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Pyrolysis Mass Spectrometry Analysis of Thiophene Capped Poly(Methyl Methacrylate) and Poly(Methylthienyl Methacrylate)

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ABSTRACT

The thermal degradations of thiophene-capped poly(methyl methacrylate) and poly(methylthienyl methacrylate) were studied via direct pyrolysis mass spectrometry. No significant effect of heating rate on the thermal degradation behaviors of the polymers under investigation have been observed in the heating range studied. It has been determined that thermal degradation of thiophene-capped poly(methyl methacrylate), (TPMMA) mainly yields monomer as in the case of pristine poly(methyl methacrylate). An analogous degradation mechanism can also be proposed for poly(methylthienyl methacrylate), (PMTM). Yet, the elimination of side chains, evolution of $OCH_2C_4H_3S$ groups was found to be also effective for this sample. Pyrolysis experiments were repeated using 17 eV electrons to determine the extent of fragmentation due to dissociative ionization

Key Words: Thiophene capped poly(methyl methacrylate); Poly(methylthienyl methacrylate); Direct pyrolysis MS; Thermal degradation.

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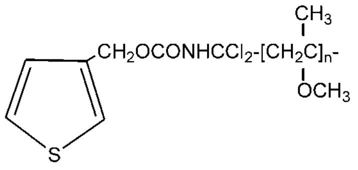
INTRODUCTION

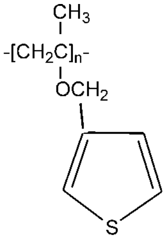
The thermal degradation of poly(methyl methacrylate), (PMMA) and its copolymers have been the subject of many studies for more than 50 years.[1–13] The accepted thermal degradation mechanism for PMMA is a depolymerization mechanism yielding mainly the monomer, methyl methacrylate. The direct pyrolysis mass spectral analysis yields a single peak in the total ion current curve revealing the similarity between the pyrolysis mass spectra of the polymer and the monomer.[11] Recently, kinetics and mechanisms of thermal degradation of poly(methyl methacrylate) have been studied by thermal analysis Fourier transform infrared spectoscopy and it was concluded that thermal degradation was initiated by a mixture of chain end and random chain scission initiation followed by depropagation and first order termination.[13]

Pyrolysis mass spectrometry techniques and their applications to polymer studies have been discussed in a number of studies.[11,12] Among the various common spectroscopic techniques, direct pyrolysis mass spectrometry (DPMS) technique also offers an alternative for polymer composition analysis. Since, DPMS directly analyzes thermal degradation products without prior separation secondary reactions and condensation of pyrolysate can be largely avoided. Thus, important information to elucidate the thermal degradation mechanism can be obtained.

In this work, we report the direct pyrolysis mass spectrometry results on the thiophene-capped poly(methyl methacrylate) and poly(methylthienyl methacrylate) samples which were used as host matrices for the preparation of block copolymers of polypyrrole.[14,15]



thiophene-capped poly(methyl methacrylate)



poly(methylthienyl methacrylate)

EXPERIMENTAL

Poly(methyl methacrylate) was purchased from Aldrich (Mn = 15 000). Thiophene capped poly(methyl methacrylate), (TPMMA), ($M_n = 28\,000$), and poly(methylthienyl methacrylate), (PMTM), ($M_n = 73\,000$) were synthesized in the Department of Chemistry; İstanbul Technical University and details of the synthesis procedure were discussed in our previous studies.[14,15] After a short time, thiophene capped PMMA was synthesized by mixing 3-thiophenemethanol and thrichloroacetylisocyanate in dry cyclohexane.

Direct insertion probe pyrolysis mass spectrometry system consists of a 5973 HP quadruple mass spectrometry coupled to a SIS direct insertion probe. The maximum temperature attainable is 445°C. Pyrolysis analyses were carried on ca. 10 μg of polymer samples in flared glass sample vials. Mass spectra of the products were recorded at a scan rate of 2 scans/s in the mass range of 10–700 amu using 70 and 19 eV electrons to determine the extent of fragmentation during ionization. Two heating rates, namely 10°C/min and 900°C/min were applied to investigate the effect of heating rate on thermal behavior.

