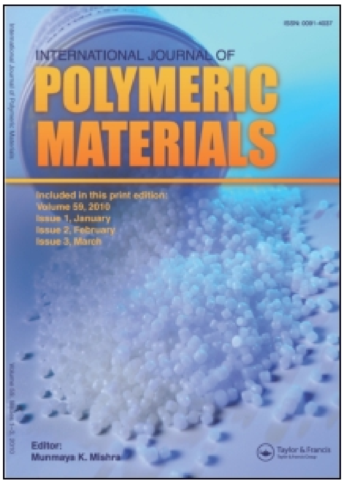

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CHARACTERIZATION OF POLYPYRROLE-THIOPHENE CAPPED POLY(METHYL METHACRYLATE) VIA PYROLYSIS MASS SPECTROMETRY

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This article reports the direct pyrolysis mass spectrometry results on p-toluene sulfonate doped polypyrrole synthesized through the thiophene moities of thiophene-capped poly(methyl methacrylate), TPMMA. Pyrolysis data gave strong evidence for decomposition of the matrix polymer TPMMA during the electrochemical polymerization of pyrrole with a TPMMA coated anode. However, evolution of products diagnostic of TPMMA around 370°C, the temperature region of PPY degradation, and presence of fragments involving both thiophene and pyrrole units confirmed the growth of polypyrrole from the end groups of the matrix polymer while the main chain dissociates.

Keywords: polypyrrole, thiophene capped poly(methyl methacrylate), direct pyrolysis MS

INTRODUCTION

Polypyrrole (PPY) is among of the most extensively studied conductive polymers. Yet its applications are still limited due to the poor mechanical properties. Several works on graft copolymerization of pyrrole have been reported in the literature to modify mechanical characteristics [1–4]. Recently, the authors' attempted to prepare polymers with an electroactive thiophene group on which electrochemical polymerization of pyrrole can be achieved. For this purpose,

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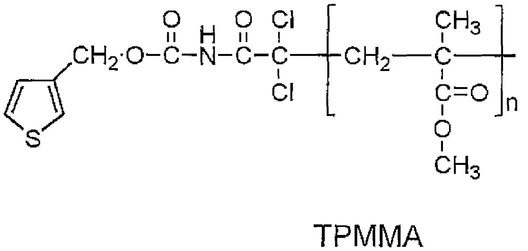


SCHEME 1 Thiophene-capped Poly (methyl methacrylate) substrate.

trichloro acetylcarbamate derivatives of thiophene were used and block copolymers of thiophene-caped poly(methyl methacrylate) (TPMMA) with pyrrole were prepared [5]. Yet, structural characterization was not possible with the use of classical spectroscopic techniques. An alternative technique that can be used for structural characterization is the pyrolysis mass spectrometry. Application of pyrolysis mass spectrometry techniques to polymer studies has been discussed in a number of recent studies [6–8].

This reports the direct pyrolysis mass spectrometry results on the sample of polypyrrole grown from the thiophene moities of thiophene-caped poly(methyl methacrylate) (TPMMA).

EXPERIMENTAL

Synthesis of thiophene capped poly(methylmethacrylate) (TPMMA) (Mn = 15 000) has been previously reported [5]. Polypyrrole (PPY), and PPY/TPMMA samples were electrochemically prepared in a conventional three-compartment cell with two platinum foils (1.5 cm^2 each) as the working and counter electrodes [9]. A Ag/Ag^+ electrode was utilized as the reference electrode. For the synthesis of PPY/TPMMA, pyrrole was electrochemically polymerized onto a TPMMA pre-coated anode. A constant potential of 1.1 V was supplied via a Wenking POS 73 potentiostat. Syntheses were carried out under nitrogen atmosphere in deionized water containing 0.02 M pyrrole and 0.05 M sodium p-toluene sulfonic acid, (PTSA).

Direct insertion probe pyrolysis mass spectrometry system consists of a 5973 HP quadruple mass spectrometer coupled to a SIS direct insertion probe (maximum temperature attained 445°C). Mass spectra of products were recorded at a scan rate of 2 scans/s in the mass range of 10–700 amu using 70 eV electrons as temperature increased at a rate of 10°C/min and kept constant for an additional 10 min at 445°C.

