Characterization of Conducting Copolymer of Thiophene via Pyrolysis Mass Spectrometry

Anil Levent[a]; Jale Hacaloglu[a]; Levent Toppare[a]

[a] Chemistry Department, Middle East Technical University, Ankara, Turkey

PLEASE SCROLL DOWN FOR ARTICLE

Characterization of Conducting Copolymer of Thiophene via Pyrolysis Mass Spectrometry

ANIL LEVENT, JALE HACALOGLU, AND
LEVENT TOPPARE

Chemistry Department, Middle East Technical University, Ankara, Turkey

In this work, structural and thermal characterization of a conducting copolymer of thiophene (PTh) with 2-methylbutyl-2-(3-thienyl)acetate prepared by two different methods has been performed by pyrolysis mass spectrometry techniques. The pyrolysis mass spectrometry data of both components of the copolymer, polythiophene, PTh, poly(2-methylbutyl-2-(3-thienyl)acetate), PMBTA and PTh/PMBTA have been analyzed and compared. It has been determined that when the electrochemical polymerization of thiophene was achieved on PMBTA coated anode through the thiophene moieties of PMBTA, characteristics of both PTh and PMBTA were retained to a certin extent. However, when thiophene was polymerized in the presence of MBTA, a polymer film with lower conductivity, but more uniform structure, was produced.

Keywords pyrolysis, polythiophene, copolymer, conducting polymers

Introduction

The application of several conducting polymers is still limited due to their poor mechanical properties. In order to improve the mechanical properties of these polymers, either structural modification of monomers or preparation of block or graft copolymers of conducting polymers with certain insulating polymer matrices having good mechanical characteristics have been achieved (1, 2). Characterization of some interesting polythiophene based conducting polymers have been discussed in the literature (3–5). Synthesis and characterization of soluble polythiophene derivatives and liquid crystalline polythiophene derivaties have also appeared in the literature (6, 7). Two new functionalized thiophene derivatives bearing epoxy and carbonate groups were synthesized by Li and coworkers (8). They have determined that the electrooxidative polymerization of these monomers led to stable electroactive polymers, while the functional groups remained unchanged during the polymerization process. Electrochemical and spectroscopic data of the resulting homopolymers revealed that these polymers possess an extended conjugated pi-electron system comparable to unfunctionalized poly(3-alkylthiophene)s (8). In our recent studies, we have attempted to grow thiophene through the heterocyclic end groups of some insulating polymers in order to improve mechanical characteristics of polythiophene (9–11).

Although, the field of conducting polymers advanced considerably in the last decades, structural characterization of the samples by classical spectrometry techniques is limited. It has been shown that pyrolysis mass spectrometry techniques offer an alternative way for polymer structure and composition analyses (12–14).

In this work, the structural and the thermal characterization of the copolymer of thiophene (Th) and (2-methylbutyl-2-(3-thienyl)acetate) (MBTA) have been performed via direct insertion probe pyrolysis mass spectrometry technique. The pyrolysis mass spectrometry data of polythiophene (PTh), poly(2-methylbutyl-2-(3-thienyl)acetate) (PMBTA) and copolymers prepared by two different methods have been analyzed and compared.

Experimental

The synthesis of (S)-2-methylbutyl-2-(3-thienyl)acetate (MBTA) have been described in our previous studies as shown in Scheme 1 (11). The crude product was purified by passing through a silicagel column using hexane as the eluent. The polymerization of the monomer was achieved by constant current electrolysis in one compartment cell consisting of platinum as working and counter electrodes. The electrolysis was carried out in dichloromethane-tetrabutylammonium tetrafluoroborate, $N(C_4H_9)_4BF_4$, (TBAFB), solvent electrolyte system. Scheme 1 also represents the galvanostatic polymerization of the monomer.

Potentiostatic copolymerization of thiophene and MBTA were carried out at 1.9 V in a $CH_3CN/0.5M$ TBAFB solvent electrolyte system using two Pt foil electrodes (1.5 cm^2) as the working and counter electrodes and Ag/Ag^+ as the capillary reference electrode using a Wenking POS 73 Potenstiostat. For this purpose, two different routes were followed. In the first, thiophene (0.02 M) was electrochemically polymerized on PMBTA coated anode through the thiophene moieties of PMBTA. The expected mechanism is shown in Scheme 2.

In the second, 0.02 M thiophene was polymerized in the presence of MBTA as shown in Scheme 3.
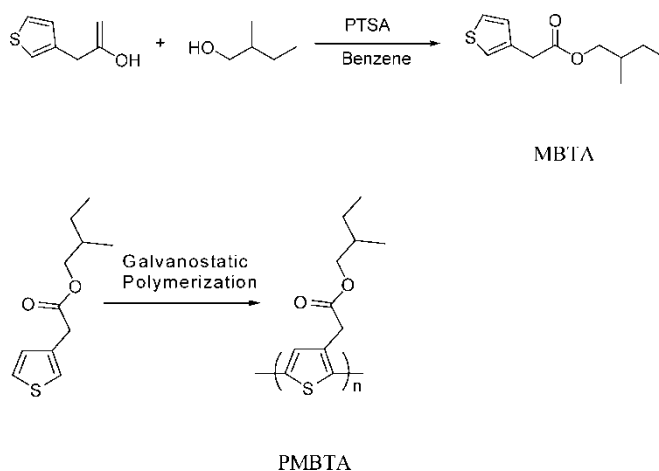
MBTA