RESULTS AND DISCUSSIONS

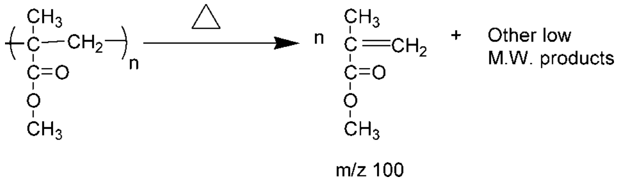
Thiophene Capped Poly(Methyl Methacrylate) (TPMMA)

It may be suggested that the thermal degradation mechanism of thiophene capped poly(methyl methacrylate) should be quite similar to that of poly(methyl methacrylate) as the only difference is the presence of end groups. It is known that poly(methylmethacrylate), (PMMA), degrades via a mixture of chain end and random chain scission initiation followed by depropagation which produces mostly monomer and low molecular weight oligomers as shown in Sch. 1.

Direct pyrolysis mass spectra of PMMA obtained at both heating rates, (10°C/min and 900°C/min) show mainly the classical fragmentation pattern of the monomer, methylmethacrylate, in accordance with the literature results.[11] Oligomer peaks up to five monomer units, though weak, are also present in the spectra. The mass spectral data are summarized in Table 1 for comparison with the corresponding ones for TPMMA.

Thermal degradation of the thiophene capped poly(methyl methacrylate) occurred in a broad temperature range starting from initial stages of heating as seen from the total ion current, TIC, curve [Fig. 1(a)]. The TGA thermogram of the sample shows a three-stage weight loss for TPMMA though main weight loss occurs at around 430°C.[14] It is known that a complex thermal degradation mechanism involving multi-steps yields pyrograms with more than one peak. Yet, the mass spectra recorded at the peak maxima of the TIC curve are nearly identical indicating to each other that the observed trend is not due to a complex thermal degradation mechanism.

The mass spectrum recorded at the temperature corresponding to maximum product yield at 425°C is shown in Fig. 1(b). The pyrolysis mass spectrum, with the base peak at m/z 41 due to CH_2CCH_3, and strong peaks at m/z 69 and 100 due to CH_2CCH_3CO and methylmethacrylate, $CH_2C(CH_3)COOCH_3$, respectively, is nearly identical to that of the poly(methyl methacrylate), PMMA as expected. Yet, weak peaks associated with the end group such as peaks at m/z 82, 83, 97, 110, 113 and 125 due to CCl_2, C_4H_3S, $CH_2C_4H_3S$,



Scheme 1.

Table 1. The characteristics and/or intense peaks present in the pyrolysis mass spectra corresponding to the maxima in ion profiles of TPMMA and PMMA recorded during pyrolysis with a heating rate of 10°C/min.

	TPMMA		PMMA	
m/z	220°C	425°C	410°C	Assignment
39	529	553		C_3H_3
41	1000	1000	1000	CH_2CCH_3
59	106	129	146	$COOCH_3$
69	850	901	969	$CH_2C(CH_3)O$
83	8	11		C_4H_3S
85	90	89	107	$CH_2C(CH_3)OO$
97	16	9		$CH_2C_4H_3S$
99	202	220	247	$CH_2C_3H_5COO$
100	373	393	470	MMA
109	5	23		$CHCH_2CCl_2$
113	7	25		$OCH_2C_4H_3S$
125	2	10		CCl_2CONH
127	2	10		CCl_2COCH
141	2	9		$COOCH_2C_4H_3S$
151		10		$COCCH_3CH_2CCl_2$
165		4		$OCC(CH_3)CH_2CCl_2$
196		1		MMA + CH_2CCl_2
200		2	6	$(MMA)_2$
266		1		Monomer
301		1	3	$(MMA)_3$ + H
401		1	1	$(MMA)_4$ + H