RESULTS AND DISCUSSION

The pyrolysis of PPY/TPMMA at a heating rate of 10°C/min yielded a total ion current (TIC) curve, the variation of total ion yield as a function of temperature, that reveals a broad peak with a maximum at 375°C (Figure 1a). This temperature is significantly low compared to

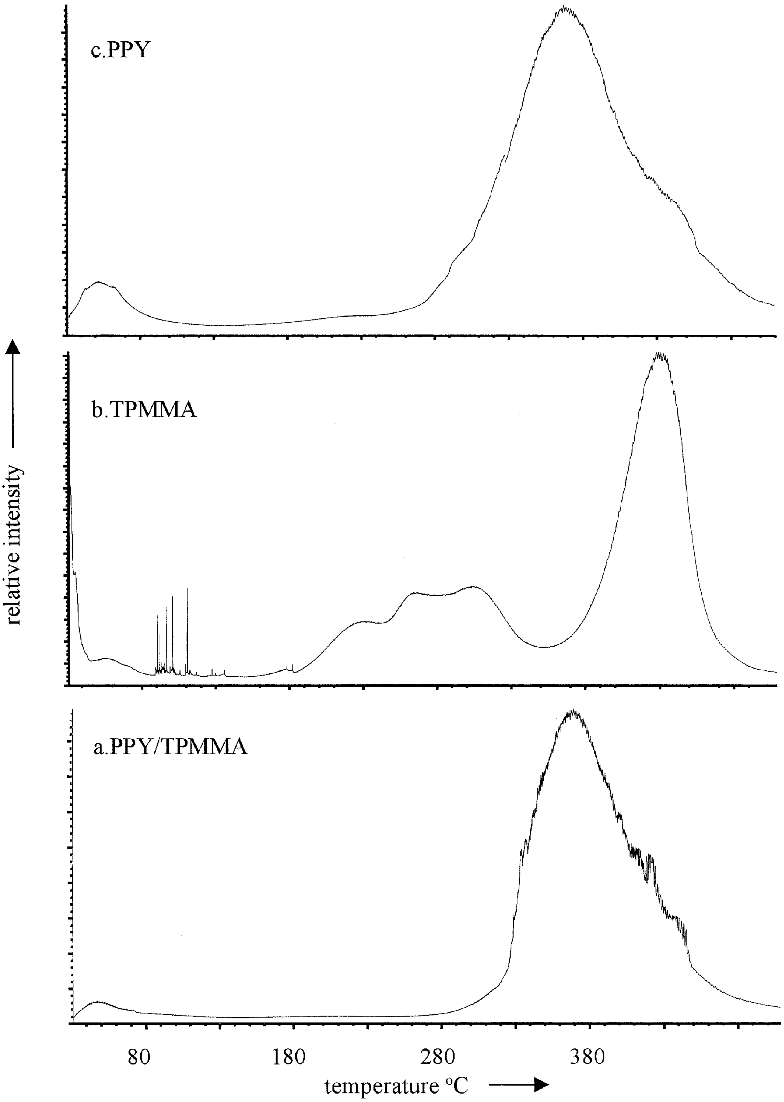


FIGURE 1 TIC curves of (a) PPY/TPMMA (b) PPY, and (c) TPMMA.

the corresponding value for the pure TPMMA (425°C) but very close to that of PPY (370°C) (Figures 1b and 1c). The mass spectrum recorded at the maximum of the TIC curve is mainly dominated by peaks characteristic of polypyrrole. Some of the diagnostic peaks of TPMMA, though very weak, are also present in the spectrum. In Figure 2, the pyrolysis mass spectrum recorded at the TIC maximum is shown. The corresponding mass spectra for PPY and TPMMA are also included for comparison (Figures 2b and 2c). In Table 1 the mass spectral data are summarized.

If polymerization of pyrrole had proceeded through the thiophene moites yielding a block copolymer then the copolymer should be composed of chains involving blocks with different thermal stabilities. Then, during the pyrolysis, each block should behave separately, similar to the corresponding homopolymer. Thus, pyrolysis of such a copolymer should give a TIC curve that is the sum those of both components. Furthermore, fragments involving characteristic units of both blocks should also be produced. If a composite has been produced instead of a copolymer, then pyrolysis should yield a TIC curve quite similar to that of the copolymer. However, peaks due to fragments involving characteristic units of both blocks should be absent in the pyrolysis mass spectra.

The decomposition of PPY/TPMMA at significantly lower temperatures than TPMMA, in the region where PPY decomposition occurs, and the disappearance of high mass fragment peaks diagnostic of TPMMA from the pyrolysis mass spectra reveal that the copolymer does not contain long chains of TPMMA. The significantly low intensities of TPMMA-based fragment peaks indicated that the PPY/TPMMA sample is mainly composed of PPY.

