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Characterization of Conducting Copolymers of Succinic Acid Bis-(-4-pyrrol-1-yl-phenyl) Ester and Thiophene via Pyrolysis Mass Spectrometry

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In this work, a direct pyrolysis mass spectrometry technique was applied to characterize a conducting copolymer of succinic acid bis-(4-pyrrol-1-yl-phenyl) ester (SM) and thiophene prepared by electrochemical polymerization. Thermal degradation behavior of both components was quite similar to those of the corresponding homopolymers, PSM, and polythiophene PTh. Yet, detection of oligomers and mixed dimers of both monomers in the high temperature pyrolysis mass spectra confirmed the formation of a copolymer. Furthermore, evolution of SM monomer in the temperature range where the fragments, due to the thermal degradation of PTh chains, have been detected. Also, the generation of dimer of thiophene in the temperature range, where the fragments associated with PSM have been observed, pointed out the presence of thiophene and SM units along the PTh and PSM chains. However, as thermal stabilities of PTh and PSM chains were nearly identical to the corresponding homopolymers, it may be concluded that the presence of other monomer or low molecular weight oligomers along the chains of each component did not significantly affect the thermal characteristics.

Keywords conducting polymers, polythiophene, dipyrrolyl monomer, pyrolysis mass spectrometry

Introduction

The mechanical properties of conducting polymers can be improved through the formation of polymer composites, graft and block copolymers (1–4). Polythiophene and polypyrrole derivatives are also used for the same purpose (5). Electrochemical synthesis of copolymer films from pyrrole and substituted pyrroles, pyrrole, thiophene, bithiophene, and other combinations of aromatic compounds have been reported. Furthermore, ladder-like polymers, synthesized with the use of N-substituted pyrroles of thiophenes, where the two electropolymerizable units are linked with phenyl derivatives, have been prepared to promote interchain electronic connections in conducting polymers (6, 7).

However, application of common spectroscopic techniques in the elucidation of the structure of conducting polymers is still limited as the samples prepared are insoluble

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in common solvents and contain high concentrations of charge carriers. During the last decades, pyrolysis mass spectrometry techniques in polymer analyses have gained significant interest (8–12). Recently, we reported the characterization of the polymer of a dipyrrolyl monomer, succinic acid bis-(4-pyrrol-1-yl-phenyl) ester by pyrolysis mass spectrometry (13). It was determined that under galvanostatic polymerization conditions, growth of the polymer through the pyrrole moieties was achieved yielding a ladder type polymer (PSM) film. The electrochemical synthesis of a copolymer of dipyrrolyl monomer and thiophene were also discussed in our previous studies (14).

In this work, characterization of the polymer film obtained by the electrolysis of succinic acid bis-(4-pyrrol-1-yl-phenyl) ester in the presence of thiophene by direct pyrolysis mass spectrometry technique is discussed.

Experimental

The synthesis of succinic acid bis-(4-pyrrol-1-yl-phenyl) ester, (SM), and the galvanostatic polymerization of the dipyrrolyl monomer, (PSM), and BF_4^- doped polythiophene, (PTh), were discussed in our previous studies (13, 15).

The electrolysis of 50 mg SM and 15 mL 0.4 M thiophene (Aldrich) in 15 mL dichloromethane (Merck) was performed in a two compartment cell equipped with platinum foils as the working and counter electrodes and Ag/Ag^+ as the reference electrode under nitrogen atmosphere. A Wenking POS 2 Potentiostat was used for that purpose. Electrolysis was carried at 2.7 V at 0°C. 0.1 M tetrabutylammonium tetrafluoroborate (TBAFB), (Aldrich) was used as the supporting electrolyte. The polymer film, PSM/Th, was washed with the solvent several times to remove unreacted monomer and excess TBAFB.

The direct insertion probe pyrolysis mass spectrometry (DP-MS) system used for thermal analyses consists of a 5973 HP quadrupole 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 heating rate was kept constant, namely 10°C/min, in all pyrolysis experiments.

Results and Discussions

A cyclic voltamogram of succinic acid bis-(4-pyrrol-1-yl-phenyl) ester in acetonitrile reveals one irreversible oxidation peak at 0.65 V (14) which implies that SM is an electroactive substance. A decrease in peak intensities was observed with a continuous scan revealing a loss of electroactivity. For comparison, the value for the pyrrole under the same conditions is 1.1 V. After the addition of thiophene to the solution, a redox peak which showed a decrease in height, with an increasing scan number, was observed at 1.9 V. This redox behavior is completely different than that of pure thiophene, which gives an oxidation peak at 2.1 V. This shift is a reasonable consequence for the copolymer formation. Analysis of the electrolysis product PSM/Th was first performed by TGA and FTIR studies (14). The TGA curve revealed five transitions indicating either a multi-step degradation process or a presence of a multi-component mixture. The FTIR studies pointed out the existence of both thiophene and succinic acid bis-(4-pyrrol-1-yl-phenyl) ester chains and dopant anion in the polymer film, PSM/Th. Yet, it is not possible to conclude whether a copolymer or a composite was formed with the use of FTIR data.

Pyrolysis mass spectra of a composite and a copolymer involving the same components should also be quite similar. Formation of a block copolymer can only be confirmed if fragments involving characteristic units of both components are detected.

On the other hand, an alternating or a random copolymer can be readily differentiated from a composite or blend as the thermal behavior should be somewhat different than the ones for corresponding homopolymers. Thus, in order to elucidate the structure of the product of electrolysis, PSM/Th, pyrolysis data of not only the product film itself, but also those of PTh and PSM and their simple mechanical mixture had to be studied and compared.

