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Investigation of Copolymers of Thiophene-Functionalized Polystyrene with Pyrrole by Pyrolysis Mass Spectrometry

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The thermal and structural characterization of electrochemically synthesized thiophene-functionalized polystyrene and pyrrole (PS/PPy) and their copolymers were investigated by direct pyrolysis mass spectrometry. The pyrolysis data confirmed the growth of polypyrrole onto the pendant thiophene moiety of polystyrene. It is determined that the electrolytic film has different properties from the mechanical mixture and the related homopolymers.

Keywords pyrolysis mass spectrometry, graft copolymer, conducting copolymers, polypyrrole

Introduction

Preparation of conducting polymers by electrochemical polymerization methods has several advantages such as simplicity, reproducibility, and control of thickness (1–3). Yet, the polymers synthesized have poor mechanical and physical properties that create processing problems. Various ways, such as introducing alkyl groups into the main chain, synthesis of soluble precursors, preparation of conducting polymer composites, blends, copolymers, can be used to improve the mechanical characteristics (4, 5).

Several works on graft copolymerization of pyrrole by electrochemical or chemical polymerization of pyrrole onto pendant pyrrole moieties located on various polymers having good mechanical properties have appeared in the literature (6–9). The development of viable "living" free radical procedures for the synthesis of well-defined polymers with controlled incorporation of functional groups has recently been the subject of various studies (10, 11). Polymer chains with a wide variety of functional groups can be prepared with the use of functionalized initiators. The three standard methods for "living" free radical polymerization are nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and radical addition fragmentation transfer polymerization (RAFT). The main advantage of NMP is the absence of any metal. In a recent study, we synthesized and characterized a new thiophene-containing stable nitroxide initiator to obtain a thienyl containing (2,2,6,6,-tetramethylpiperidinyl-1-oxy),

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(thi-TEMPO), polystyrene and a graft copolymer of pyrrole prepared by electrochemical polymerization of pyrrole on the pendant thiophene moities of polystyrene. Enhancements in the mechanical properties were obtained, though conductivities of the products and polypyrrole (PPY) were in the same order of magnitude with pristine PPy (0.7–2 S/cm) (12). However, a detailed characterization of the graft polymer was not possible as the application of classical spectroscopic techniques for characterization of electrochemically prepared conducting polymers is still limited due to the insolubility of the films in common solvents.

Pyrolysis mass spectrometry techniques and their applications to polymer studies have been discussed in a number of publications (13–16). In several of our studies, we have shown that pyrolysis mass spectrometry can be utilized not only to study thermal behavior but also for structural characterization of conducting polymers (17–20). In the present study, direct pyrolysis mass spectrometry technique was applied in order to investigate the characteristics of the graft copolymer containing (2,2,6,6,-tetramethylpiperidinyl-1-oxy) initiated polystyrenes and polypyrrole.

Experimental

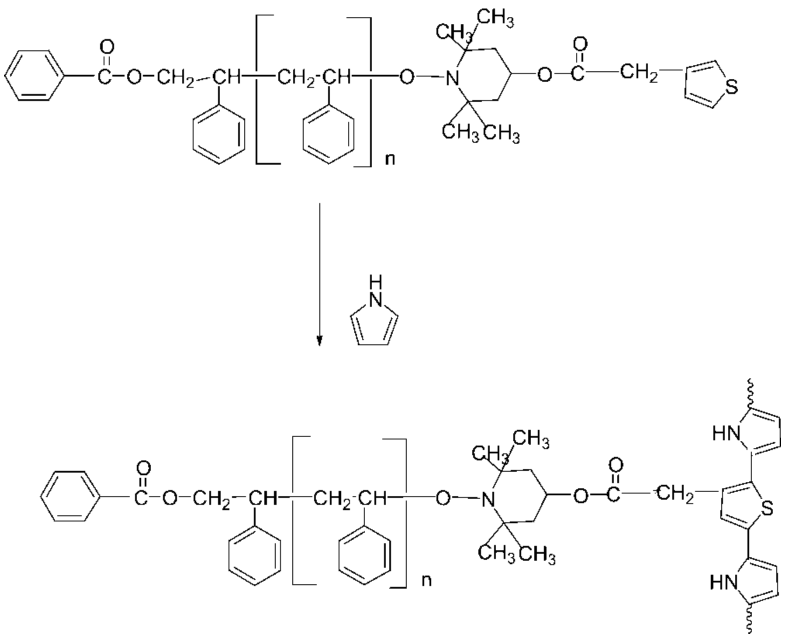
Synthesis of thi-TEMPO (2,2,6,6,-tetramethylpiperidinyl-1-oxy) initiated polystyrenes, PS1 ($M_{n},_{GPC} = 22420$), and PS2 ($M_{n},_{GPC} = 11520$) and polymerization of pyrrole onto PS1 and PS2 coated electrodes have been discussed in a recent publication (12). Dichloromethane (Aldrich) and p-toluene sulfonic acid (PTSA) were used as received. Pyrrole (Py) was distilled before use and stored at 4°C. Graft copolymers were prepared in water-PTSA (para-toluene sulfonic acid) (0.05M) solvent-electrolyte couple in an H-shaped electrolysis cell by constant potential electrolysis (1.1V vs. Ag/Ag^{+}) of pyrrole (0.02M) onto electrodes coated with the thienyl containing polystyrene samples, PS1 and PS2. The films (PS1/PPy and PS2/PPy) were immersed in the solvent of PS1 and PS2 (dichloromethane) for several hours in order to remove unreacted polymers. In Scheme 1 representation of the synthesis is given.