PMBTA

Scheme 1. Synthesis of (S)-2-methylbutyl 2-(3-thienyl)acetate (MBTA) and its homopolymer.
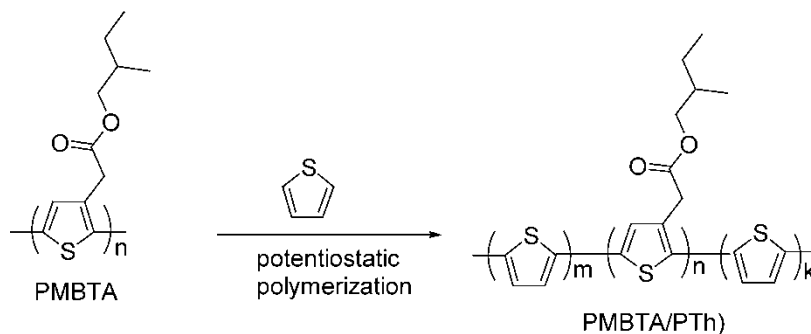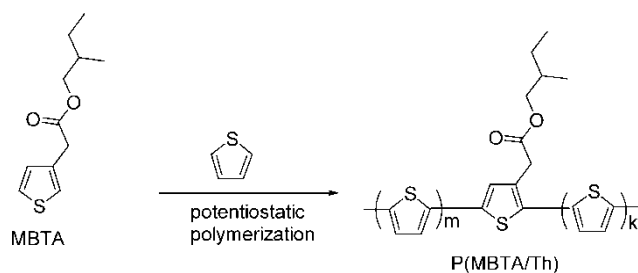
Scheme 2. The expected mechanism for the synthesis of PMBTA/PTh.

5973 HP quadruple mass spectrometry system is coupled to a JHP SIS direct insertion probe for thermal analyses. 0.01 mg samples were pyrolyzed in flared glass sample vials. The temperature was increased at a rate of 100C/min and the scan rate was 2 scans/s.

Conductivities of the samples were measured using a four-probe technique as 10^2, 8×10^{-3}, 2×10^{-1}, and 2×10^{-2} S cm^{-1} for PTh, PMBTA, PMBTA/PTh and P(MBTA/Th), respectively.

Results and Discussions

For a reliable structural analysis of the polymer via pyrolysis mass spectrometry, the fragmentation pattern of the monomer and all ingredients must be known. Thus, the pyrolysis mass spectra of both the monomer and the supporting electrolyte were also recorded in the temperature range of 25–445°C. The mass spectrum of the monomer involves peaks reflecting the classical ester, hydrocarbon and thiophene fragmentation patterns. It is clear that the main degradation mechanism of the monomer (S)-2-methylbutyl 2-(3-thienyl)acetate involves bond cleavages next to C=O, and McLafferty rearrangement reactions yielding C_2H_2OH (m/z = 43 Da), $C_4H_3SCH_2$ (m/z = 97 Da), $C_4H_3SCH_2COOH$ (m/z = 142 Da), COOH (m/z = 45 Da), C_5H_{11} (m/z = 71 Da). The mass spectral data for the monomer is summarized in Table 1. On the other hand, mass spectrum of the supporting electrolyte is mainly dominated with peaks due to dissociative ionization of tetrabutylammonium cation and peaks at m/z = 100, 142, 185, and 242 Da due to $N(C_4H_9)C_2H_5$, $N(C_4H_9)_2CH_2$, $N(C_4H_9)_3$, and $N(C_4H_9)_4$ were quite significant.

Scheme 3. The expected mechanism for the synthesis of P(MBTA/Th).

Table 1

Mass spectral data at some selected temperatures recorded during the pyrolysis of PMBTA, PTh, PMBTA/PTh, and P(MBTA/Th)

m/z	MBTA	PMBTA				PTh		PMBTA/PTh			P(MBTA/Th)		Assignments
		60°C	280°C	320°C	420°C	240°C	430°C	55°C	320°C	440°C	70°C	440°C	
34			0	4	14	4	418	6	34	68		12	H_2S
39		85	58	356	317	55	167		343	311	258	389	C_3H_3
41	383	233	133	694	358	309	754	1000	676	421	328	530	C_3H_5
44	139		133	331	478			876	449	456	302	464	CS, CO_2
49		1000		36	0	1000	683	623	405	27	1000	8	BF_2
55	141	174	208	910	1000			11	1000	1000	965	1000	C_4H_7
70	191	176	75	487	471			95	513	491	418	521	C_5H_{10}, NC_4H_8
83	6	9	2	170	1		2	16	6	4	10	2	C_4H_3S
84	5	5	57	170		8	51	14	9	8	8	3	C_4H_4S
97	954	199	80	171	10			25	16	18	51	6	$CH_3C_4H_2S$
100	298		320	353		8	53	12	4	2	2	2	$N(C_4H_9)C_2H_5$
142	241	43	1000	1000		25	71	2	9	2	2	1	$N(C_4H_9)_2CH_2$
166		46	1	6		7	23		3	2		0.1	Thiophene dimer
242			952	85			6						$N(C_4H_9)_4$
212	133	42	2	1				3					MBTA

Actually, PMBTA is basically a 3-substituted thiophene. However, as the substituent involves labile bonds, one should expect a somewhat different thermal degradation mechanism compared to PTh. Pyrolysis of polythiophene has been studied in detail in our previous works (15, 16). The TIC curve and the mass spectra recorded at the maxima of the TIC curve and the evolution profiles of some selected products recorded during the pyrolysis of PTh are shown in Figures 1 and 2, respectively. It has been determined that the thermal degradation of the polymer occurs in two steps; at around 240°C dopant leaves the polymer, and in the final stage of pyrolysis, degradation of the polymer occurs. Products due to the cleavage of the thiophene ring are more abundant than the low molecular weight oligomers. This behavior is attributed to presence of a network structure (15, 16).

The total ion current (TIC) curve and the mass spectra recorded at the maxima of the TIC curve recorded during the pyrolysis of PMBTA are shown in Figure 3. The TIC curve shows three broad and intense peaks. The peak recorded around 250°C is the most intense and has a shoulder around 330°C (Figure 3(a)). It is clear that the first peak in the TIC curve corresponds to evolution of unreacted monomer, low molecular weight oligomers, solvent and the dopant ion. The mass spectra, recorded around 300°C pointed out evolution of adsorbed counter ion of dopant, TBAFB, and those recorded in the final stage of pyrolysis indicated degradation of the polymer. No monomer or low molecular weight oligomers were detected. Yet, peaks due to thiophene and its dimer are present in the mass spectra recorded in a broad temperature range. At elevated temperatures, peaks due to dissociation of thiophene ring are more abundant. The characteristic and/or intense peaks in the pyrolysis mass spectra recorded at the maxima of the TIC curve are also given in Table 1.