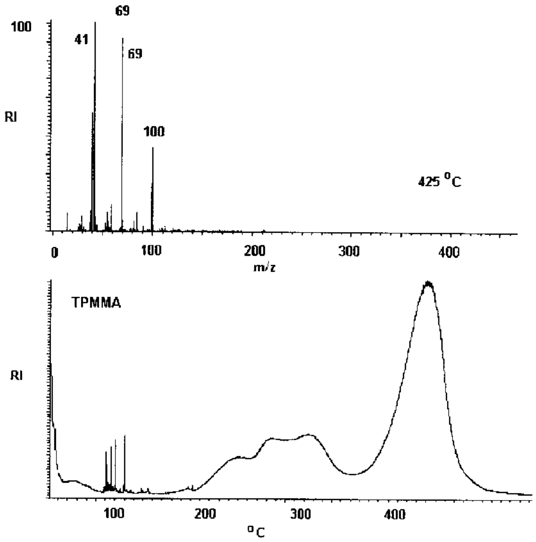
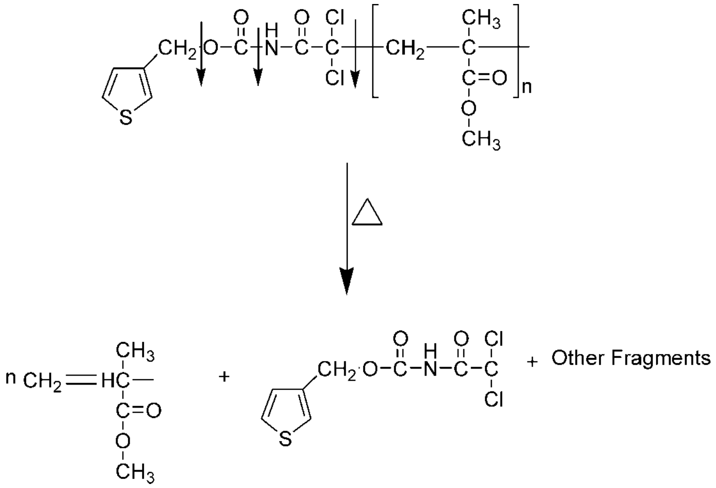


Figure 1. a) The total ion current during the pyrolysis of TPMMA with a heating rate of 10°C/min and b) the mass spectra corresponding to maximum yield.

CCl_2O, $OCH_2C_4H_3S$ and CCl_2CONH, respectively are also present in the spectrum. The intense and/or characteristic peaks present in the mass spectra recorded at 220°C and 425°C are summarized in Table 1. Considering the similarities in the pyrolysis mass spectra of TPMMA and PMMA it may be proposed that the thermal decomposition of TPMMA occurs via a depolymerization mechanism yielding mainly monomer as in the case of pristine poly(methyl methacrylate) as shown in Sch. 2. It is clear that no significant effect of the end groups on the thermal decomposition of the main chain exists.

To get a better insight on thermal decomposition processes and products, the time-temperature resolved evolution profiles, the single ion pyrograms, of intense and characteristic peaks were studied. In Fig. 2, pyrograms of the peaks at m/z 100, 401, 41, 97, and 125, due to $CH_2C(CH_3)COOCH_3$, $(CH_2C(CH_3)COOCH_3)_4H$, CH_2CCH_3, $CH_2C_4H_3S$ and CCl_2CONH respectively, are given. As seen from the figure, all the fragments show similar trends above 325°C. At moderate temperatures below 325°C, the fragments involving thiophene, chlorine and MMA follow different paths. It may be proposed that the polymer sample contains either chains with variable chain length and thermal stabilities or chains with different end groups. Another possibility may be the presence of adsorbed reactants. The MMA bearing fragments appearing in the pyrolysis mass spectra at low temperatures may be attributed to the decomposition of low molecular weight chains. However, the presence of both MMA and thiophene bearing fragments around 220°C, in the region where chlorine involving fragments were nearly absent, may only be attributed to PMMA chains with only thiophene end groups formed during the synthesis of the compound. Furthermore, detection of relatively intense peaks due to thiophene involving fragments at initial stages of pyrolysis may be associated with the presence of 3-thiophenyl methanol used for the synthesis of N-trichloroacetyl 3-thiophenylmethyl carbamate, the starting material for the insertion of end groups.[15]

Similar observations have been found in the case of a ballistic heating rate (900°C/min) indicating that the heating rate has no significant impact on the thermal



Scheme 2.