5973 HP quadruple mass spectrometry system is coupled to a JHP SIS direct insertion probe pyrolysis system for thermal analyses. 0.01 mg samples were pyrolyzed in the flared glass sample vials. Heating rate was 10°C/min and the scan rate was 2 scans/s. In each experiment, the temperature was increased up to 445°C, (the maximum attainable temperature) and kept constant for an additional 10 min at this temperature.

Conductivities were measured using four-probe technique as 0.7 and 2.0 $S\,cm^{-1}$ for PS1/PPy and PS2/Ppy, respectively (12).

Results and Discussion

In order to investigate the thermal and structural characteristics of the graft copolymer of thienyl containing (2,2,6,6,-tetramethylpiperidinyl-1-oxy) initiated polystyrenes and polypyrrole, pyrolysis analysis of PS1, PS2, PPy, PS1/PPy and PS2/PPy were performed. Pyrolysis analysis of PS1 and PS2 yielded nearly identical total ion-current, (TIC) curves, the variation of total ion yield as a function of temperature, and the pyrolysis mass spectra revealing that chain length of the polymers under investigation had no significant effect on thermal characteristics. Similarly, for PS1/PPy and PS2/PPy, pyrolysis



Scheme 1. Synthesis of copolymers of thienyl containing polystyrene and polypyrrole.

data were almost identical. Thus, in the following discussions abbreviation PS is used for representing both PS1 and PS2 films.

thi-TEMPO Initiated Polystyrenes

Thermal degradation of polystyrene has been the topic of several studies (21). It is known that the PS degrades in a single stage by a depolymerization reaction yielding mainly the monomer, styrene and some low molecular weight oligomers.

Pyrolysis mass analysis of (2,2,6,6,-tetramethylpiperidinyl-1-oxy) initiated polystyrenes, PS indicated that the thermal degradation mainly occurred in a narrow region and the product yield reached to a maximum at 445°C for both samples. Yet, around 225 and 320°C weak peaks were detected in the total ion current (TIC) curves. In general, a TIC curve with more than one peak indicates a sample containing more than one component or presence of blocks or side chains with different thermal stabilities. Analysis of the pyrolysis mass spectra indicated that the low temperature evolutions were mainly due to the cleavage of end groups containing COO groups. On the other hand, the pyrolysis mass spectra recorded around 445°C involved diagnostic product peaks of polystyrene. In Figure 1, the TIC curve and the pyrolysis mass spectra at the weak shoulders at around 225 and 320°C and at 445°C are shown. The related data are summarized in Table 1.

In Figure 2, the single ion pyrograms, the variation of intensity of a single product ion as a function of temperature, of some selected products due to cleavage of end groups such as CO_2 (m/z = 44 Da), $(C_4H_3S)CHCO$ (m/z = 124 Da), $C_6H_5CO_2CH_2$-$CH(C_6H_5)CH_2CH{=}CH_2$ (m/z = 266 Da), and decomposition of polystyrene chains namely, C_7H_7 (m/z = 91 Da), styrene (m/z = 104 Da), and styrene dimer