It is known that a great degree of similarity between the mass spectrum of the monomer and pyrolysis mass spectrum of the polymer can only be observed if the thermal degradation process proceeds through a depolymerization mechanism, yielding mainly a monomer. On the other hand, the thermal degradation of polymers involving labile side chains usually occurs in two steps, the first being the cleavage of weak bonds substituted on the main chain. Thus, the monomer and oligomer peaks are either weak or absent in the pyrolysis mass spectra of such polymers. For conducting polymers, as the polymer film contains dopant ions, an exact resemblence of the pyrolysis mass spectra of the polymer and the mass spectrum of the monomer cannot be expected. For the BF_4^- doped PMBTA, the pyrolysis mass spectra are totally different than the mass spectrum of the monomer indicating that depolymerization type degradation did not take place.

For a better understanding, single ion pyrograms of all intense and characteristic products have been studied. In Figure 4, the time temperature resolved evolution profiles of fragments BF_2 (m/z = 49 Da), C_4H_7 (m/z = 55 Da), C_5H_{10} (m/z = 70 Da), $C_4H_3SCH_2$ (m/z = 97 Da), $(C_4H_3S)_2$ (m/z = 166 Da), and H_2S (m/z = 34 Da). All dopant based fragments such as HF, BF, BF_2, and BF_3 showed identical trends with BF_2 (Figure 2a). It is clear that the evolution of dopant occurs in two steps; around 60 and 280°C. The first peak in the evolution profile of BF_2 was associated with the evolution of physically adsorbed BF_4^- and the second with the loss of the dopant ion. The relative intensity of the second peak is significantly low, indicating that doping process is not very efficient. The fragments that can be directly attributed to a loss of side chains show identical trends. Evolution of H_2S was also detected in the final stages of pyrolysis. Though the MBTA monomer peak was not recorded, fragment peaks due to the loss of hydrocarbon chains such as peaks at 55 and 70 Da due to C_4H_7, and C_5H_{10}, respectively, thiophene and $C_4H_3SCH_2$ were detected especially above 200°C.
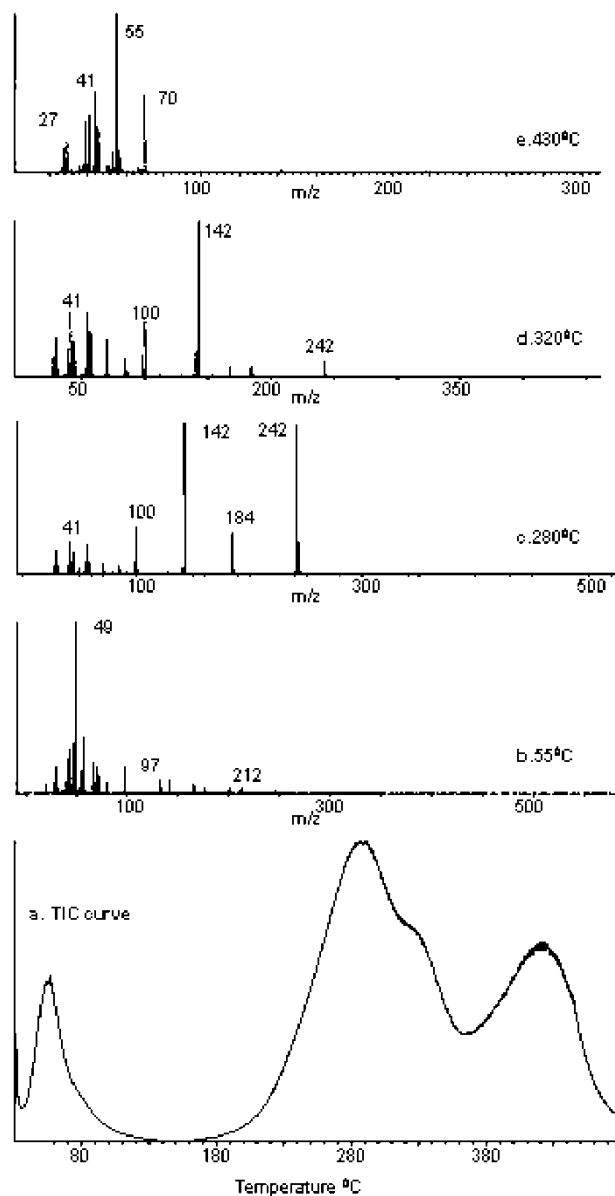
Figure 1. a) The TIC curve and the mass spectra recorded at, b) 55°C, c) 280°C, d) 320°C, and e) 420°C for PMBTA.