Pyrolysis mass spectrometry analysis of polythiophene, PTh, and the homopolymer of succinic acid bis-(4-pyrrol-1-yl-phenyl) ester, PSM, has been discussed in our previous studies (13, 15).

Pyrolysis of electrochemically prepared BF_4^- doped polythiophene by direct insertion probe MS and Curie point pyrolysis GCMS techniques indicated that the thermal decomposition of polythiophene occurs in two steps (15). 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 in accordance with the literature results (16, 17). The detection of products such as H_2S and C_2H_2 at elevated temperatures, pointed out cleavage of the thiophene ring. Oligomer peaks involving more than three repeating units were not detected. In general, the dopant based fragment peaks were significantly more intense. The peak at $m/z = 49$ Da due to BF_2 was the base peak. Furthermore, peaks due to the evolution of NBu_4^+ ion was detected around 250°C . Peaks that can be associated with the solvent, dichloromethane were quite significant even at high temperatures.

Pyrolysis analysis of the polymer film prepared by galvanostatic polymerization of succinic acid bis-(4-pyrrol-1-yl-phenyl) ester has shown that the decomposition of the monomer occurred under the synthesis conditions yielding mainly butadionic acid and pyrrole. The low temperature pyrolysis mass spectra recorded below 100°C was dominated with peaks, not only due to these products, but also with peaks due to the supporting electrolyte TBAFB, and the solvent, although the sample has been washed for several times and dried under vacuum. Yet, the high temperature pyrolysis data revealed that polymerization of the monomer has also occurred. The presence of a peak at $m/z = 131$ Da supported the growth of the polymer from both of the pyrrole end groups producing a ladder type polymer (13). This was due to the pyrrole dimer in the final stages of pyrolysis and the lack of monomer peak, which was among the most intense peaks in the mass spectrum of the succinic acid bis-(4-pyrrol-1-yl-phenyl) ester monomer as expected for an ester. As the two polypyrrole chains are linked with phenyl ester derivatives, involving relatively weak C–O bonds, the generation of a monomer unit during thermal degradation is actually unlikely. It has also been determined that the polypyrrole chains, linked with phenyl ester spacers, had both quinoid and aromatic structures. The thermal degradation of PSM started by the cleavage of $\text{C}_4\text{H}_4\text{NC}_6\text{H}_4\text{O}$ end groups and was followed by the decomposition of both phenyl ester units and polypyrrole chains having a quinoid structure. The maximum yield for PSM-based degradation products was detected around 320°C . The final stage of thermal degradation has been attributed to decomposition of polypyrrole chains having an aromatic structure. Desorption of the solvent dichloromethane and BF_4^- based fragments were detected throughout the pyrolysis. NBu_4^+ evolution occurred around 350°C , indicating very strong adsorption, most probably due to the ladder type structure producing cages along the polymer chain.

Mechanical Mixture

Pyrolysis of the mechanical mixture of PSM and PTh yielded a total ion current, TIC, curve (the variation of the total ion yield as a function of temperature) indicating the

evolution of the thermal degradation products in a broad temperature range. The TIC curve and the mass spectra recorded at the maxima and the shoulders of the peaks in the TIC curve are given in Fig. 1. As expected, the mass spectra involved characteristic peaks due to both components. The base peak was due to BF_2 at $m/z = 49$ Da. Diagnostic peaks of the supporting electrolyte and the solvent were also present. However, since some of the fragment peaks are diagnostic for both of the components, for a better understanding, the variation of the relative intensities of each intense or characteristic peak with respect to temperature, (the single ion pyrograms or evolution profiles) have been studied.

In Fig. 2, the single ion pyrograms of some selected characteristic fragments for PTh, namely H_2S ($m/z = 34$ Da) and $(\text{C}_4\text{H}_3\text{S})_2$ ($m/z = 166$ Da), and in Fig. 3, those for PSM, such as $\text{OCCH}_2\text{CH}_2\text{COO}$ ($m/z = 100$), $\text{C}_6\text{H}_4\text{OCHO}$ ($m/z = 122$ Da), $\text{C}_8\text{H}_8\text{N}_2$ ($m/z = 131$), $\text{C}_4\text{H}_4\text{NC}_6\text{H}_4\text{OH}$ ($m/z = 159$ Da), and $\text{HNC}_6\text{H}_4\text{OCOC}_2\text{H}_4$ ($m/z = 191$) are shown. The pyrograms of HCl ($m/z = 36$) and $(\text{C}_4\text{H}_9)_2\text{NCH}_2$ ($m/z = 142$ Da), are shown in both figures for a better comparison. The evolution profiles of dopant ion based fragments, HF ($m/z = 20$ Da) and BF_2 ($m/z = 49$ Da) are also included in Fig. 2.

The pyrograms of the fragments that can only be generated from one component are nearly identical to those of the corresponding ones observed from the related homopolymers (13, 15). The fragments that can be generated from both components show evolution profiles as a summation of both the corresponding ones from each homopolymer as in the case of pyrogram of $(\text{C}_4\text{H}_9)_2\text{NCH}_2$ ($m/z = 142$ Da). Evolution of $(\text{C}_4\text{H}_9)_2\text{NCH}_2$ at low temperatures around 250°C can be directly attributed to the desorption of electrolyte from the polythiophene units, whereas the high temperature evolution around 350°C can be associated with the desorption from PSM units. It is clear that the thermal behavior of each component of the mixture, PSM and PTh, were identical to the pure counterparts and were not affected by the presence of the other. Thus, it can be concluded that no secondary reactions has occurred under the experimental conditions.

