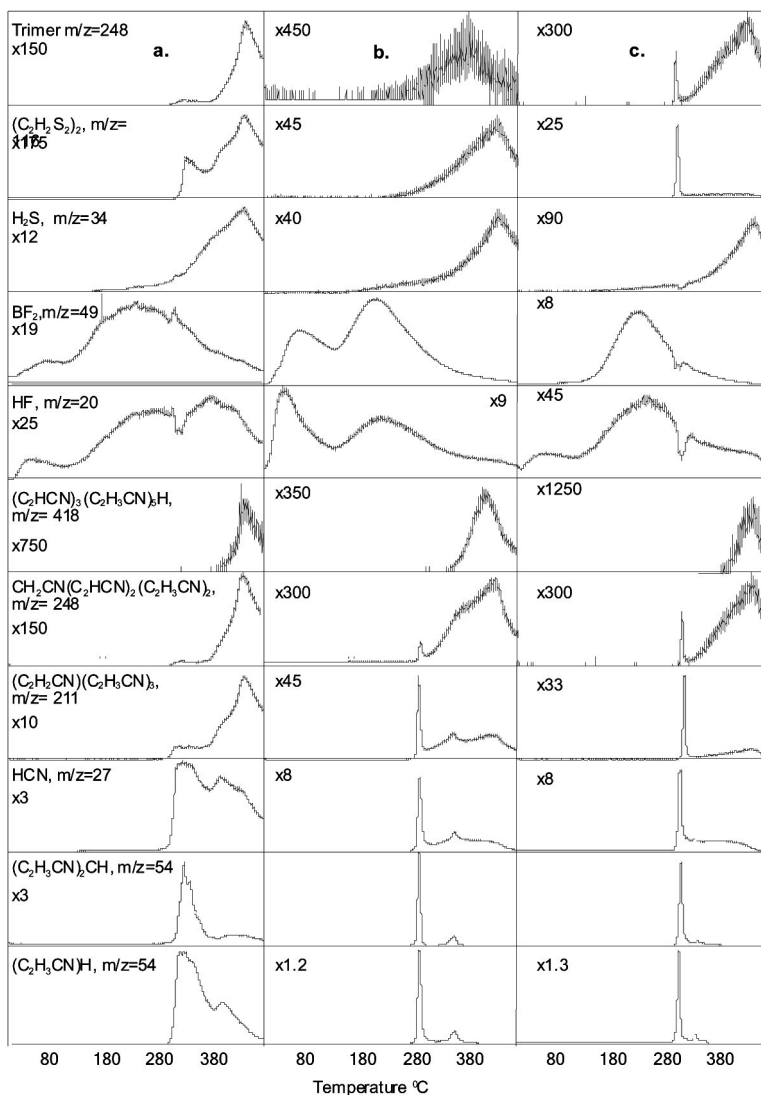
Figure 4. Evolution profiles of some characteristic fragments recorded during the pyrolysis of a) PTh/PAN, b) corresponding homopolymers PTh and PAN, and c) mechanical mixture.

generated during the pyrolysis of the mechanical mixture showed nearly identical trends with those recorded for the homopolymer PAN. Again acrylonitrile monomer, its low molecular weight oligomers, and the fragments due to the homolytic cleavages along the polymer backbone were mainly generated in a narrow temperature range around 320°C, whereas the fragments associated with relatively high molecular weight unsaturated cyclic imine structures were recorded at high temperatures and were quite weak. It is clear that each component degraded independently during the pyrolysis of the mixture.

On the other hand, evolution profiles of PAN based products recorded during pyrolysis of PTh/PAN films showed significant differences compared to those recorded for the pure homopolymer, PAN. In general, the evolution profiles of products
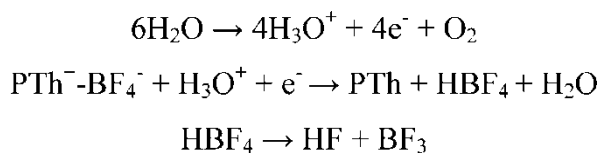
generated by homolytic cleavages shifted slightly to higher temperatures and broadened. Furthermore, the relative intensities of high molecular weight fragments involving unsaturated cyclic structures detected especially in the final stages of pyrolysis decreased considerably. Significant increase in HCN evolution even at elevated temperatures was also detected. Thus, it may be thought that polymerization of pending CN groups yielding single conjugated structure of imine moieties was restricted.

Some variations in the evolution profiles of PTh based products were also detected. Yet, the changes were almost negligible. Meanwhile, the relative intensities of dopant based fragments such as BF_3, BF_2, and BF were decreased noticeably while HF generation was enhanced even at elevated temperatures. The decrease in the dopant yield may be associated with a decrease in the extent of doping. However, if this was the case then evolution of HF should also be decreased accordingly. In general, it is known that HF generation is attributed to reactions of dopant with adsorbed H_2O usually during storage as shown in Scheme 2.

Thus, evolution of HF mainly expected to occur at initial stages of pyrolysis. Detection of HF at elevated temperatures, especially in the regions where evolution of other dopant based products already diminished, was associated with fluorine substituted thiophene rings in our previous studies (12). Thus, it may be concluded that fluorination of the polymer matrix has occurred under the experimental conditions.