No significant difference could be observed upon increasing the heating rate or decreasing ionization energy. It can be concluded that the thermal degradation of the PMBTA polymerized by the coupling of thiophene end groups, occurs through a multi-step degradation mechanism. Though, the generation of thiophene and its dimer was significant at moderate temperatures, that of H_2S can only be detected at elevated temperatures. The H_2S yield was higher than the thiophene yield and attributed to a network structure in our previous studies on polythiophene (15, 16). Yet, for those samples thiophene was also
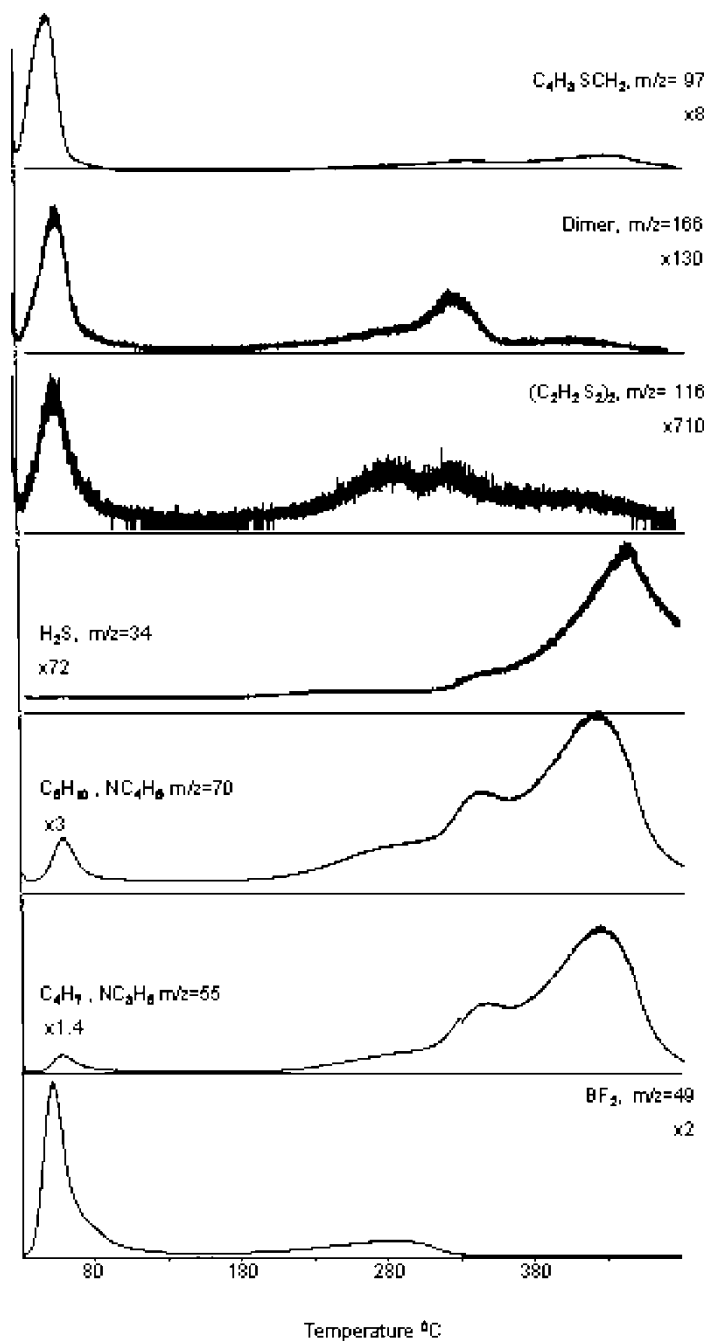
Figure 2. Single ion pyrograms of some selected products recorded during pyrolysis of PMBTA.

detected in the same region. Thus, it may also be thought that for this paticular thiophene derivative, the extent of the network structure is limited.

The TIC curve and the mass spectra recorded at the maxima of the TIC curve and the evolution profiles of some selected products recorded during the pyrolysis of
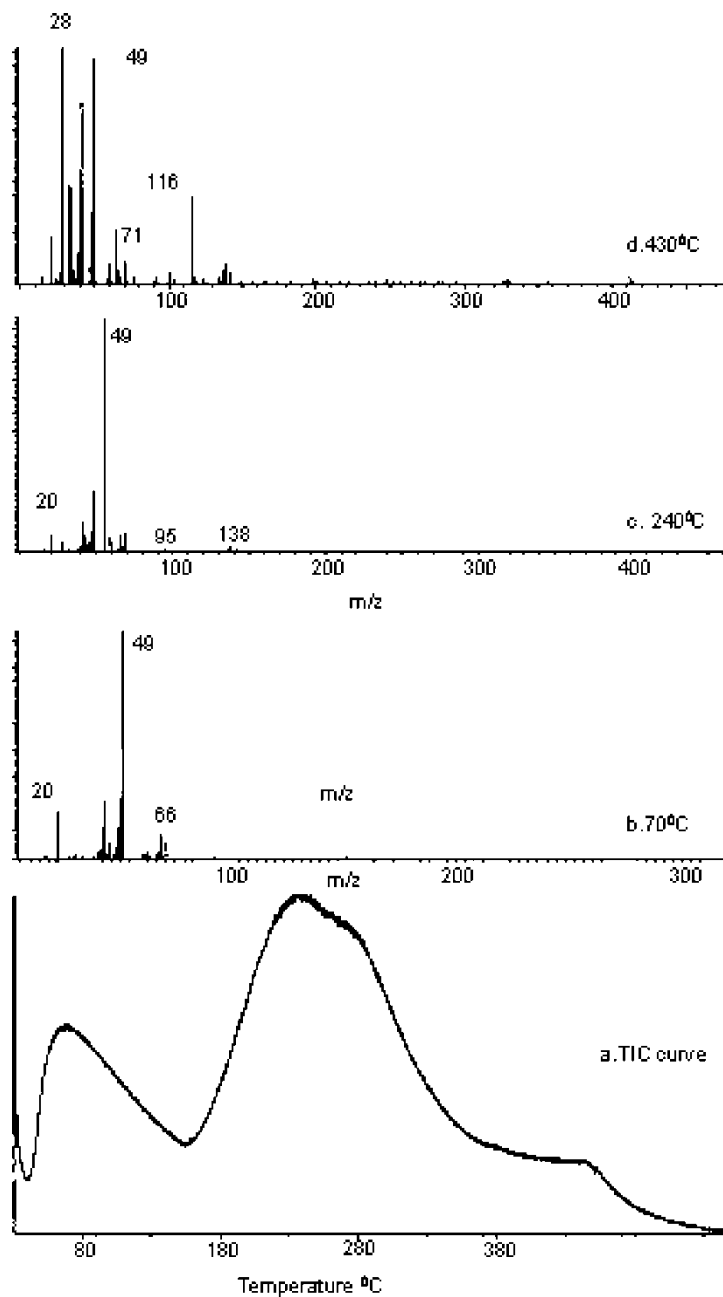
Figure 3. a) The TIC curve and the mass spectra recorded at b) 70°C, c) 24°C, and d) 430°C, for PTh.