PSM/PTh

The TIC curve of PSM/PTh film showed an intense peak at initial stages of pyrolysis with a maximum at 60°C as in the case of PSM. The following broad evolution band with several shoulders had a maximum at 300°C , pointed out the complex nature of the PSM/PTh sample. In general, the low temperature peaks below 100°C can directly be attributed to desorption of the unreacted monomer, solvent or any other low molecular weight species adsorbed on the polymer film. However, the presence of more than one peak or a broad peak with several shoulders can be associated either with a multi-step thermal degradation process, as in the case of polymers having labile side groups, or with the presence of more than one compound or segments with different thermal stabilities. For conducting polymers, thermal decomposition involves at least two steps, the first being due to the loss of dopant. The TIC curve and the mass spectra recorded at the maxima and the shoulders of the TIC curve are shown in Fig. 4. Intense and/or characteristic peaks of both PSM and PTh samples are again present in the pyrolysis mass spectra. Moreover, contrary to pyrolysis data of PSM, PTh and their mechanical mixture, high molecular weight fragment peaks were detected in the high temperature pyrolysis mass spectra. Again, peaks due to supporting electrolyte such as BF_3 , HF and NBu_4^+ , and those due to dissociative ionization of them are quite significant. The mass spectral data are summarized in Table 1.

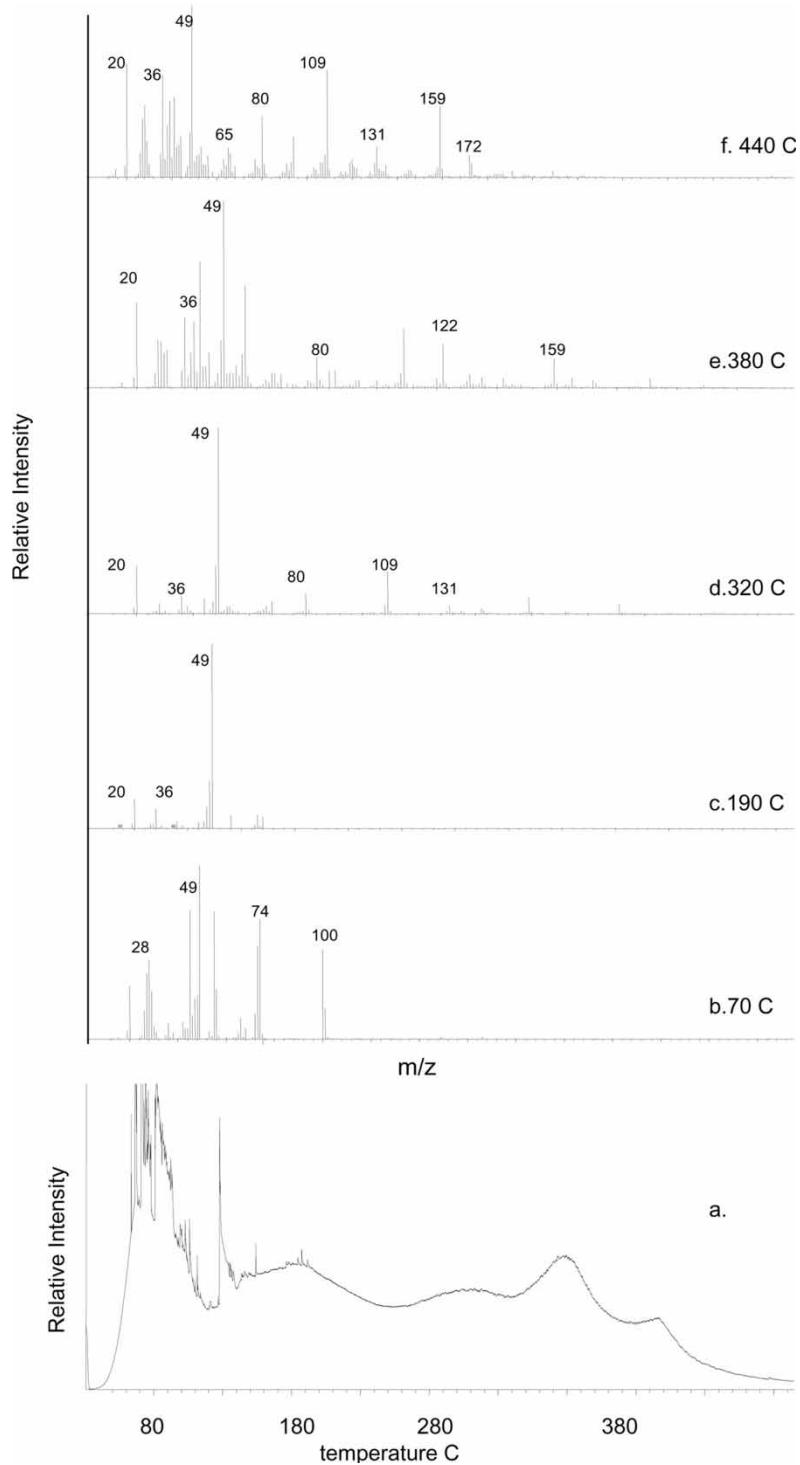


Figure 1. The TIC curve and some selected pyrolysis mass spectra for the mechanical mixture of PTh and PSM.