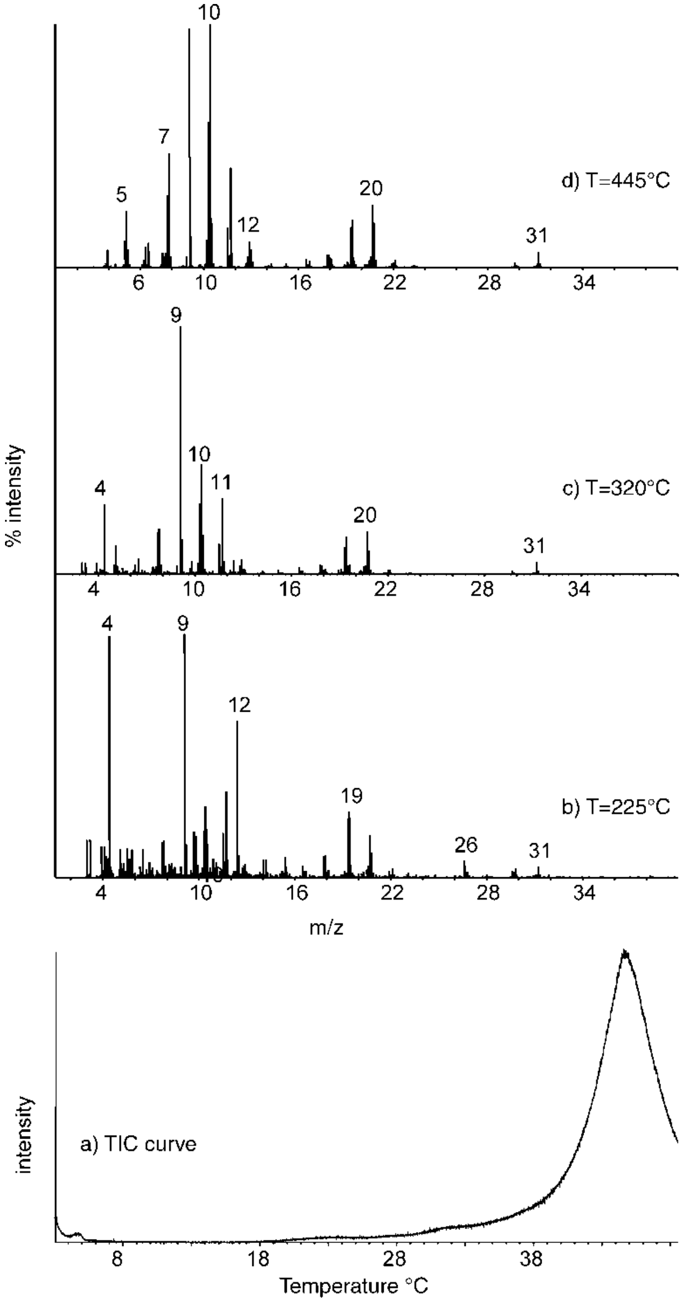


Figure 1. The TIC curve and the mass spectra recorded at the selected temperatures for PS.

(m/z = 207 Da) styrene tetramer (m/z = 415 Da) are shown. The trends in single ion pyrograms confirmed that the loss of end groups occured more readily at moderate temperatures just above 200°C, whereas, PS chains degraded at elevated temperatures in a single step. Thus, it can be concluded that thermal degradation mechanism of PS

Table 1
The relative intensities of some characteristic product peaks in the pyrolysis mass spectra of PS, PPy and PS/PPy

	PS	PPY		PS/PPy		
m/z	440°C	340°C	435°C	370°C	445°C	Assignments
34		19	384	10	473	H_2S
40		86	77	94	93	C_2HNH
48	1	90	125	114	111	SO
64	16	220	332	284	271	SO_2
65	104	135	77	133	121	C_5H_5
66	5	25	31	26	26	Pyrrole, C_5H_6
77	291	31	10	24	20	C_6H_5
84	2				1	Thiophene
91	986	1000	1000	1000	1000	C_7H_7
104	1000			1	4	Styrene
172		70	5	46	19	PTSA
207	250				1	Styrene dimer
312	61					Styrene trimer

involves two steps, the first being the loss of end groups containing labile C-O bonds and the second being the chain scission followed by depolymerization in accordance with literature results (21).

Polypyrrole

Thermal degradation of polypyrrole has been discusssed in detail in our previous studies (17, 18). The TIC curve of PPY shows a single broad peak starting just above 250°C and with a maximum at 340°C and a shoulder at 410°C (Figure 3). Nearly all the abundant peaks were diagnostic to dopant, PTS. However, a completely different fragmentation pattern compared to that of p-toluene sulfonic acid, PTSA was observed. (It has been assumed that p-toluene sulfonate ion evaporate in the protonated form.) In general, PPY based peaks were weak and only moderate monomer and very weak dimer peaks can be identified. The peaks at $m/z = 26$ and 39 Da were associated with the cleavage of the pyrrole ring. In Table 1, the data related to the characteristic and intense peaks due to the evolved products during pyrolysis of PPY are also included for comparison.

