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A pyrolysis mass spectrometry study of polythiophene–polyamide composites

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The thermal behavior of composites of polythiophene and polyamide prepared by mechanical blending and electrochemical synthesis of polythiophene onto an electrode coated with polyamide have been studied thoroughly by the pyrolysis approach under both direct and indirect pyrolysis mass spectrometric analysis conditions. It is determined that the electrolytic film has different properties from the mechanical mixture and the related homopolymers.

(Keywords: direct and indirect pyrolysis; composites; mass spectrometry)

INTRODUCTION

Heterocylic polymers have gained interest because of their high electrical conductivity[1–4]. Yet their electronic and chemical applications are limited because of their poor mechanical properties and processability[5–10]. It has been shown that by electrochemical synthesis of a conducting polymer on an electrode coated with a conventional insulating polymer, the conductivity of the resultant electrolytic film is maintained while the mechanical properties are improved. Recently we have discussed the synthesis and characterization of homogenous composites of polythiophene (PTh) on a polyamide (PA) coated electrode[11]. Here we report a detailed study of the thermal behavior and decomposition products of PTh–PA composites; mechanical mixture, and electrolytic film to investigate the effects of each component on each other. Samples have been studied thoroughly by the pyrolysis approach under both direct and indirect pyrolysis mass spectrometric analysis conditions. Pyrolysis techniques and their applications to polymer degradation studies have been discussed in a number of recent publications[12–16]. It has been shown that pyrolysis mass spectrometry is an excellent method not only for analysis of thermal behavior of polymer samples but also for rapid characterization purposes. Yet the extensive fragmentation suffered by most pyrolysis products at the ion source of the quadrupole is a serious drawback, since the chemical identification of individual pyrolysis products may be impossible. Thus, comparisons have been made both with pyrolysis mass spectra of corresponding homopolymers (polythiophene and polyamide), and polyamide–polythiophene mechanical mixtures to get a better understanding.

EXPERIMENTAL

PTh–PA composites were prepared by electrochemical polymerization of thiophene onto a polyamide coated electrode at a constant potential of 1.8 V vs Ag^0/Ag^+ (10^{-2}M) reference electrode. The electropolymerizations were carried out with a potentioscan Wenking POS 73. Preparative details for the composites were given in our previous publication[11].

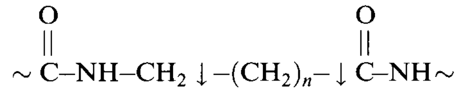
The degradation studies were carried out using two pyrolysis techniques: direct pyrolysis with the use of a pyrolysis probe and indirect pyrolysis (evolved gas analysis). The details of the systems were reported previously[12,13]. Pyrolysis analysis was performed using a BALZERS QMG311 quadrupole mass spectrometer controlled by a PC. 0.1 mg and 1.0 mg samples were used in direct and indirect pyrolysis m.s. studies, respectively.

RESULTS AND DISCUSSIONS

Direct pyrolysis

Polyamide. Low molecular weight fragments, below 100 amu, started to appear in the direct pyrolysis mass spectra of PA just above 120°C. Yet main degradation occurred in a narrow temperature range of 215–235°C. The most intense and/or characteristic peaks detected at 226°C (the temperature at which maximum decomposition yield was observed) and the chemical formulas assigned are given in *Table 1.*

The fragmentation pattern was quite similar to those of secondary amides; α-cleavages in the acid functional group and β-cleavages in the *N*-alkyl chain resulting in the production of saturated hydrocarbon radicals was confirmed by the presence of peaks in the pyrolysis mass spectra differing by 14 amu.



$$\sim \overset{\displaystyle O}{\overset{\|}{C}}-NH-CH_2 \downarrow -(CH_2)_n- \downarrow \overset{\displaystyle O}{\overset{\|}{C}}-NH\sim$$

It is known that the second characteristic feature of a hydrocarbon mass spectrum is the distribution of relative intensities of these ions. In a saturated unbranched chain