PMBTA/PTh are shown in Figures 5 and 6, respectively. The TIC curve resembles that of PTh, as both involve three degradation stages. Yet for PTh, the second peak attributed to dopant loss was the most intense, whereas for the PMBTA/PTh sample, the high temperature evolution peak is the most intense one. Analyses of the mass spectra and the single ion
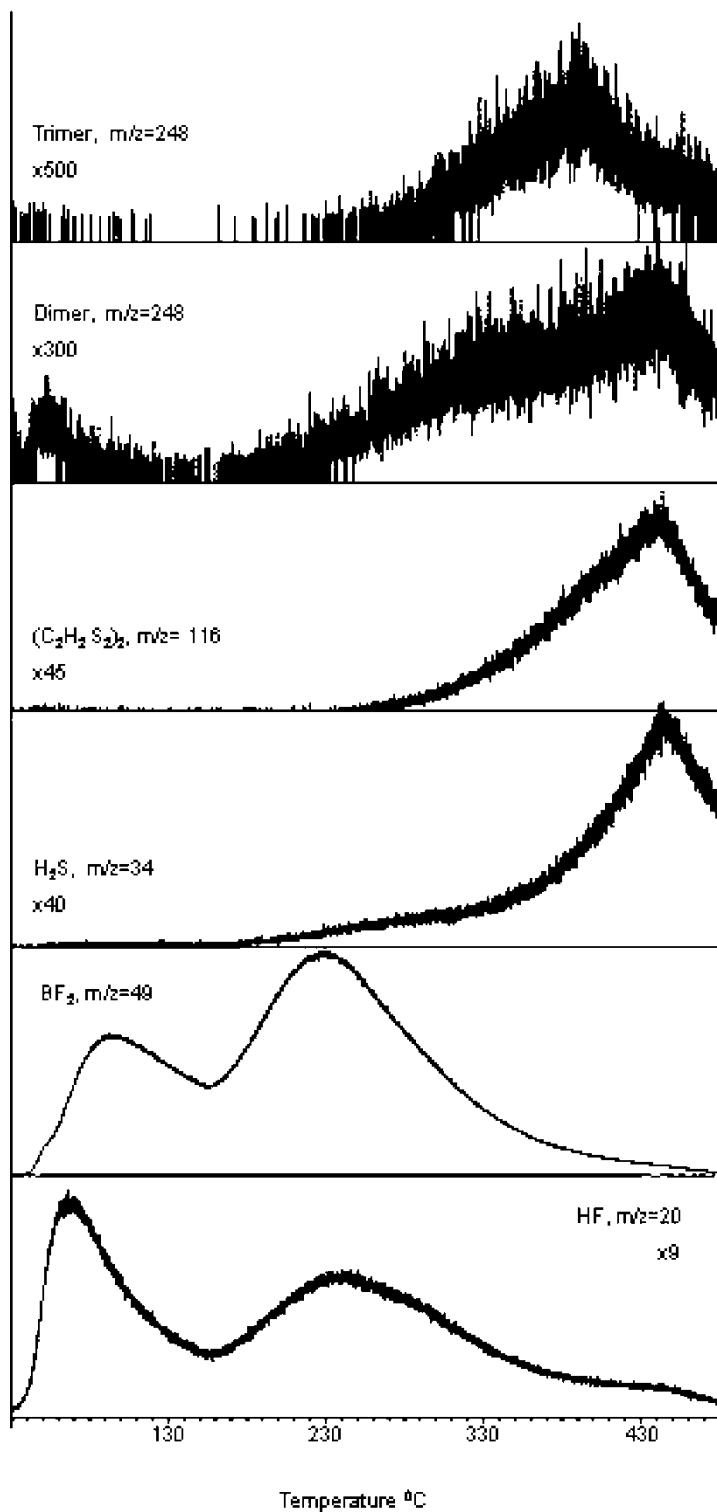
Figure 4. Single ion pyrograms of some selected products recorded during pyrolysis of PTh.
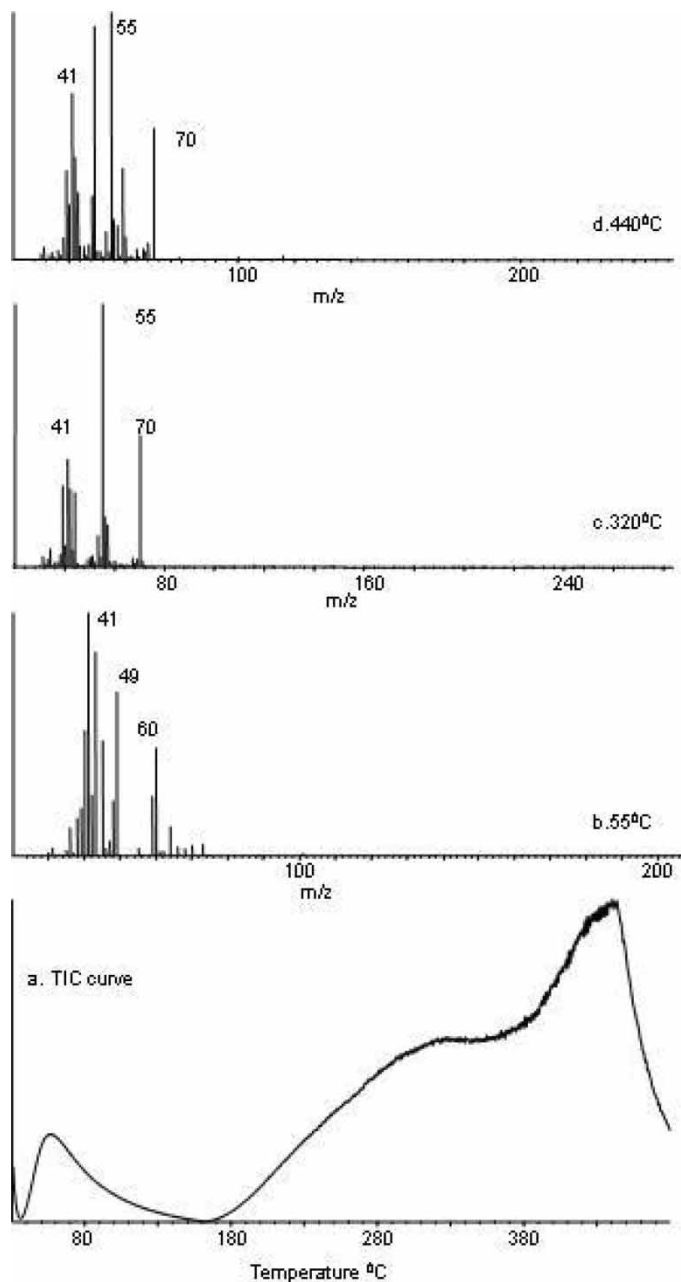
Figure 5. a) The TIC curve and the mass spectra recorded at b) 50°C, c) 320°C, and d) 440°C for PMBTA/PTh.