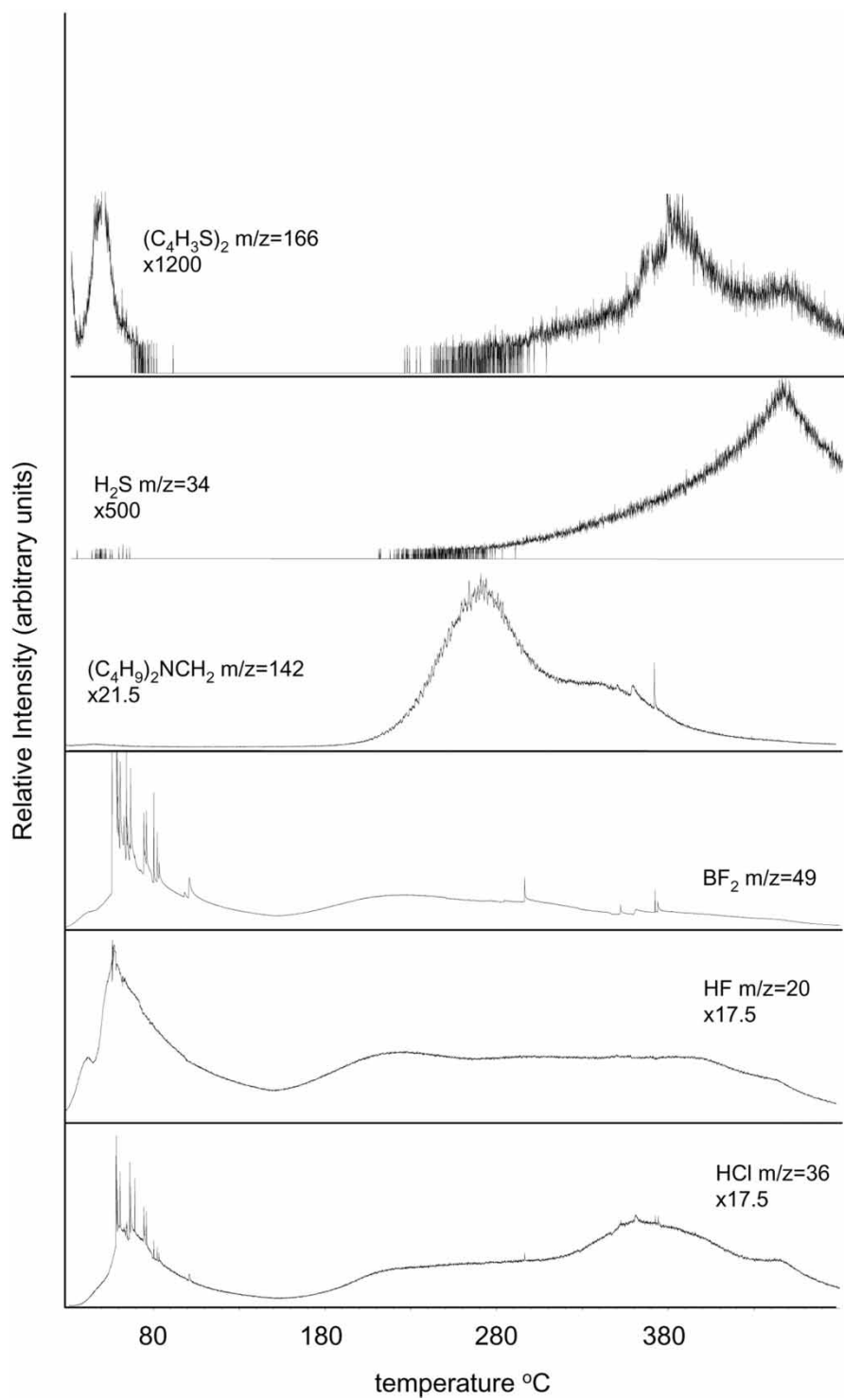


Figure 2. The single ion pyrograms of some selected characteristic fragments of PTh based fragments for the mechanical mixture of PSM and PTh.