In Figure 4, the single ion pyrograms of H_2S^+ (m/z 34 Da), C_2HNH^+ (m/z 40 Da), $C_4H_3NH^+$ (m/z 66 Da), $C_7H_7^+$ a(m/z 91 Da), and $CH_3C_6H_4SO_3H^+$ (m/z 172 Da), are shown. As can be noted, the evolution of tropylium ion has shifted to higher temperatures (maximum at 340°C) compared to that of the dopant ion molecular ion at m/z 172 Da (maximum at 290°C). Furthermore, evolution of H_2S was quite significant in the final stages of pyrolysis. The trends in single ion pyrograms of dopant based fragments indicated that the interaction between the dopant and the pyrrole is most probably not unique. It has been proposed that pyrolysis removed the dopant that has been adsorbed or physically bound more readily at lower temperatures. The significant differences in the mass spectra recorded around 340°C, compared to the mass spectrum of PTSA, and

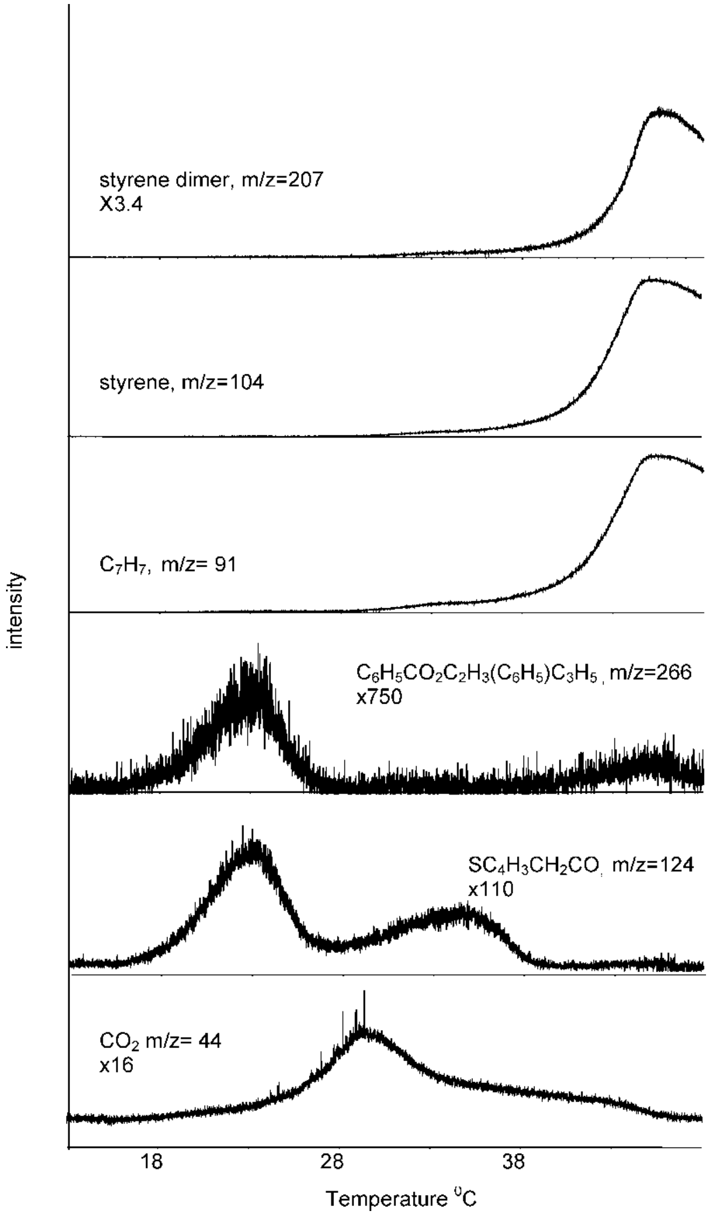


Figure 2. Single ion pyrograms of some selected fragments recorded during pyrolysis of PS.

the evolution of H_2S at elevated temperatures were then associated with blocks involving chemically bound dopant that degraded before evolution. On the other hand, the lack of high-mass product peaks related to polypyrrole, the presence of very weak monomer peak and the decomposition of the pyrrole ring, have been attributed to a net work structure, since depolymerization reaction yielding mainly a stable aromatic monomer and low molecular weight oligomers should be almost impossible for a network structure (17, 18).