pyrograms indicated that the PTh based products show quite similar fragmentation trends with those recorded for PTh. However, single ion pyrograms of the products, that can directly be associated with PMBTA, show significant changes. Again, no monomer peak due to PMBTA can be detected in the final stage of pyrolysis. The shift of evolution profiles of PMBTA based products to higher temperatures indicating an increase in thermal
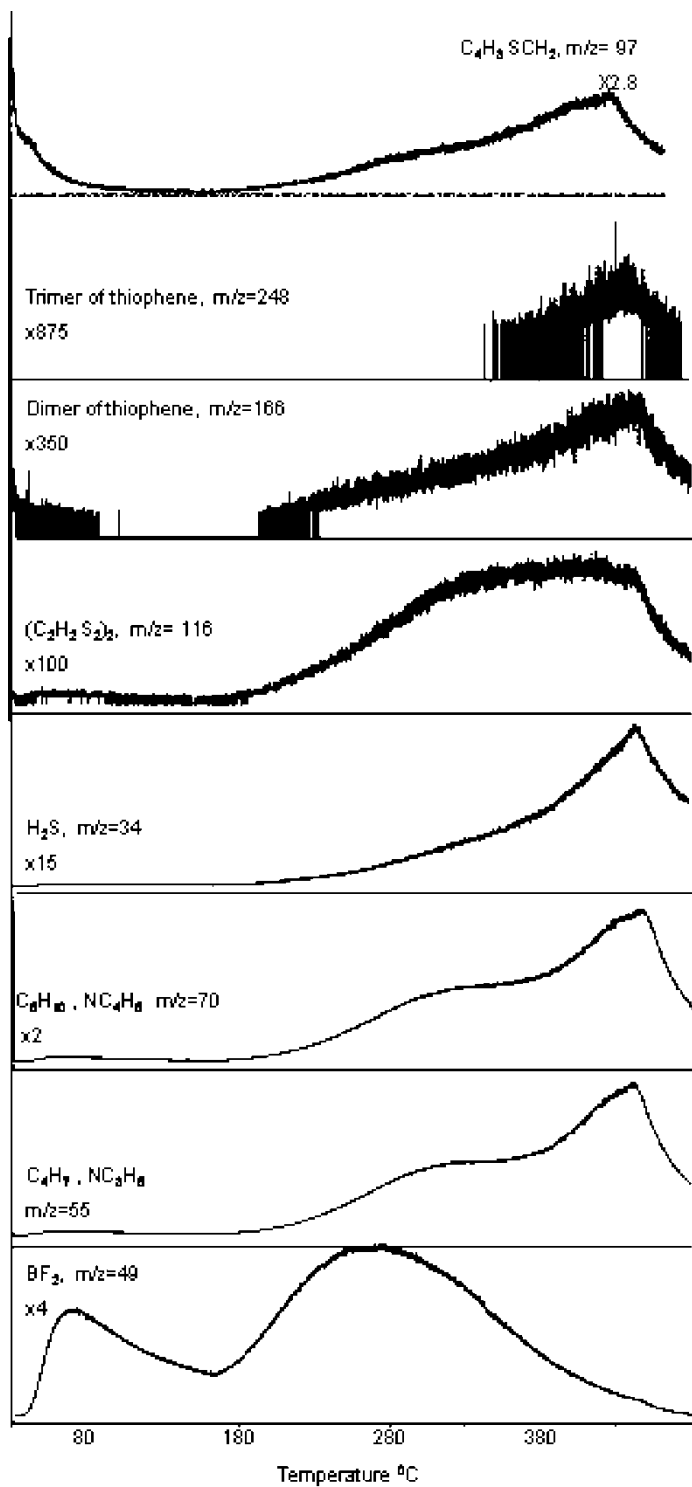
Figure 6. Single ion pyrograms of some selected products recorded during pyrolysis of PMBTA/PTh.
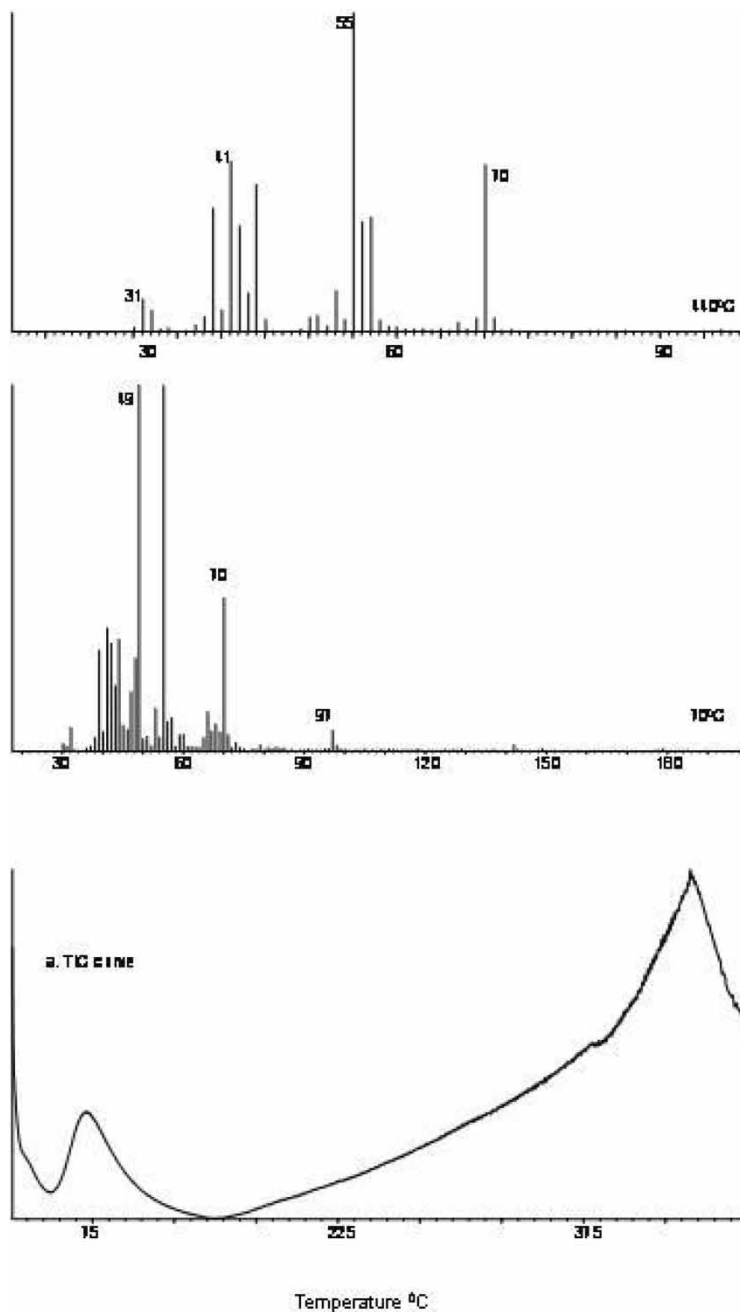
Figure 7. a) The TIC curve and the mass spectra recorded at b) 70°C, and c) 440°C for P(MBTA/Th).