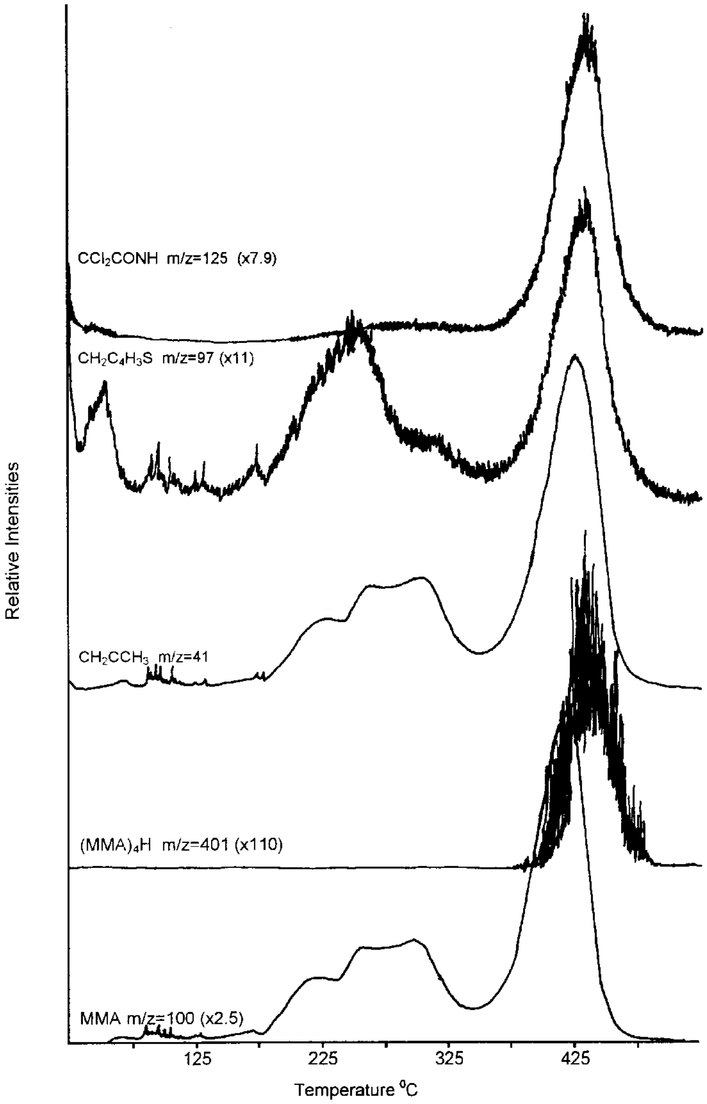


Figure 2. Time–temperature resolved evolution profiles of the ions at m/z 100, 401, 41, 97, and 125 obtained during the pyrolysis mass spectrometry of TPMMA with a heating rate of 10°C/min.

decomposition mechanism at least in the range studied. To decrease the extent of fragmentation of the thermal decomposition products in the ion source, pyrolysis experiments were repeated by decreasing ionization energy to 19 eV at both heating rates. Similar TIC curves involving sharper peaks were obtained. The 19 eV pyrolysis mass spectra are dominated with peaks which are also present in the corresponding 70 eV spectra. Changes in the relative intensities of the product peaks and the increase in the relative intensity of the monomer peak confirmed the proposed depolymerization mechanism.

Poly(Methylthienyl Methacrylate) (PMTM)

Pyrolysis of poly(methylthienyl methacrylate) yielded a total ion current, TIC, curve that shows a sharp but weak peak at the initial stages of pyrolysis and a broad peak with a maximum around 380°C [Fig. 3(a)]. Analysis of the low temperature peak below 50°C indicated the presence of unreacted monomer adsorbed on the polymer. The main thermal decomposition occurs in a single stage, in accordance with the thermogravimetry results that reveals a single stage huge weight loss at 412°C.[15] The base peak in all the pyrolysis mass spectra recorded is due to $CH_2C_4H_3S$ fragment at m/z 97 [Fig. 3(b)]. The monomer peak at m/z 182 is among the most intense. Identical product peaks were detected when a ballistic heating rate was applied indicating that the thermal decomposition mechanism is independent of the heating rate. In the corresponding 19 eV pyrolysis mass spectra the base peak is at m/z 69 due to $CH_2C_2OCH_3$ and noticeable decrease in the relative intensity of the monomer peak is observed. In Table 2, the data related to characteristic and/or intense peaks in the 19 and 70 eV pyrolysis mass spectra recorded at the maximum of the total ion current curves obtained at a heating rate of 10°C/min are collected.