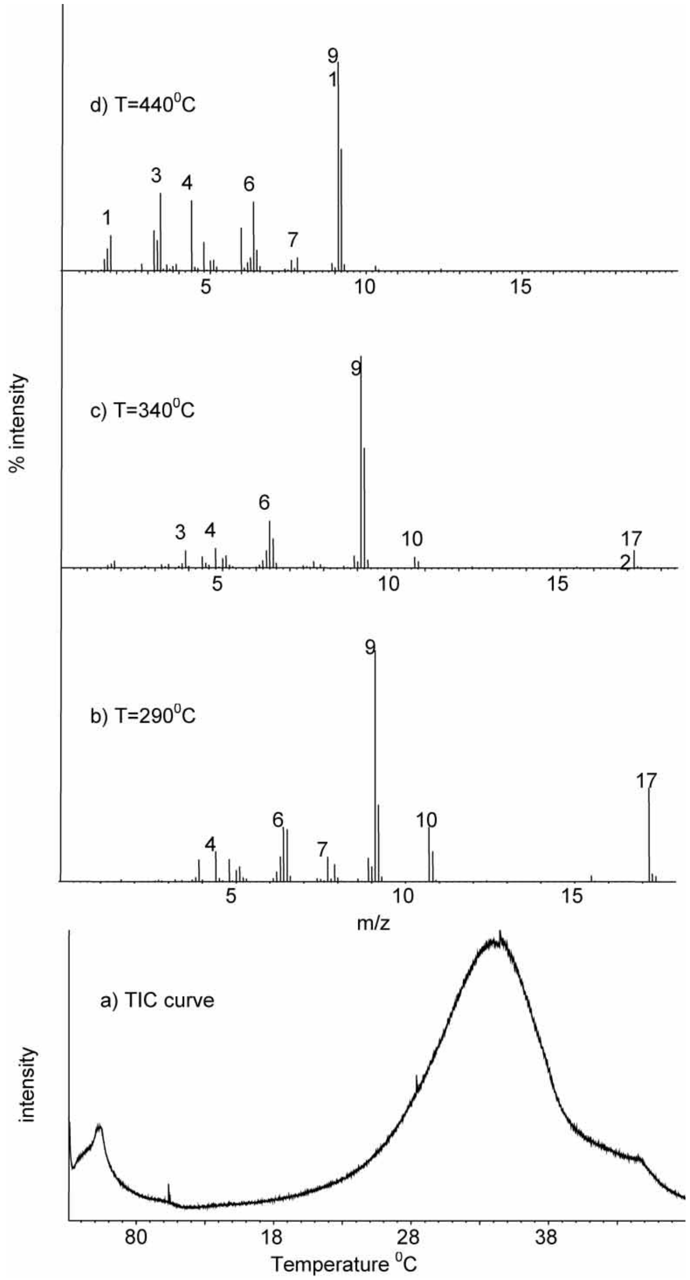


Figure 3. The TIC curve and the mass spectra recorded at the selected temperatures for PPy.

PS/PPy Graft Copolymer

The TIC curves of the polymers synthesized by eletrochemical polymerization of pyrrole onto a PS coated electrode showed a broad peak with a shoulder at elevated temperatures and were quite similar to that of PPy. Furthermore, the pyrolysis mass spectra were mainly