stability, may be attributed to the growth of thiophene through PMBTA matrice backbone. Adsorption of low molecular weight species on the polymer is also significantly decreased.

The TIC curve and the mass spectra recorded at the maxima of the TIC curve and the evolution profiles of some selected products recorded during the pyrolysis of

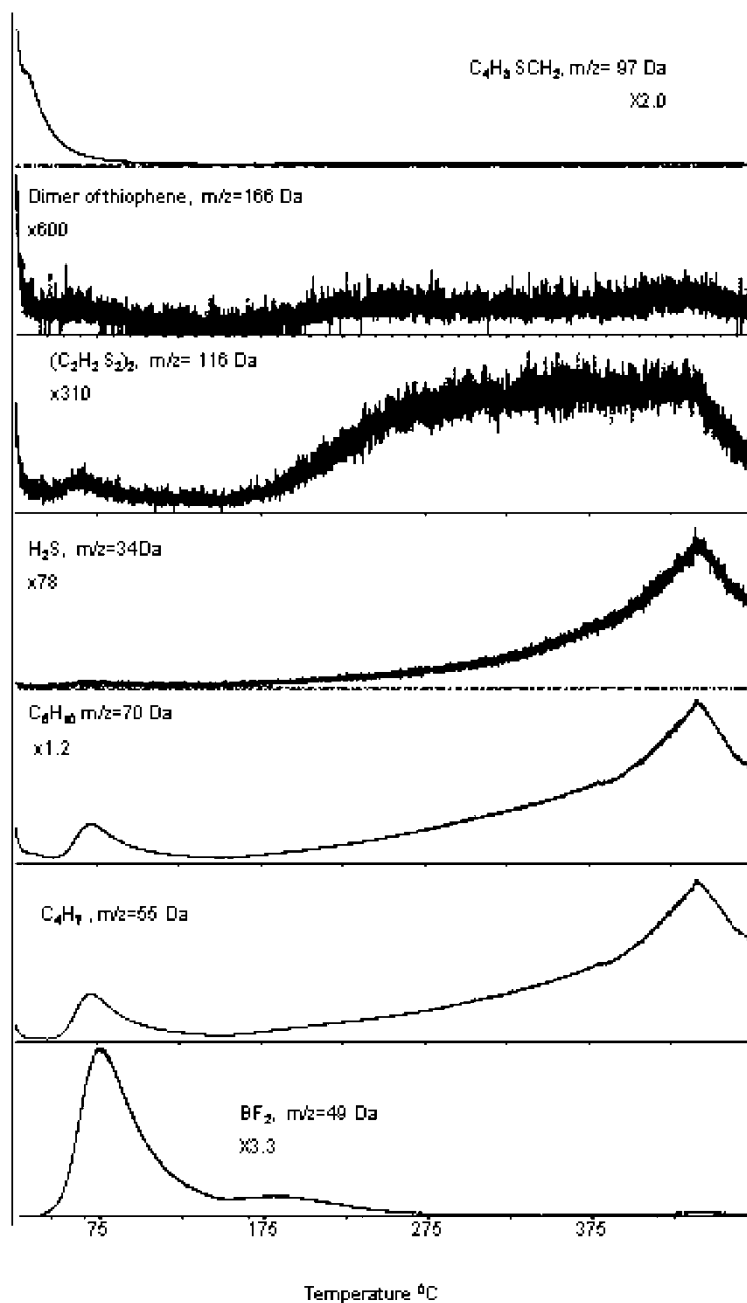**Figure 8.** Single ion pyrograms of some selected products recorded during pyrolysis of P(MBTA/Th).