To get a better insight, the time-temperature resolved evolution profiles of single ions are studied. In Figure 3a pyrograms of thermal degradation products that are diagnostic of TPMMA component, namely C_3H_5 ($m/z = 41$), MMA ($m/z = 100$) and C_2H_3S ($m/z = 83$) are shown. The single ion pyrograms of the same fragments generated during the pyrolysis of pure TPMMA are given in Figure 3b for comparison, whereas, in Figure 4, the programs of pyrrole-based products, C_7H_7, C_4H_3NH, and H_2S having m/z values 91, 66, and 34, respectively, are shown [9]. Again, the corresponding ones for pure PPY are also included for a better understanding. It can be noted from Figure 4 that polypyrrole-based products have nearly identical profiles with those of the corresponding ones evolved during the pyrolysis of PPY. However, the pyrograms of the products attributed to degradation of TPMMA blocks show significant differences. Even the fragments associated with methylmethacrylate units such as

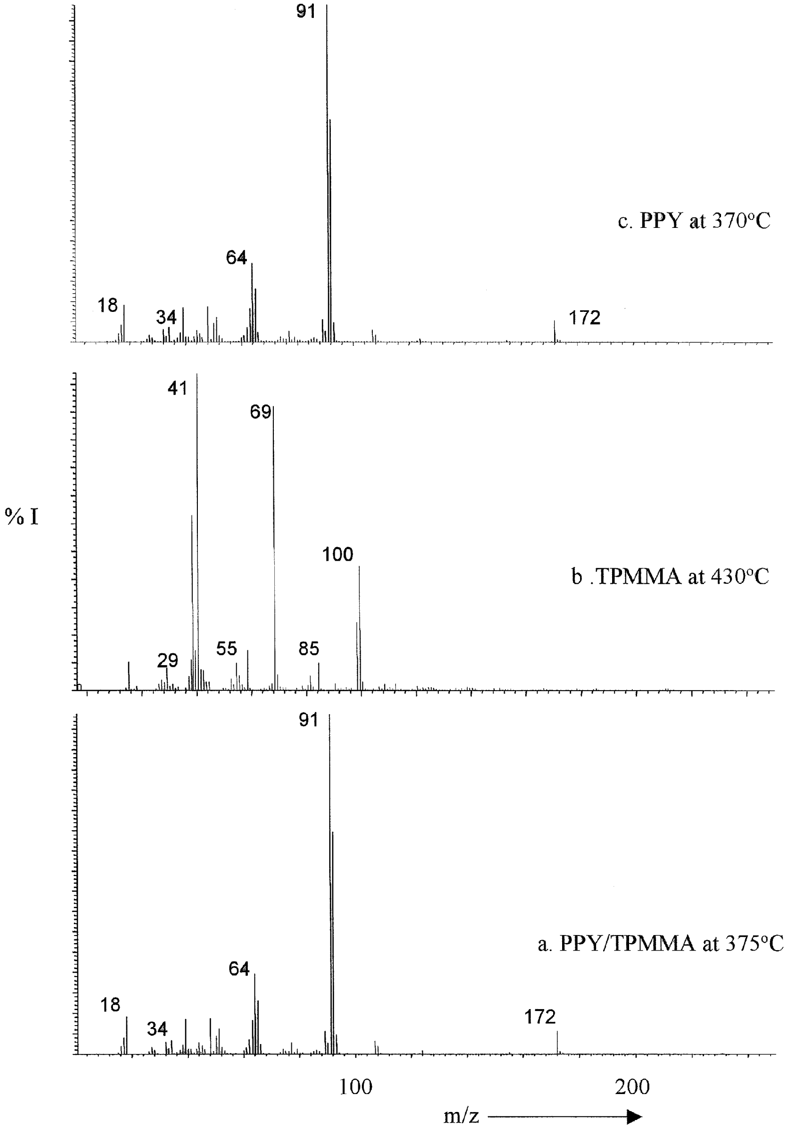


FIGURE 2 The pyrolysis mass spectra for (a) PPY/TPMMA, (b) PPY, and (c) TPMMA at the maximum of the corresponding TIC curves.

$CH_2(CH_3)OOCH_3$ (m/z = 100) and C_3H_5 (m/z = 41) that show similar thermal trends when generated from TPMMA, yield totally different pyrograms when produced during the pyrolysis of the PPY/TPMMA.