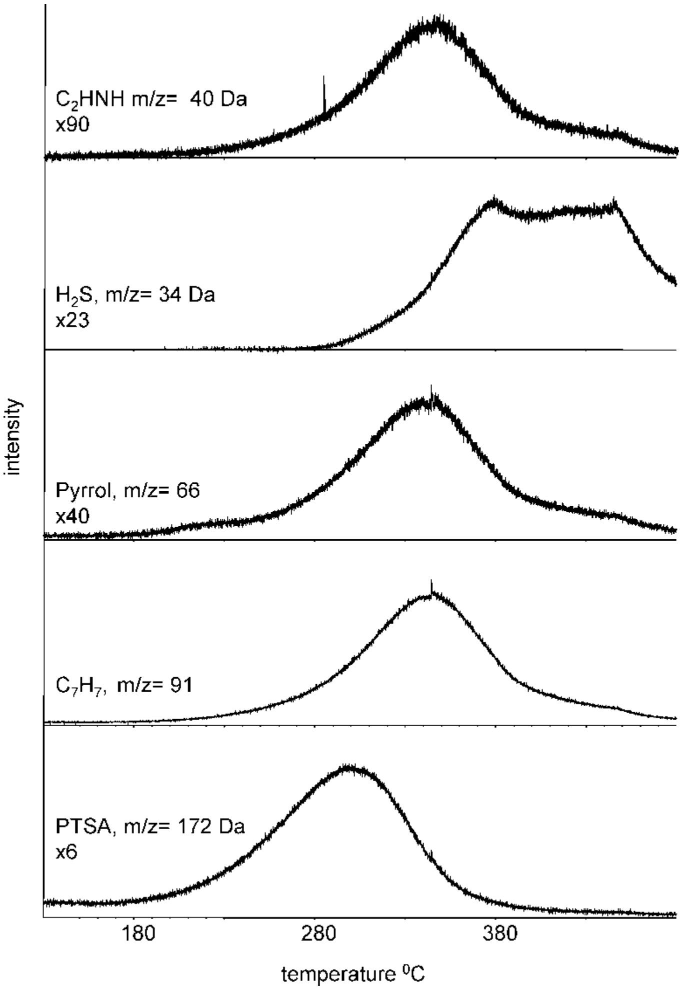


Figure 4. Single ion pyrograms of some selected fragments recorded during pyrolysis of PPy.

dominated by the peaks diagnostic to PPy. Yet, the maximum shifted to 370°C and the peak was broadened in the high temperature range (Figure 5). The styrene monomer peak, which was the base peak in the pyrolysis mass spectra of PS, was present although weak. Peaks at $m/z = 91$, 77, 64 and 48 Da are both diagnostic to PS and PTSA-doped PPy. However, except for the tropylium and phenyl peaks, the relative intensities of these peaks were quite low in the pyrolysis mass spectra of PS unlike PPY. Thus, taking into account the very low yield of styrene, it can be suggested that contributions of these fragments due to the degradation of PS chains was negligible. On the other hand, no diagnostic peak for the end groups could be detected. The related data is summarized in Table 1.

Single ion pyrograms of some selected products are given in Figure 6. Except for the shift to higher temperatures, the evolution of PTSA ($m/z = 172$ Da) showed an identical trend with that was observed for PPy (Figures 4 and 6). However, evolution of dopant based fragments such as C_7H_7 ($m/z = 91$ Da), and SO_4 ($m/z = 64$ Da), SO