P(MBTA/Th) are shown in Figures 7 and 8, respectively. It is noteworthy that the intensity of the second peak around 280°C in the TIC curves of PMBTA/PTh and PMBTA diminished significantly. The second peak was mainly due to the evolution of labile side groups from PMBTA chains. For the P(MBTA/Th) sample, the structure

seemed to be more uniform and fragments like C_4H_7 and C_5H_{10}, due to a loss of side chains, showed similar evolution profiles, even with H_2S due to cleavage of the thiophene ring. However, relative intensities of characteristic peaks due to dopant, cleavage of thiophene ring and thiophene oligomers diminished relative to fragments derived from MBTA units. Thus, it may be concluded that when the polymerization of thiophene was achieved in solution containing MBTA, a random copolymer having more uniform physical characteristics but lower conductivity was produced.

Conclusion

Direct insertion probe pyrolysis mass spectrometry analysis of PMBTA, PTh, PMBTA/PTh and P(MBTA/Th) showed that when thiophene was electrochemically polymerized on PMBTA coated anode through the thiophene moieties of PMBTA, thermal characteristics of both PTh and PMBTA were retained to a certain extent. The conductivity of this sample was higher than that of PMBTA, but lower than that of PTh. On the other hand, when thiophene was polymerized in the presence of MBTA, a polymer film with significant conductivity, but a more uniform structure was produced.

Acknowledgment

References

1. Satoh, M., Ishikawa, H., Yageta, H., and Hasegawa, E. (1997) Structure and Properties of Polypyrrole Synthesized Under Air and Oxygen-Free Conditions. *Synth. Met.*, 84: 167–168.
2. Cirpan, A., Alkan, S., Toppare, L., Cianga, I., and Yagci, Y. (2002) Synthesis and Characterization of Conducting Copolymers of Thiophen-3-yl Acetic Acid Cholesteryl Ester with Pyrrole. *J. Mat. Sci.*, 37: 1767–1775.
3. Koide, N. and Hirai, Y. (1999) Synthesis and Physical Properties of Side-Chain Type Liquid Crystalline Polythiophene Derivatives. *Mol. Cryst. Liq. Crys. Sci. Tech.*, 332: 2873–2885.
4. Osaka, I., Shibata, S., Toyoshima, R., Akagi, K., and Shirakawa, H. (1999) Synthesis and Properties of Liquid Crystalline Polythiophene Derivatives. 1 *Synth. Met.*, 02 (1–3): 1437–1438.
5. Buvat, P. and Hourquebie, P. (1999) Metallic Properties of Polythiophene Based Conducting Polymers. *Synth. Met.*, 101 (1–3): 17–18.
6. Ahn, S.H., Czae, M.Z., Kim, E.R., Lee, H., Han, S.H., Noh, J., and Hara, M. (2001) Synthesis and Characterization of Soluble Polythiophene Derivatives Containing Electron-Transporting Moiety. *Macromolecules*, 34 (8): 2522–2527.
7. Ko, H.C., Park, S., Paik, W., and Lee, H. (2002) Electrochemistry and Electrochromism of the Polythiophene Derivative with Viologen Pendant. *Synth. Met.*, 132 (1): 15–20.
8. Li, G.T., Kossmehl, G., Kautek, W., Plieth, W., Melsheimer, J., Dolbhofer, K., Hunnius, W.D., and Zhu, H.S. (1999) Reactive Groups on Polymer-Coated Electrodes, 9-New Electroactive Polythiophenes with Epoxy and Cyclic Carbonate Groups. *Macr. Chem. Phys.*, 200 (2): 450–459.
9. Uyar, T., Toppare, L., and Hacaloglu, J. (2001) Thermal and Structural Characterization of Polypyrrole by Direct-Insertion Probe Pyrolysis Mass Spectrometry. *Synth. Met.*, 119: 307–308. ibid., (2001) Spectroscopic Investigation of Oxidation of p-toluene Sulfonic Acid Doped Polypyrrole. 123 (2): 335–342.

10. Cirpan, A., Alkan, S., Toppare, L., Hepuzer, Y., and Yagci, Y. (2002) Conducting Graft Co-polymers of Poly(3-methylthienyl metacrylate) with Pyrrole and Thiophene. *J. Polym. Sci. Part A. Polym. Chem.*, 40 (23): 4131–4140.

11. Levent, A., Toppare, L., Cianga, I., and Yagci, Y. (2003) Synthesis and Characterization of Conducting Copolymers of (S)-2-methylbutyl-2(3-thienyl)acetate with Pyrrole and Thiophene. *Macr. Chem. Phys.*, 204 (8): 1118–1122.

12. Peacock, P.M. and McEwen, C.N. (2004) Mass Spectrometry of Synthetic Polymers. *Anal. Chem.*, 76 (12): 3417–3427.

13. Zoller, D.L., Sum, S.T., and Johnston, M.V. (1999) Determination of Polymer Type and Comonomer Content in Polyethylenes by Pyrolysis Mass Spectrometry. *Anal. Chem.*, 71: 866–872.

14. Uyar, T., Toppare, L., and Hacaloglu, J. (2002) Characterization of Electrochemically Synthesized p-toluene Sulfonic Acid Doped Polypyrrole by Direct Probe Pyrolysis Mass Spectrometry. *J. Anal. Appl. Pyrol.*, 64 (1): 1–13.

15. Gozet, T., Hacaloglu, J., and Onal, A.M. (2004) Pyrolysis Mass Spectrometry Analysis of BF_4^- Doped Polythiophene. *J. Macr. Sci. Pure and Appl. Chem.*, A41 (6): 713–725.

16. Gozet, T. and Hacaloglu, J. (2004) Direct Pyrolysis Mass Spectrometry of Fresh and Aged PF_6^- Doped Polythiophene Films. *Polym. Int.*, 53 (12): 2162–2168.