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Table 1 The relative intensities (RI) and assigned chemical formulas of the most intense and/or characteristic ions observed during direct pyrolysis m.s. analyses of PA

m/z	RI	Assigned formula
43	41	C_3H_7, NHC_2H_4
44	155	$O=C=NH_2$
57	208	C_4H_9, NHC_3H_6
59	72	$CH_2=C(OH)NH_2$
70	412	C_5H_{10}
84	1000	C_6H_{12}, NHC_5H_9, $C_2H_3CONHCH_2$
86	652	$C_2H_4CONHCH_3$, $H_2C=C(OH)NHC_2H_4$, NHC_5H_{11}
97	599	C_7H_{13}, NHC_6H_{10}
113	58	C_8H_{17}, NHC_7H_{14}, $C_2H_4CONHC_3H_6$, $C_4H_8CONHCH_2$, $CH_2=C(OH)NHC_4H_7$
128	63	$CH_2=C(OH)NHC_5H_{10}$, NHC_8H_{17}, $C_2H_4CONHC_4H_9$, $C_5H_{11}CONHCH_2$
140	188	$C_{10}H_{20}$, NHC_9H_{17}, $C_2H_3CONHC_5H_{10}$, $C_6H_{11}CONHCH_2$
154	222	$C_{11}H_{22}$, $NHC_{10}H_{19}$, $C_2H_3CONHC_6H_{12}$, $C_7H_{13}CONHCH_2$
168	77	$C_{12}H_{24}$, $NHC_{11}H_{21}$, $C_2H_3CONHC_7H_{14}$, $C_8H_{15}CONHCH_2$
182	53	$NHC_{12}H_{23}$, $C_2H_3CONHC_8H_{16}$, $C_9H_{17}CONHCH_2$
196	43	$C_2H_3CONHC_9H_{18}$, $C_{10}H_{19}CONHCH_2$
210	34	$C_2H_3CONC_{10}H_{20}$, $C_{11}H_{21}CONHCH_2$
224	24	$C_2H_3CONHC_{11}H_{22}$
238	19	$C_2H_3CONHC_{12}H_{24}$

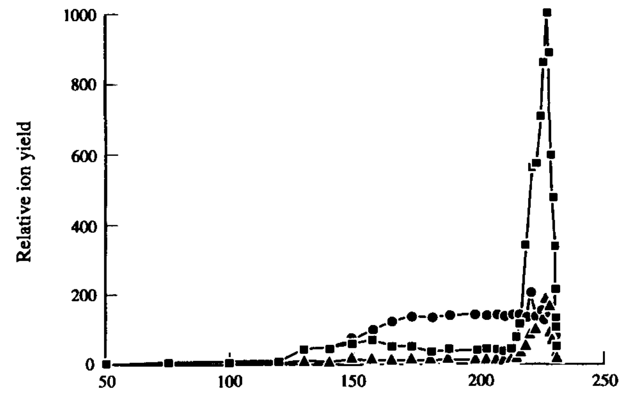
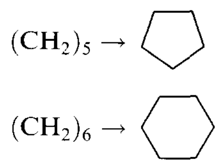


Figure 1 Ion–temperature profiles of 44: (●), 84: (■), and 140: (▲) amu fragments observed during the direct pyrolysis of PA

the most intense ion is C_4 fragments, since those with higher mass will fragment further. A similar behavior might be expected in the pyrolysis mass spectra. Yet, contrary to these expectations the peak at 84 amu was the base peak in PA spectra. Furthermore, the peak at 70 amu was also abundant. These peaks may be due to more than one chemical species or may also be produced during electron-impact ionization of high-mass thermal decomposition products. However, one may also propose that cyclization reactions accompanying thermal decomposition may yield cyclohexane and cyclopentane:



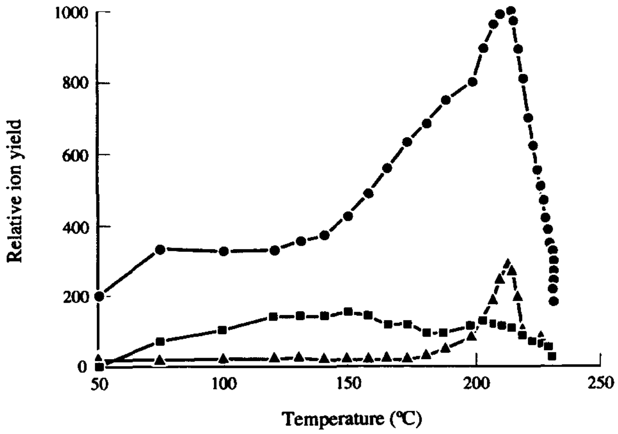
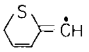
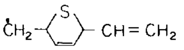
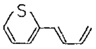
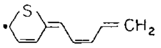
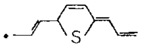
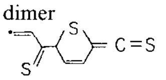
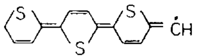
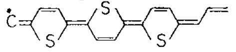
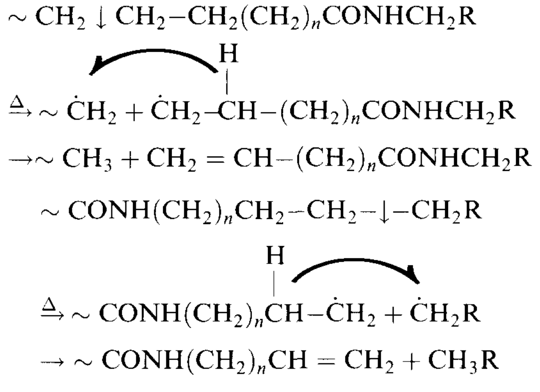


Figure 2 Ion–temperature profiles of 44: (●), 84: (■), and 163: (○) amu fragments observed during the direct pyrolysis of PTh

Table 2 The relative intensities (RI) and assigned chemical formulas of the most intense and/or characteristic ions observed during direct pyrolysis m.s. analyses of PTh

m/z	RI	Assigned formula
44	1000	CS
45	213	HCS
63	72	C_5H_3
84	115	monomer
97	136	
125	55	
136	72	
149	72	
163	289	
168	38	dimer
197	25	
261	77	
297	230	

Fragment ions due to cleavage between α and β atoms of the acid portion, and McLafferty rearrangement ions were also identified. The presence of a large variety of ions arising during the ionization of thermal decomposition products may indicate that thermal decomposition occurred by random scissions producing a large variety of neutral species. Moreover, as the relative intensities of fragments 1 amu less than the mass of the fragment ions arising from the expected degradation patterns were more intense: disproportionation of the macroradicals formed by random scission may be proposed as the mechanism of thermal decomposition.



$$\sim CH_2 \downarrow CH_2{-}CH_2(CH_2)_nCONHCH_2R$$

$$\xrightarrow{\Delta} \sim \dot{C}H_2 + \dot{C}H_2{-}\overset{\overset{H}{|}}{C}H{-}(CH_2)_nCONHCH_2R$$

$$\rightarrow \sim CH_3 + CH_2 = CH{-}(CH_2)_nCONHCH_2R$$

$$\sim CONH(CH_2)_nCH_2{-}CH_2{-}\downarrow{-}CH_2R$$

$$\xrightarrow{\Delta} \sim CONH(CH_2)_n\overset{\overset{H}{|}}{C}H{-}\dot{C}H_2 + \dot{C}H_2R$$