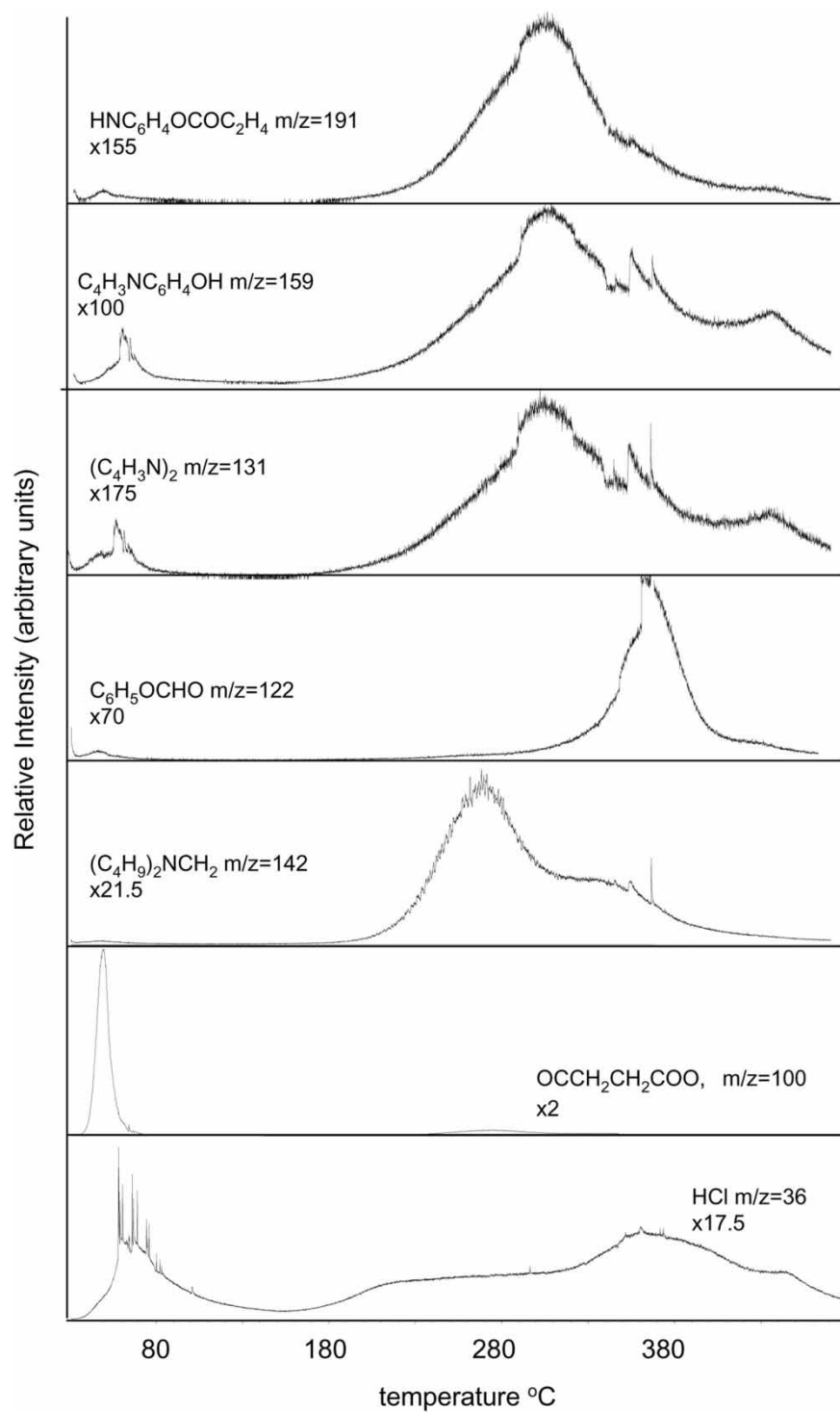


Figure 3. The single ion pyrograms of some selected characteristic fragments of PSM based fragments for the mechanical mixture of PSM and PTh.