TABLE 1 The Characteristics and/or Intense Peaks Present in the Pyrolysis Mass Spectra Corresponding to the Maxima in Ion Profiles of PPY/TPMMA Recorded during Heating at a Rate of 10°C/min

	PPY		TPMMA	PPY/TPMMA			
m/z	370°C	440°C	425°C	90°C	375°C	436°C	Assignment
26	9	1	—	32	18	11	C_2H_2, CN
27	19	28	32	25	49	32	C_2H_3
34	41	244	—	—	44	148	H_2S
41	14	21	1000	1000	30	28	CH_2CCH_3
64	231	235	5	15	421	280	SO_2
66	27	27	5	3	44	30	C_4H_4N or C_4H_3NH
69	2	3	901	16	3	9	$CH_2C_2OCH_3$
70	1	1	49	7	2	2	C_4H_6O, Cl_2
83	1	1	11	13	2	2	C_4H_3S
85	7	7	89	14	10	8	$CH_2CCOOCH_3$
89	65	52	2	6	80	48	$C_4H_3NHCCH_3$
91	1000	1000	24	59	1000	1000	C_7H_7
92	656	589	7	8	772	601	$C_6H_5CH_3$
100	—	—	393	9	3	5	MMA
124	9	1	6	3	14	41	CCl_2COCH_2, $C_4H_3S(C_3H_3NH)$, $CHOC_4H_3NH$
125	2	5	10	5	1	2	CCl_2CONH
132	0,6	0,2	—	—	1	1	Dimer of pyrrole
141	—	—	9	3	1	1	$COOCH_2C_4H_3S$
149	—	—	—	5	1		$C_4H_3S{-}C_4H_2NH$
161	—	—	—	—	1	1	$CH_2C_4H_2S{-}C_4H_2NH$
172	67	2	—	—	38	16	$CH_3C_6H_4SO_3H$

The maximum of the pyrograms of TPMMA-based products shifted significantly to low temperatures when generated during the pyrolysis of PPY/TPMMA indicating a decrease in the thermal stability. The maximum of the TIC curve for TPMMA at 425°C shifted to 375°C in copolymer, as in the case of PPY. In general, the evolution of thermal degradation products at lower temperatures indicates a decrease in the thermal stability that can be associated with a decrease in the molecular weight of the polymer. On the other hand, presence of a second peak in the pyrograms of low molecular weight thermal degradation products, such as C_3H_5 and C_4H_3S, at initial stages of pyrolysis is even more noteworthy. Actually, below 100°C degradation of polymer is not likely. The low temperature peaks in the TIC curves are mainly attributed to evolution of low molecular weight volatile species that had been adsorbed on the polymer under investigation. In the present, as the TPMMA-related low molecular weight species can

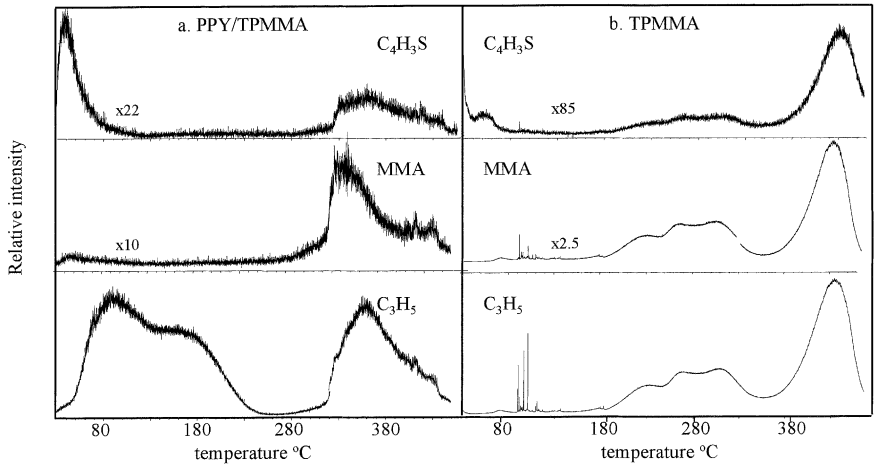


FIGURE 3 Single ion pyrograms of the fragments at m/z 100 due to MMA, 41 due to C_3H_5 and 83 C_4H_3S of (a) PPY/TPMMA and (b) PPY.

only be present in the reaction medium if the degradation of the matrix polymer, TPMMA, has occurred during the electrochemical polymerization of pyrrole. Thus, not only the evolution at lower temperatures and the significant decrease in the relative intensities of TPMMA based products, but also the trends observed in the single ion