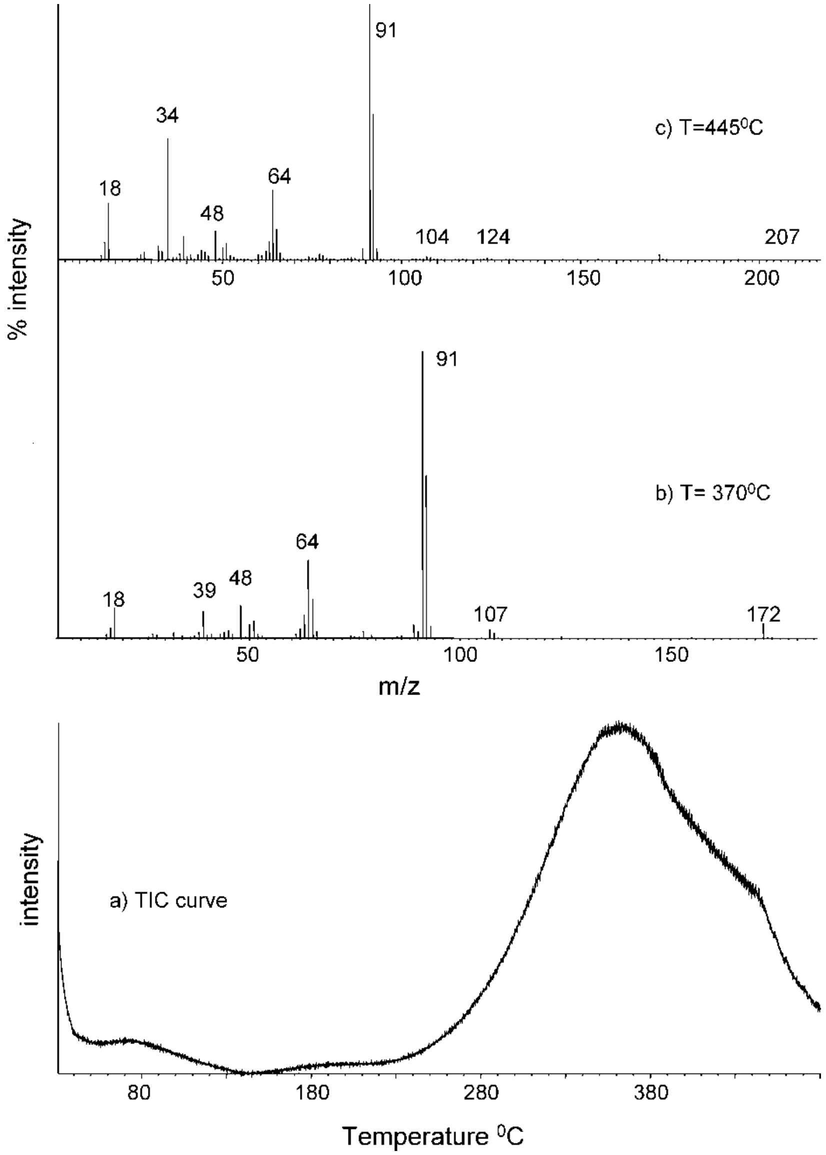


Figure 5. Single ion pyrograms of some selected fragments recorded during pyrolysis of PPy.

(m/z = 48 Da) and polypyrrole based fragments such as C_4H_4N (m/z = 66 Da) and C_2HNH (m/z = 40 Da) increased noticeably at elevated temperatures. The most drastic change was detected in the evolution profile of H_2S. The relative intensity of the high temperature peak in the evolution profile increased significantly. Actually, H_2S formation is not detected for PTSA, thiophene and PS samples. Its evolution during the pyrolysis of PPy was attributed to reactions of dopant ion with the polymer film in our previous studies (17, 18) Generation of H_2S was also detected for BF_4^-, and PF_6^- doped polythiophene samples and associated with the cleavage of the thiophene ring due to the presence of a network structure (19, 20).

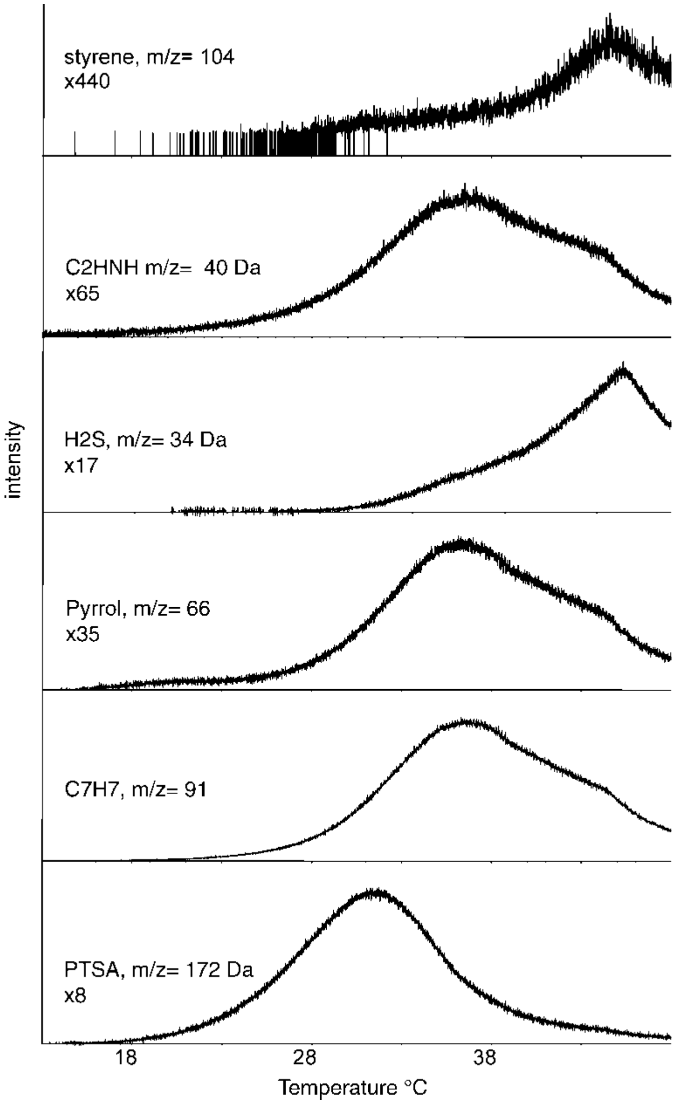


Figure 6. Single ion pyrograms of some selected fragments recorded during pyrolysis of PPy.