The single peak in the TIC pyrogram and mainly the monomer evolution reveals that the polymer degrades via a depolymerization mechanism as in the case of PMMA.

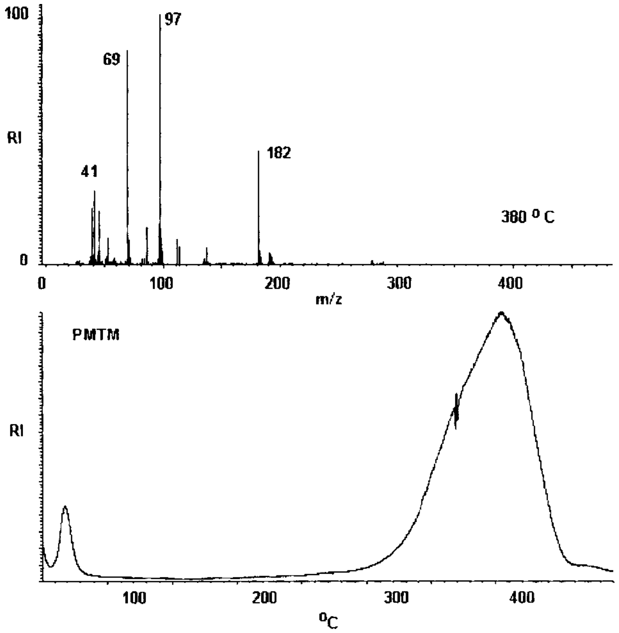


Figure 3. a) The total ion current recorded during the pyrolysis of PMTM with a heating rate of 10°C/min and b) the mass spectra corresponding to maximum yield.

Table 2. The characteristics and/or intense peaks present in the 70 and 19 eV pyrolysis mass spectra at TIC maxima of PMTM recorded during pyrolysis with a heating rate of 10°C/min.

	PMTM		
	70 eV	19 eV	
m/z	380°C	379°C	Assignment
39	220	28	C_3H_3
41	283	216	CH_2CCH_3
44	49	28	CO_2, C_2H_4O
53	102	39	C_4H_5
58	29	5	CO_2CH_2
69	853	1000	$CH_2C(CH_3)CO$
83	24	6	C_4H_3S
85	144	115	$CH_2C(CH_3)COO$
97	1000	749	$CH_2C_4H_3S$
99	52	38	$C_5H_7O_2$
109	7	4	$C_4H_4COCH_2CH_3$
111	63	28	$C_4H_5CO(CH_3)_2$
113	58	51	$OCH_2C_4H_3S$
126	4	3	$C_5H_8O_2C_2H_2$
137	63	63	$C_4H_4(CO)_2CH_2CH_3$
141	1	1	$COOCH_2C_4H_3S$
154	3	2	$C_5H_8OC_3H_2O$
182	435	384	MTM
185	3	3	$C_5H_8O_2C_4H_5O_2$
191	45	37	$(CH_2C_2H_3)_3CH_2C_2OCH_2$
192	38	36	$(CH_2C_2H_3)_3CH_2C_2OCH_3$
255	2	1	$(MMA)_2 + C_2H_3CO$
278	14	11	$MTM + C_4H_4CH_2(CH_3)_2$

Comparison with the monomer spectrum was not possible. Yet, the observed trends, the significant increase in the relative intensity of the m/z 69 fragment peak and the decrease in that of the monomer peak may be associated with the cleavage of C—O bonds and loss of the side groups during pyrolysis.

The temperature-time resolved single ion curves of C_3H_5 at m/z 41, C_4H_3S at m/z 83, $CH_2C_4H_3S$ at m/z 97 and monomer, MTM at m/z 182, recorded at 10°C/min are shown in Fig. 4. Inspection of the single ion profiles with quite similar pattern indicated that the polymer is a homogeneous homopolymer with the absence of impurities other than unreacted monomer evolving immediately below 60°C. Thus, the following decomposition mechanism can be suggested for PMTM (Sch. 3).