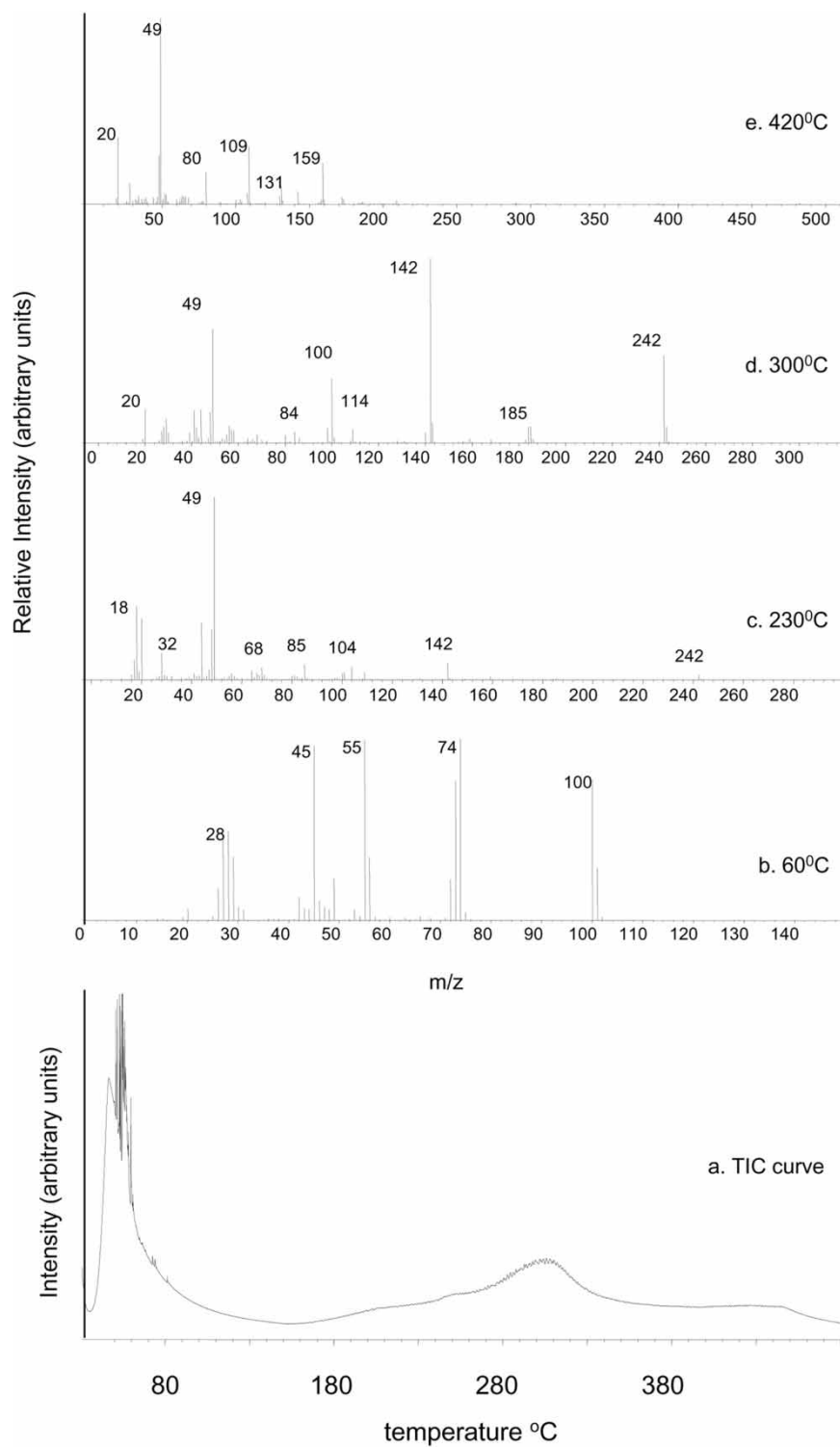


Figure 4. The TIC curve and some selected pyrolysis mass spectra for PSM/PTh.

Table 1
Pyrolysis mass spectral data for PSM/PTh at some selected temperatures

m/z	Relative intensities				Assignments
	60°C	230°C	300°C	420°C	
20	61	363	183	373	HF
30	75	1	53	19	BF, CH ₂ NH, NO, CH ₂ O
34			1	45	H ₂ S
36	10	16	13	29	HCl
39	6	10	53	58	C ₃ H ₃
41	19	36	178	1	C ₃ H ₅ , CH ₃ CN
45	963	5	3		COOH, CHS,
49	221	1,000	614	1,000	BF ₂
55	1,000	37	28	51	CH ₂ CHCO
66	24	35	16	43	C ₄ H ₄ N
68	16	51	43	49	BF ₃
74	1,000	2		9	CH ₃ CH ₂ COOH
80	1	9	39	184	H ₂ N-C ₅ H ₄
83	5	18		11	C ₄ H ₃ SH
84	6	8	63	15	C ₄ H ₄ SH, OCH ₂ CH ₂ CO, FC ₄ H ₃ N
85	2	209	1	11	CH ₂ C ₄ H ₉ N
100	780	18	354	19	OCCH ₂ CH ₂ COO
101	291	18	31	4	FC ₄ H ₂ S
109	1	7	66	340	H ₂ N-C ₆ H ₄ -OH
131		1	9	110	C ₄ H ₄ N-C ₅ H ₅ , HNH ₃ C ₄ -C ₄ H ₃ N
142		22	1,000	67	(C ₃ H ₃ S) ₂ , (C ₄ H ₉) ₂ N=CH ₂ , C ₄ H ₄ NC ₆ H ₄
159	1	10	21	236	C ₄ H ₄ N-C ₆ H ₄ -OH
166	1	1		3	(C ₄ H ₄ SH) ₂
184		1	80	12	NC-C ₄ H ₃ N-C ₆ H ₄ -OH
185	2	2	88	6	NBu ₃
186		1	21	15	C ₄ H ₄ N-C ₆ H ₄ OCO
242		3	424	1	NBu ₄ , C ₄ H ₄ N- C ₆ H ₄ OCOCH ₂ CH ₂ CO
304				4	C ₄ H ₂ N-C ₆ H ₄ (C ₄ H ₂ S) ₂
386				4	C ₄ H ₂ N-C ₆ H ₄ (C ₄ H ₂ S) ₃
400				4	SM
468				2	C ₄ H ₂ N-C ₆ H ₄ (C ₄ H ₂ S) ₄
482			1	5	Mixed dimer

In Fig. 5, the single ion pyrograms of HF ($m/z = 20$ Da), BF₂ ($m/z = 49$ Da), H₂S ($m/z = 34$ Da) and (C₄H₃S)₂ ($m/z = 166$ Da) are shown. Whereas, Fig. 6 shows evolution profiles of characteristic of thermal degradation products of PSM, namely C₆H₄OCHO ($m/z = 122$ Da), C₈H₈N₂ ($m/z = 131$), C₄H₄NC₆H₄OH ($m/z = 159$ Da), monomer, SM, ($m/z = 400$ Da), C₄H₂S(C₄H₂NC₆H₄)(C₄H₂S)₂ ($m/z = 386$ Da) and mixed dimer ($m/z = 482$ Da). The pyrograms of fragments (C₄H₉)₂NCH₂