It is clear that thermal characteristics, thus, structural characteristics of both PAN and PTh blocks were affected during the electrochemical polymerization of thiophene onto PAN coated anode. However, in order to propose a copolymer formation, fragments involving characteristic units of both components should be detected. Thus, the presence of such products namely mixed dimers and trimers such as $C_2H_3CN-C_4H_2S$, (m/z = 135 Da), $(C_2H_3CN)_2-C_4H_2S$ (m/z = 188 Da), $C_2H_3CN-(C_4H_2S)_2$ (m/z = 217 Da) and $(C_2H_3CN)_2-(C_4H_2S)_2$ (m/z = 270 Da) has been questioned. Unfortunatelly, these peaks were also present in the pyrolysis spectra of PAN itself. Fragments $(C_2H_3)_5$ (m/z = 135 Da), and $(C_2H_3CN)(C_2H_3)_5$ (m/z = 188 Da) generated by decomposition of segments involving CN defficiency, and fragments at $(C_2HCN)_4CH$ (m/z = 217 Da) and $(C_2HCN)_4(C_2H_3CN)$ (m/z = 270 Da) produced by the degradation of dehydrogenated cyclic segments were weak but detectable in the pyrolysis mass spectra of PAN.

In Figure 5 single ion pyrograms of $C_2H_3CNC_4H_2S$, $(C_2H_3CN)_2C_4H_2S$, $C_2H_3CN(C_4H_2S)_2$ and $(C_2H_3CN)_2-(C_4H_2S)_2$ (m/z = 135, 188, 217, and 270 Da respectively) recorded during pyrolysis of PTh/PAN and the mechanical mixture are shown together. Evolution profiles for C_2H_3CNH and $(C_2H_3CN)_2$ are also included for comparison. It is clear that their relative intensities of these peaks were increased drastically. Actually, for PAN films, under the electrolysis conditions, even in the absence of thiophene, decrease in the yields of monomer and oligomers, and increase in the amount of products stabilized by cyclization reactions were also detected. Thus, it is hard to propose that these peaks in the pyrolysis mass spectra of PAN/PTh are mainly due to the mixed dimers.

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

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

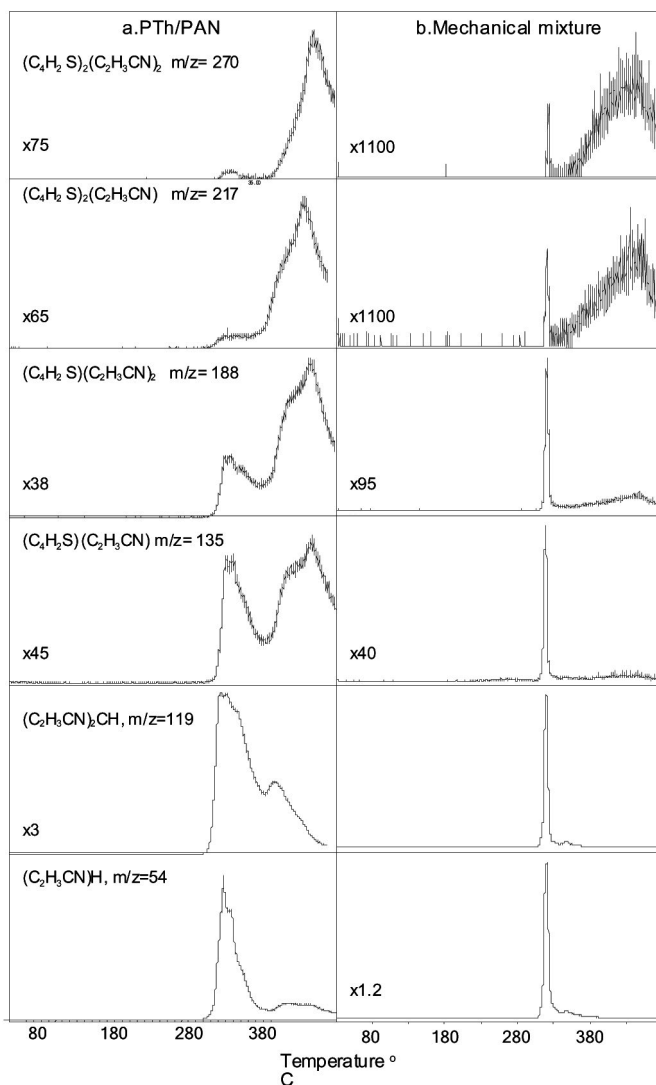$$HBF_4 \rightarrow HF + BF_3$$

Scheme 2.

Figure 5. Evolution profiles of some fragments that can be attributed to mixed dimers recorded during the pyrolysis of a) PTh/PAN and b) mechanical mixture.

Conclusion

Structural and thermal analyses of a polymer sample (PTh/PAN) prepared by electro-chemical polymerization of thiophene onto a poly(acrylonitrile) have been performed by direct insertion probe pyrolysis mass spectrometry technique indicated that thermal behavior of PAN was affected significantly. Evolution of HCN and fragments associated with homolytic cleavages of the polymer backbone were enhanced while generation of products involving unsaturated cyclic imine structures were decreased indicating that the presence of PTh inhibited characteristic cyclization reactions recorded during pyrolysis of PAN. PTh based products from PTh/PAN showed nearly identical trends

with those recorded for the pure PTh. Yet, low temperature evolution of dopant based products decreased indicating a lower extent of adsorption.

Acknowledgments

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