$$\rightarrow \sim CONH(CH_2)_nCH = CH_2 + CH_3R$$

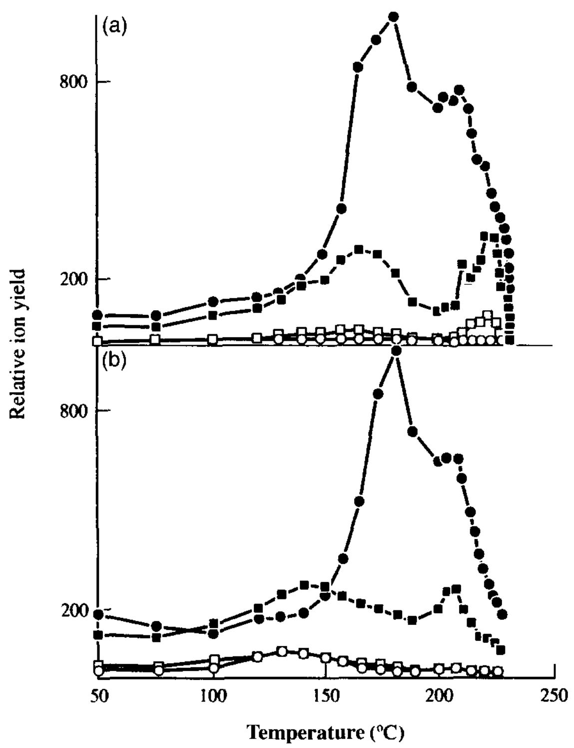
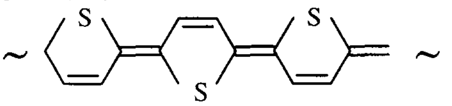


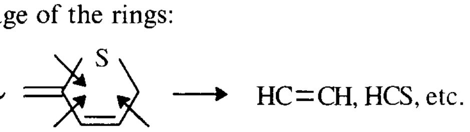
Figure 3 Ion–temperature profiles of 44: (●), 84: (■), 140: (□), and 163: (○) amu fragments observed during the direct pyrolysis of PTh–PA composites: (a) mechanical mixture and (b) electrolytic film

The ion–temperature profiles (variation of the relative intensities as a function of temperature) of the same characteristic fragments (mainly fragments at 84 and 140 amu) are shown in *Figure 1*.

Polythiophene. Thermal decomposition of PTh started at very low temperatures, just above 50°C by the evolution of low-mass fragments. The degradation yield increased steadily and reached its maximum value at 210°C. The most intense and characteristic ions observed in the pyrolysis mass spectrum recorded at 210°C are given in *Table 2*. Furthermore, ion–temperature profiles of some of the diagnostic peaks are plotted in *Figure 2*. The relatively broad decomposition range may be related to the polydispersity of the polymer sample, whereas the low intensity of the monomer and high-mass fragments may be directly related to the unsaturation along the polymer chain:



Loss of small neutral fragments was then expected due to cleavage of the rings:



PTh–PA composites. (a) PTh–PA mechanical mixture. Diagnostic peaks of both PA and PTh were present in the direct pyrolysis mass spectra of the mechanical mixture. In order to compare the behavior of the PTh–PA mechanical mixture with the corresponding homopolymers, ion–temperature profiles of the fragments selected from PTh and PA pyrolysis mass spectra were studied (*Figure 3a*). It is evident from *Figure 3* that the temperature at which the maximum decomposition yield was observed shifted to lower temperature (to 186°C). Actually this temperature corresponds to the shoulder in the ion–temperature profile of a 44 amu fragment of PTh. Notice that in the profiles two more maxima at 210 and 223°C are present. These may be directly related to maxima observed in ion–temperature profiles of pure homopolymer PTh and PA. The d.s.c. studies indicated that the peaks of both PTh and PA are separately seen from the mechanical mixture. Similarly, loss peaks due to both PTh and PA are clearly evident from thermal gravimetric analysis[11]. Thus, it may be concluded that the thermal behaviour of each component resembled the corresponding pure homopolymer. The changes in relative intensities of the decomposition products may be expected as a result of the summation of fragments that arise from both components.