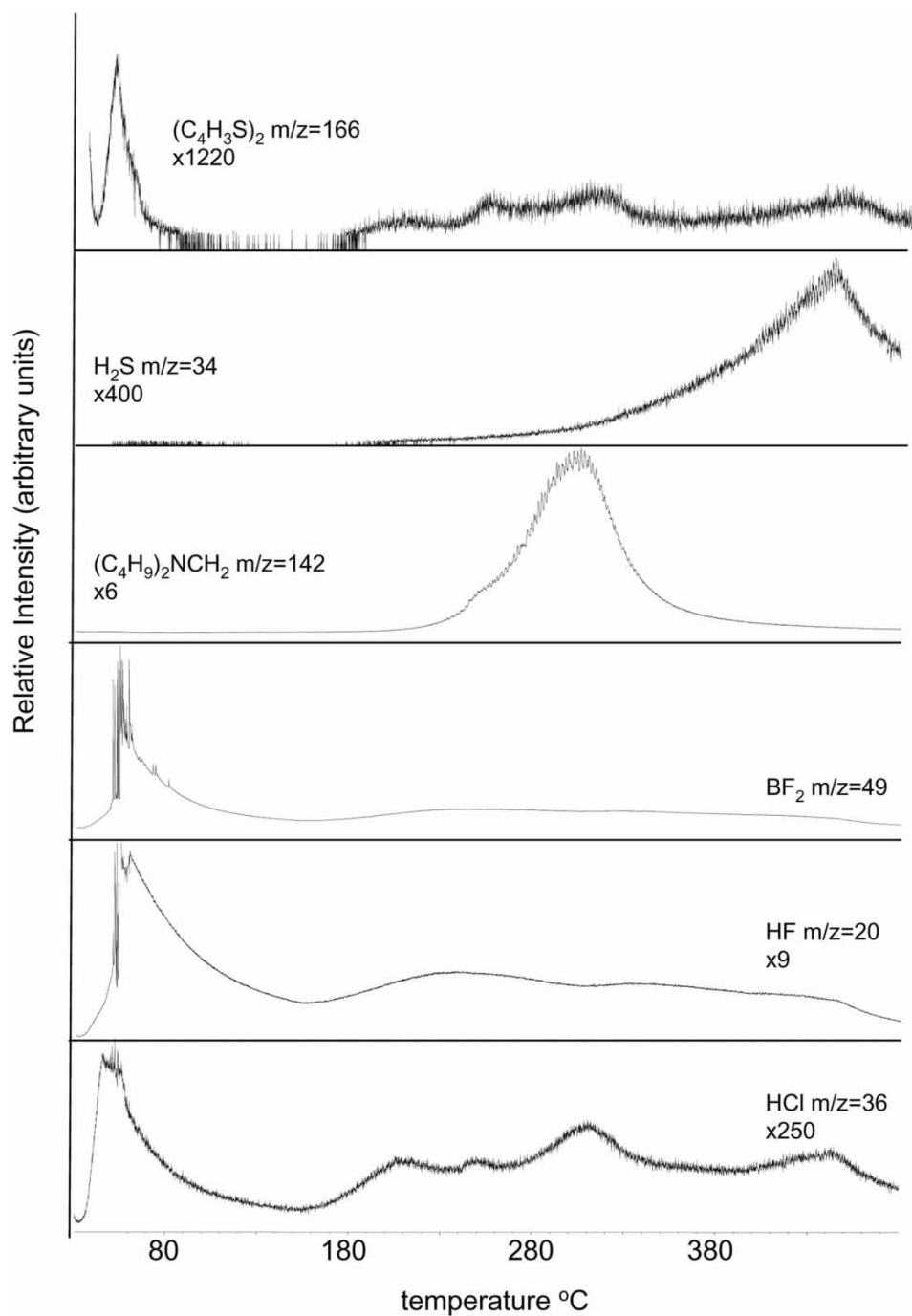


Figure 5. The single ion pyrograms of some selected characteristic fragments of PTh based fragments for PSM/Th.