It is known that polymers containing tertiary carbon atoms in the polymer skeleton structure generally follow a one-step pyrolysis and show a single peak in the TIC curve. However, it may be thought that if thermally labile side chains exist, then elimination of these groups should also occur readily. Normally, polymers containing thermally labile

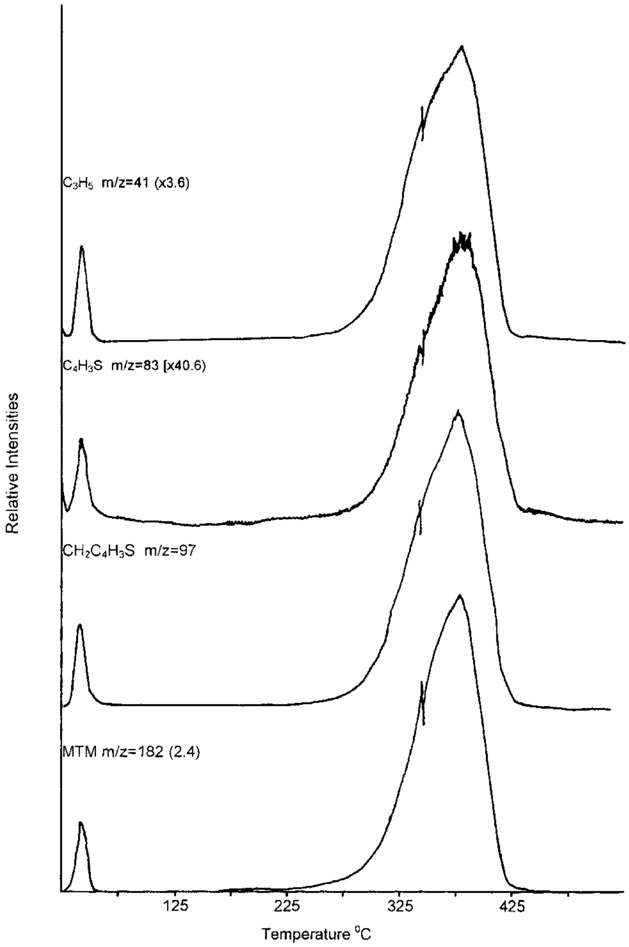
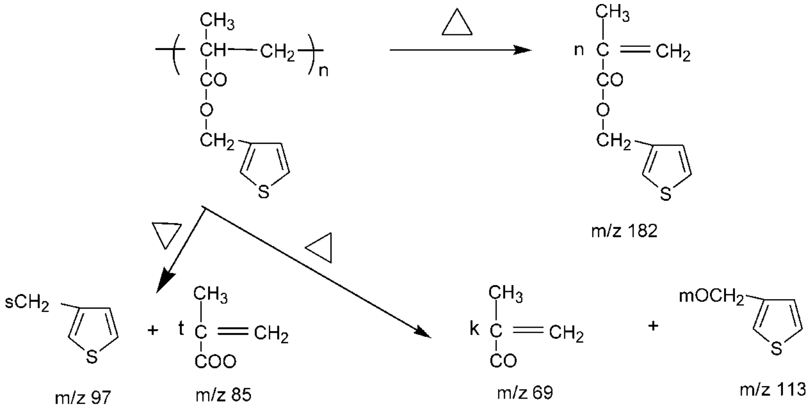


Figure 4. Time–temperature resolved evolution profiles of the ions at m/z, 182, 97,83 and 41 obtained during the pyrolysis of PMTM with a heating rate of 10°C/min.



Scheme 3.

side chains, pyrolyzes via two or more consecutive steps. For PMTM, the single peak in the TIC curve indicates that energetics of both depolymerization and elimination of thermally labile side chains are quite similar.

CONCLUSION

The data collected in this work reveal that thermal decompositions of thiophene capped poly(methyl methacrylate) and poly(methylthienyl methacrylate) initiated by chain end and main chain scissions followed by depropagation yielding mainly the corresponding monomers. Yet, the elimination of the side chains has also been detected for the poly(methylthienyl methacrylate) indicating that pyrolysis of this polymer yields a combination of both mechanisms.

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