(b) PTh–PA composite film. Direct pyrolysis of electrolytic film prepared by electrooxidation of thiophene onto a polyamide-coated anode produced notably different pyrolysis mass spectra. Ion–temperature profiles of PA- and PTh-based fragments are given in *Figure 3b*. The disappearance of characteristic peaks of PA at high temperatures was particularly significant. It is known that thermal stability depends on the molecular weight of the polymer. The very low temperature formation of PA-based fragments may indicate that a decrease in the molecular weight of PA occurred, which may further be related to the decomposition of PA during electrolysis. T.g.a. and d.s.c. studies also confirmed this proposal; no T_g due to PA and loss of the PA peak were observed.

Another point that should be noted is the lack of high-mass fragments. The dissappearance of high-mass fragments may be related to the crosslinked structure of the composite as indicated by the insolubility of the samples in common organic solvents. However, thermal stability of the electrolytic film was low compared to the situation that would be expected for a crosslinked structure. This unexpected low stability of the composite may be an indication of the presence of weak links between PA and PTh which would decompose more readily and initiate decomposition. Yet, the thermal behaviour of low-mass PTh-based fragments were quite similar to those produced from pure PTh, except for a small shift to lower temperature ranges[11].

Indirect pyrolysis

Polyamide. Indirect pyrolysis mass spectrometric analysis of PA indicated that the evolution of low-mass species started at around 200°C, while main decomposition occurred over a broad temperature range of 350–550°C. Maximum product yield was detected at 453°C. No fragment above 100 amu was observed at any temperature. The base peak was 43 amu due to $C_3H_7^+$. The 28 amu peak due to both CO^+ and $C_2H_4^+$ was also abundant. Peaks at 70 and 84 amu were weak but still present and were among the highest mass fragments. It has been shown that identification of only volatile and stable decomposition products is possible by indirect pyrolysis mass spectrometric analysis. Thus, the presence of these peaks in the indirect pyrolysis mass spectra may be a

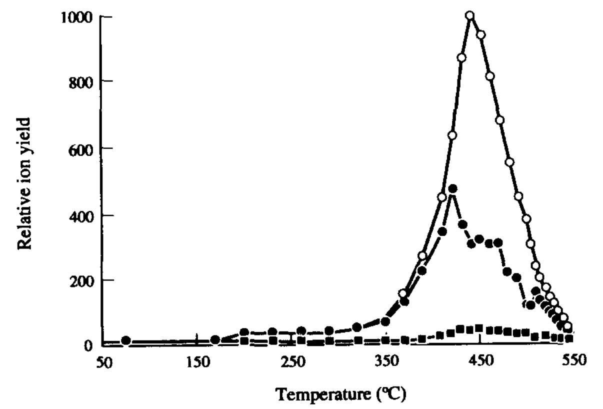


Figure 4 Ion–temperature profiles of 43: (○), 44: (●), and 84: (■) amu fragments observed during the indirect pyrolysis of PA

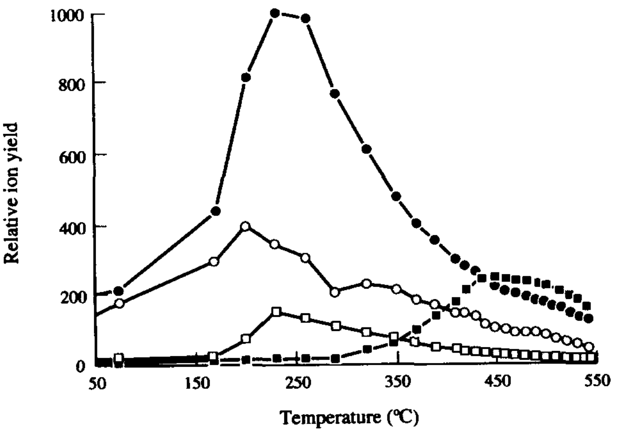


Figure 5 Ion–temperature profiles of 34: (■), 43: (○), 44: (●), and 64: (△) amu fragments observed during the indirect pyrolysis of PTh

direct indication of the production of cyclohexane and cyclopentane during thermal decomposition and confirms assignments of direct pyrolysis. Ion–temperature profiles of 43, 44 and 83 amu fragments are shown in *Figure 4*.