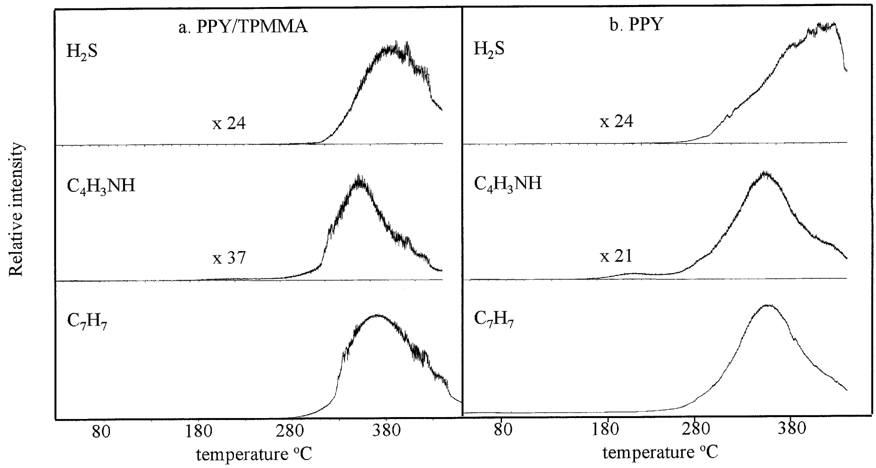
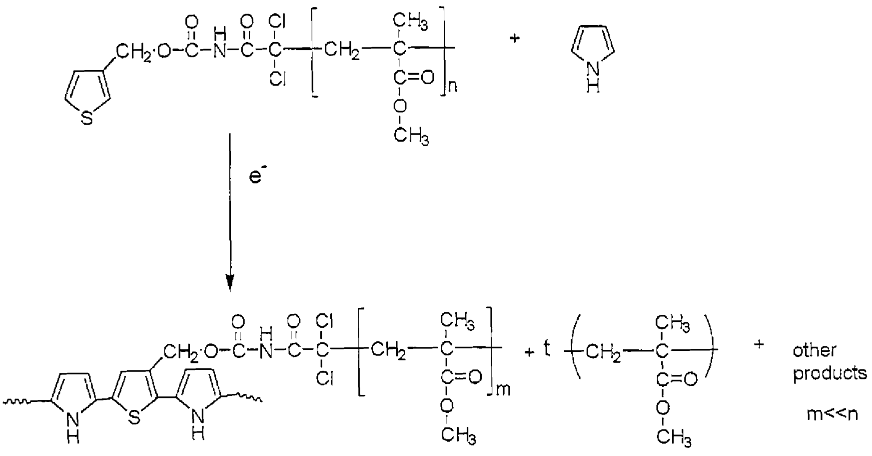


FIGURE 4 Single ion programs of the fragments at m/z 91 due to C_7H_7, 66 due to C_4H_3NH, and 34 due to H_2S of (a) PPY/TPMMA and (b) PPY.

pyrograms suggest a degradation of the matrix polymer during the electrochemical polymerization of pyrrole.

However, although weak, evolution of TPMMA-based products was also detected in the temperature region where the thermal decomposition of PPY has occurred. Thus it is clear that the final product also contains TPMMA polymer chains. Furthermore, two new peaks that were absent in the pyrolysis mass spectra of PPY and TPMMA were identified at m/z 161 and 149 Da that may be attributed to $CH_2C_4H_2S{-}C_4H_2NH$ and $C_4H_3S{-}C_4H_3NH$, respectively. Presence of these peaks is a strong evidence for the growth of pyrrole through the thiophene moities of the TPMMA. Yet, the decrease in thermal stability and the significantly low relative intensities of TPMMA-based product peaks point out that these TPMMA chains are quite short.

Pyrolysis experiments were repeated while decreasing electron energy to 19 eV in order to limit the fragmentation during the ionization in the mass spectrometer. Increase in the relative intensities of fragment peaks assigned to stable molecules evolved during pyrolysis, such as peaks at m/z 34 (due to H_2S), 64 (due to SO_2), 92 (due to C_7H_7), and 172 (due to PTSA), is noted as expected. Yet, the evolution profiles are quite similar to the corresponding ones recorded at 70 eV. Again, TPMMA-based degradation products of PPY/TPMMA showed identical behavior with those of the corresponding ones produced during pyrolysis of TPMMA. Therefore, it can be concluded that dissociative ionization has no significant effect on the observed trends. In light of



SCHEME 2 Mechanism of electrochemical polymerization of polypyrrole on TPMMA substrate.

the present results, electrochemical polymerization of pyrrole on TPMMA-coated anode can be explained by Scheme 2.

CONCLUSION

Pyrolysis data gave strong evidence for decomposition of the matrix polymer TPMMA during the electrochemical polymerization of pyrrole using a TPMMA-coated anode. However, evolution of products diagnostic of TPMMA in the same temperature region with those of PPY, and presence of fragments involving both thiophene and pyrrole units confirmed the growth of polypyrrole from the end groups of the matrix while the main chain dissociates.

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