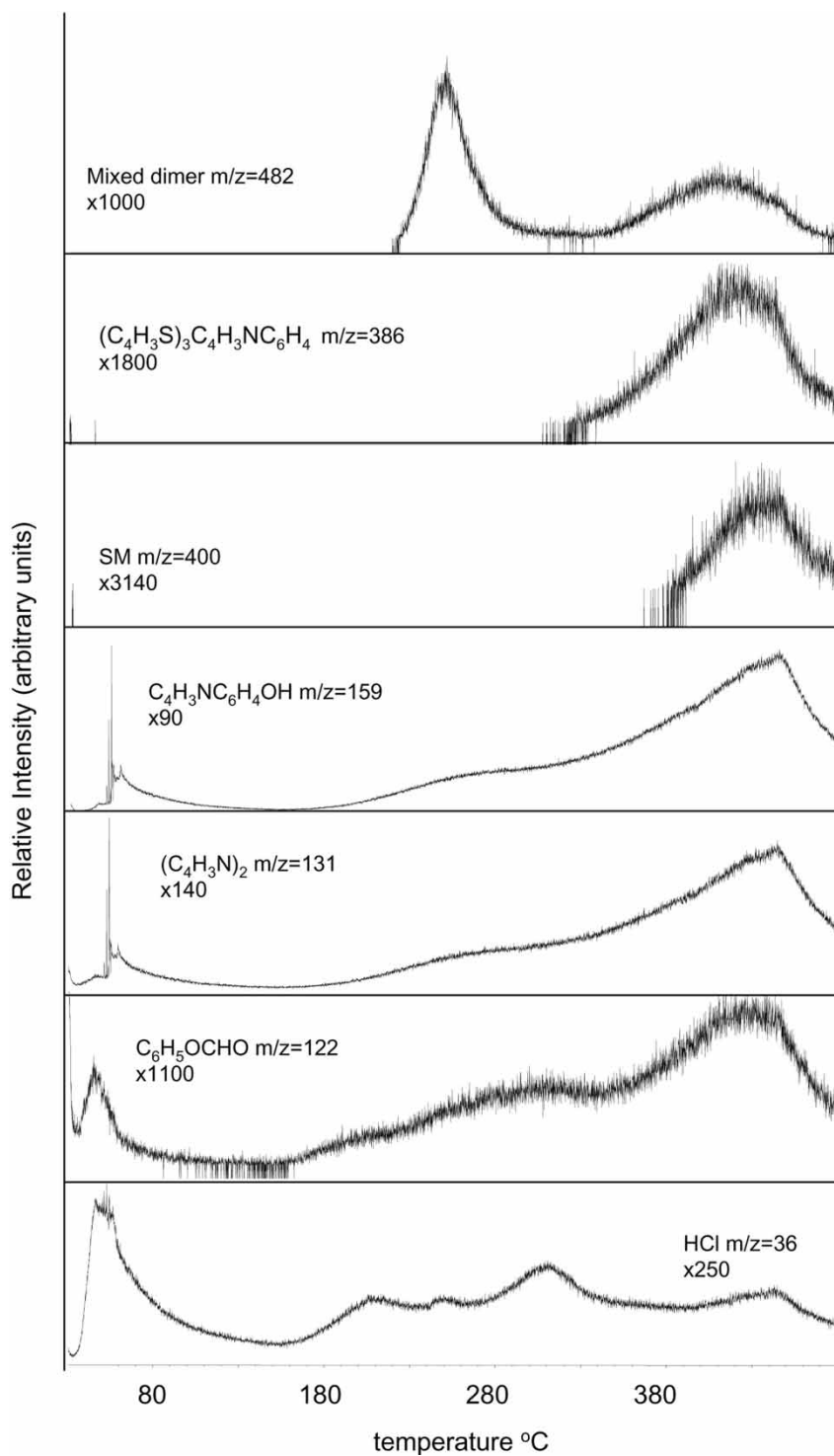


Figure 6. The single ion pyrograms of some selected characteristic fragments of PSM based fragments for PSM/Th.

($m/z = 142$ Da) due to the supporting electrolyte, and HCl ($m/z = 36$ Da) due to the solvent are again included in both figures for a better understanding.

Inspection of single ion pyrograms indicated that at the initial stages of pyrolysis, around 60°C , evolution of butadionic acid and pyrrole occurs as in the case of PSM. Thus, it can be concluded that formation of this compound was also possible during the electrochemical polymerization process as in the case of the galvanostatic one. Again, at initial stages of pyrolysis peaks due to the solvent and supporting electrolyte, peaks were quite intense. Actually, evolution of dopant BF_4^- and solvent based fragments were detected throughout the pyrolysis as in the case of the mechanical mixture.

The thermal degradation behavior of PTh based fragments was quite similar to those detected for the mechanical mixture especially in the high temperature range. Again, except for a weak dimer peak, no higher molecular weight oligomer peak was detected. However, evolution of the dimer was also recorded at moderate temperatures. This may be attributed to the presence of the thiophene chains with different thermal stabilities. The evolution profile of H_2S was nearly identical to that of PTh confirming the decomposition of the thiophene ring at elevated temperatures. Taking into account the similarities of the evolution profiles of thiophene based fragments in the high temperature region, it can be concluded that the sample involved thiophene chains having nearly identical thermal and thus, structural characteristics with the homopolymer thiophene.

The single ion pyrogram of BF_2 is also quite similar to that observed from PTh. Yet, the relative intensity of the NBu_4^+ ion peak at $m/z = 242$ Da and those of other related peaks were significantly enhanced and showed somewhat an intermediate behavior compared to those detected from PTh and PSM; the maximum yield was recorded at 300°C , which is 30°C higher than that observed for PTh, and 50°C lower than was detected from PSM, pointing out a decrease in the extent of cage structure for SM chains along the copolymer backbone.

Contrary to PTh based fragments, significant changes have been observed in the evolution profiles of PSM based fragments. Firstly, a significant decrease in the relative intensities of the low temperature bands and shoulders around 250°C were detected, while enhancements in those of the high temperature bands were recorded. One of the most important points that have to be noticed is the presence of molecular peak of SM at $m/z = 400$ Da in the high temperature pyrolysis mass spectra which is absent in PSM spectra. An even more important point is the presence of a peak at $m/z = 482$ Da that may be attributed to a mixed dimer of pyrrole and thiophene and the weak peaks at $m/z = 304, 386,$ and 468 Da that may be associated with $(\text{C}_4\text{H}_2\text{NC}_6\text{H}_4)(\text{C}_4\text{H}_2\text{S})_x$ where $x = 2$ to 4 , respectively. Except for the pyrogram of the mixed dimer, all of the others showed identical trends with those associated with PTh. Thus, it may be proposed that the SM monomer and/or low molecular weight oligomers had been added to PTh chains randomly during the electrochemical polymerization process. Though high molecular weight fragment peaks were detected only in the final stage of pyrolysis, peaks due to $\text{C}_4\text{H}_4\text{NC}_6\text{H}_4\text{OCOC}_2\text{H}_4$ at $m/z = 159$ Da and $(\text{C}_4\text{H}_4\text{N})_2$ at $m/z = 131$ Da were also recorded at moderate temperatures in the range where the homopolymer PSM degradation occurs (13). In this region, the mixed dimer evolution (Fig. 5) was also detected indicating the addition of thiophene to PSM chains. Thus, it may be concluded that homopolymerization of SM also occurred to a certain extent.

Conclusions

Direct pyrolysis mass spectrometry analysis of the electrolysis product of thiophene (Th), and succinic acid bis-(4-pyrrol-1-yl-phenyl) ester, (SM) indicated that the thermal

degradation behaviors of both components were quite similar to those of the corresponding homopolymers. Furthermore, detection of oligomers of both monomers and mixed dimers in the high temperature pyrolysis mass spectra confirmed the formation of a copolymer. Thermal decomposition of PSM started at lower temperatures as expected. Mixed dimer evolution was observed in two distinct regions. Furthermore, SM monomer, which was not detected during the pyrolysis of PSM, evolved in the temperature region in which PTh degrades indicated the presence of each monomer along the polymer chain of the other confirming formation of a random copolymer.

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