Polythiophene. Due to the low thermal stability of PTh, decomposition started below 100°C and maximum product yield was observed at around 220°C. The main volatile decomposition products at this temperature were HCS, monomer, S_2 and low-mass hydrocarbons. Above 350°C, H_2S formation was dominant. Ion–temperature profiles of some characteristic peaks are given in *Figure 5*.

PTh–PA composites. (a) PTh–PA mechanical mixture. Indirect pyrolysis mass spectra of both PTh–PA mechanical blend and electrolytic film involved characteristic peaks of both polymers. Ion–temperature profiles of these diagnostic peaks are given in *Figures 6a* and *b*. Note that the mechanical mixture yielded ion–temperature profiles which are mainly summation of those observed from PTh and PA. The only significant change was H_2S formation. Its production shifted to lower temperatures in the presence of PA. This behaviour may be due to an increased amount of hydrogen-containing species, basically hydrocarbons degrading from PA.

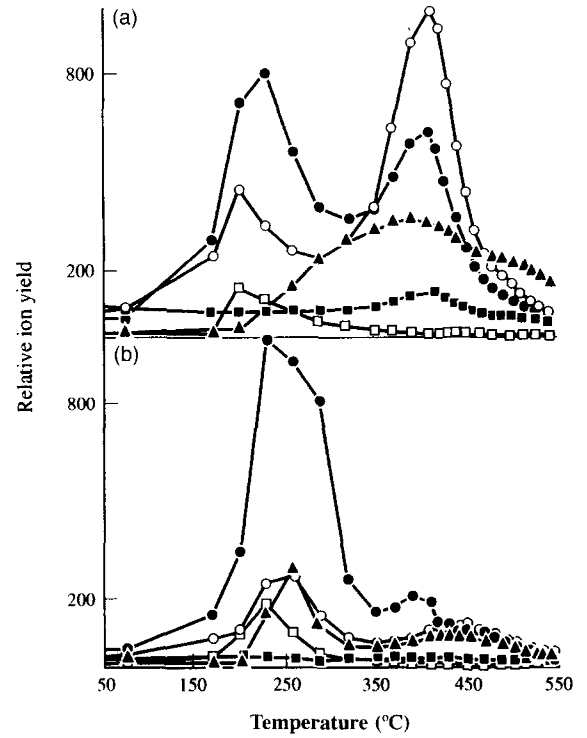


Figure 6 Ion–temperature profiles of 34: (▲), 43: (○), 44: (●), 64: (□), and 84: (■) amu fragments observed during the indirect pyrolysis of PTh–PA composites: (a) mechanical mixture and (b) electrolytic film

(b) PTh–PA composite film. In the case of electrolytic film, a considerable decrease in PA-based peaks was detectable (*Figure 6b*). Furthermore, H_2S generation changed significantly. The ion–temperature profile of an H_2S fragment may be explained by proposing two different reaction pathways for the formation of this molecule. The low-temperature production may be directly related to the evolution of H_2S during thermal decomposition, which may further indicate the presence of chemical interactions between PTh and PA, whereas high-temperature production may be through similar reaction pathways as in the case of pure PTH.

CONCLUSION

Pyrolysis studies indicated that the thermal behavior of PTh–PA electrolytic film was significantly different from the PTh–PA mechanical mixture and related homopolymers. The disappearance of PA-based fragments from the pyrolysis mass spectra of the electrolytic film pointed out that decomposition of PA occurred during electrochemical coating of polythiophene on the host polymer PA, whereas the pyrolysis analysis of the mechanical mixture indicated that each component behaved quite independently and showed an identical thermal behaviour with the related pure homopolymers.

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