Evolution of styrene monomer, though very weak, was observed at elevated temperatures and hence, confirmed the presence of PS chains together with PPy. Actually, nearly in all our previous pyrolysis studies on samples prepared by electrochemical polymerization of pyrrole on a matrix polymer coated electrode, we have detected the degradation of matrix polymer during the synthesis process (22–24). Thus, the low yield for PS based products may be an indication of degradation of these films during the electrochemical polynmerization at least to a certain extent. As the relative intensity of styrene monomer peak was quite low, it is reasonable not to detect any characteristic peak due to the end groups which were already quite weak in the pyrolysis mass spectra of PS. Furthermore, contributions of PS based fragments maynot be significant. Then, it may be concluded that the high temperature shift of dopant and PPy based fragments was mainly due to the increase in thermal stability of polypyrrole chains. On the other hand, the trends in H_2S evolution profile, especially the significant increase in the relative yield around 440°C, can be associated with the cleavage of thiophene ring during the pyrolysis. Cleavage of thiophene ring occurs only when thiophene is polymerized in a network structure. Thus, it may further be concluded that polymerization of pyrrole on the thiophene moities occured during the synthesis process, even if the matrix polymer degraded to a certain extent.

Conclusions

The pyrolysis mass spectrometry analysis of the films prepared by electrochemical polymerization of pyrrole on thi-TEMPO (2,2,6,6,-tetramethylpiperidinyl-1-oxy) initiated polystyrenes coated electrodes, confirmed the growth of polypyrrole onto the pendant thiophene moiety of polystyrene. The electrolytic film has different properties from the mechanical mixture and the related homopolymers.

References

1. Rodriguez, J., Grande, H.J., and Otero, T.F. (1997) *Handbook of Organic Conductive Molecules and Polymers*. Nalwa, H.S. (ed.), John Wiley: Chishester; Vol. 2, Ch. 10.
2. Diaz, A.F. and Hall, B. (1983) *IBM J. Res. Develop.*, 27: 342–347.
3. Kumar, D. and Sharma, R.C. (1998) *Eur. Polym. J.*, 34: 1053–1060.
4. Stanke, D., Hallensleben, M.L., and Toppare, L. (1995) *Synth. Met.*, 73: 261–266.
5. Billingham, N.C. and Calvert, P.D. (1989) Electrically Conducting Polymers. In *Adv.* in Polym. Sci. Springer-Vertag: Heidelberg3–33.
6. Nazzal, A.I. and Street, G.B. (1984) *J. Chem. Soc., Chem. Commun.*, 2: 83–84.
7. Street, G.B., Lindey, S.E., Nazzal, A.I., and Wynne, K.J. (1985) *Mol. Cryst. Liq. Cryst.*, 118: 137–148.
8. Geissler, U., Hallensleben, M.L., and Toppare, L. (1993) *Synth. Met.*, 55: 1483–1488.
9. Kızılyar, N., Toppare, L., Önen, A., and Yağcı, Y. (1998) *J. Appl. Polym. Sci.*, 71: 713.
10. Matyajasewski, K. (1998) *In Controlled Radical Polymerization*. American Chemical Society: Washington, DC, 1–25.
11. Harthi, E.C., Hawker, W., Fan, W., and Waymouth, R.M. (2001) *Macromolecules*, 34: 3856–3861.
12. Papila, O., Toppare, L., Yagci, Y., and Cianga, L. (2004) *Int. J. Polym. Anal. Charact.*, 9: 13–28.
13. Tsuge, S. (1995) *J Anal. Appl. Pyroly.*, 32: 1–6.
14. Boon, J.J. (1992) *Int. J. Mass Spectrom. Ion Processes*, 118: 755–787.
15. Montaudo, G. (1986) *Brit. Polym. J.*, 18: 231–235.
16. Qian, K.N., Killinger, W.E., Casey, M., and Nicol, G.R. (1996) *Anal. Chem.*, 68: 1019–1027.
17. Uyar, T., Toppare, L., and Hacaloğlu, J. (2002) *J. Anal. and Appl. Pyrol.*, 64 (1): 1–13 and references cited therin.
18. Uyar, T., Toppare, L., and Hacaloğlu, J. (2001) *Synth. Met.*, 119: 307–308.
19. Gozet, T. and Hacaloglu, J. (2004) *Polymer Inter.*, 53 (12): 2162–2168.
20. Gozet, T. and Hacaloglu (2005) *J. Anal. Appl. Pyrolysis.*, 73 (2): 256–261.
21. McNeil, I.C., Zulfiqar, M., and Kousar, T. (1990) *Polym. Deg. Stab.*, 28 (2): 131–151 and references cited therin.
22. Levent, A., Hacaloglu, J., Toppare, L., and Yağcı, Y. (2003) *Synth. Met.*, 135 (136C): 457–458.
23. Özdilek, C., Toppare, L., Hacaloglu, J., and Yağcı, Y. (2004) *Synth. Met.*, 140 (1): 69–78.
24. Athar, I., Hacaloglu, J., and Toppare, L. (2004) *Polym. Inter.*, 53 (7): 926–930.