

# Analysis of Polymers Using Evolved-gas and Direct-pyrolysis Techniques\*

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Thermal analysis of polystyrene, poly(*p*-methylstyrene) and poly( $\alpha$ -methylstyrene) has been carried out using evolved-gas analysis by infrared and mass spectrometry, and direct-pyrolysis analysis by mass spectrometric techniques. Evolved-gas analysis, both by infrared and mass spectrometry, reveals features due mainly to the corresponding monomers or stable, volatile, and low relative molecular mass degradation products. In direct-pyrolysis mass spectrometry, however, primary decomposition products and heavier fragments such as dimers and trimers can also be detected. The ion-temperature profiles of the corresponding monomer ions reveal information about the thermal stability of the polymers.

**Keywords:** Polymer; pyrolysis; Infrared technique; mass spectrometry

## Introduction

In a thermal-degradation study there may be many different objectives such as polymer identification, determination of thermal stability, degradation mechanism and products, or measurement of the temperatures at which physical or mechanical properties change. The techniques available for the study of the thermal decomposition<sup>1-6</sup> of polymers have increased substantially during the last decades, each having its own potential and limitations. Pyrolysis techniques are among the most common methods, especially if degradation products are sought. Indirect pyrolysis or evolved-gas analysis<sup>2,6-10</sup> can be carried out with gas chromatography-mass spectrometry (GC-MS), mass spectrometry (MS) or infrared (IR) techniques. The information that can be obtained is limited and questionable, as only volatile fragments can be analysed and secondary reactions are likely to confuse the interpretation of results. In direct-pyrolysis MS<sup>6,11-13</sup> high relative molecular mass fragments are also detected, as condensation is prevented. Furthermore, as the possibility of secondary reactions is diminished, due to the high vacuum conditions and the rapid MS detection system, the data are more reliable for the investigation of degradation mechanisms.

The thermal degradation of polystyrene (PS), has been the subject of numerous investigations for many years with the use of different thermal-analysis techniques.<sup>8,14-19</sup> The thermal analyses of its methyl-substituted derivatives such as poly(*p*-methylstyrene) (PPMS) and poly( $\alpha$ -methylstyrene) (PAMS) have also been studied to some extent.<sup>20-23</sup> In this work, our

principal aim was to compare evolved-gas and direct-pyrolysis techniques by studying the results of the thermal analysis of PS, PPMS, and PAMS using MS and IR techniques.

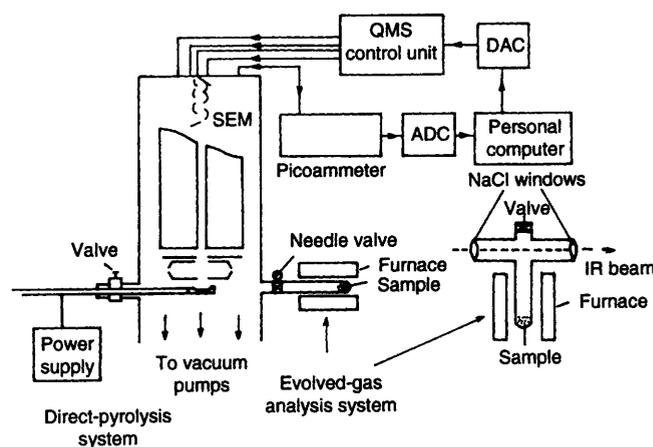
## Experimental

### Apparatus

The mass spectrometer used throughout was a Balzers QMG 311 spectrometer coupled to a personal computer for instrument control, and data acquisition and processing. A Nicolet 510 FTIR spectrometer was employed for IR studies. Fig. 1 shows a schematic diagram of the experimental set-up.

### Evolved-gas Analysis by MS and IR

The experimental system used in evolved-gas analysis (EGA)<sup>18,19</sup> consisted of a pyrolysis chamber and a furnace. A needle valve was used to control the flow of the evolved gases into the mass spectrometer. The maximum temperature that could be reached was 700 °C. The same system could also be connected directly to an IR gas cell. Samples (10 mg) in the form of fine powders were used. After sample introduction and before the start of the experiment, the pyrolysis chamber and the IR gas cell were evacuated to 0.01 Pa; the cell was heated to 50 °C, while evacuated, to dry the solvent or the unreacted monomer. The gases evolved were recorded at



**Fig. 1** Experimental set-up. The quadrupole mass spectrometer (QMS) is controlled by a personal computer via the digital-to-analogue converter (DAC). The ions are multiplied by the secondary electron multiplier (SEM), amplified by the picoammeter and read by the computer via the analogue-to-digital converter (ADC)

\* Presented at the XXVIII Colloquium Spectroscopicum Internationale (CSI), York, UK, June 29-July 4, 1993.

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10 °C intervals and the data were stored for further manipulation. Typically, a heating rate of 10 °C min<sup>-1</sup> was applied.

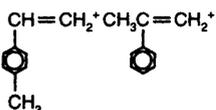
### Direct-pyrolysis MS

A direct insertion probe has been designed for direct pyrolysis experiments.<sup>13</sup> It consists of a stainless-steel tube Ag-soldered to a copper sample holder assembly, a heater, a power supply, and a chromel–alumel thermocouple. The probe can be inserted directly into the mass spectrometer using a valve that allows differential pumping of the probe-inlet line. The samples, in the form of films cast from 0.1% m/v polymer–benzene solutions onto the flat base of the copper sample holder (6 mm diameter), are subjected to thermal degradation under high vacuum ( $\leq 10^{-2}$  Pa). For direct pyrolysis, a slightly higher heating rate, 15 °C min<sup>-1</sup>, is employed. It is known that not only homogeneity, but also sample thickness are important in thermal analysis. To check the effect of sample thickness, films generated by the evaporation of 20, 30, and 50  $\mu$ l of 0.1% monodispersed PS (number average molecular mass,  $M_n = 300\,000$ )–benzene solutions were used. The relative intensities of the peaks at  $m/z$  78, 91, 104, and 208, recorded during the thermal degradation of PS at temperatures corresponding to maximum ion yields for the three samples, are given in Table 1. As the relative intensities of these main peaks in the PS spectrum are seen to be independent of the solution volume evaporated, the results indicate that the sample thickness does not have any significant effect on the degradation processes in this volume range. Hence 20  $\mu$ l of 0.1% m/v polymer solution were used

**Table 1** Relative intensities of some characteristic peaks observed during the direct pyrolysis of PS cast from 20, 30, and 50  $\mu$ l 0.1% m/v solutions

Volume/ $\mu$ l	$T_{\max}/^{\circ}\text{C}$	Relative peak intensity (%)			
		$m/z$ 78	$m/z$ 91	$m/z$ 104	$m/z$ 208
20	230	584	890	1000	22
30	228	593	896	1000	17
50	229	588	878	1000	30

**Table 2** Relative intensities of the most characteristic peaks observed during the indirect pyrolysis (above 400 °C) of PS, PPMS, and PAMS, with the assigned chemical formulae

$m/z$	Relative intensity (%)			Assignment
	PS	PPMS	PAMS	
77	326	170	335	$\text{C}_6\text{H}_5^+$
78	547	105	398	$\text{C}_6\text{H}_6^+$
91	81	697	294	$\text{C}_7\text{H}_7^+$
92	34	110	28	$\text{C}_6\text{H}_5\text{CH}_3^+$
103	718	174	543	$\text{C}_6\text{H}_5\text{CH}=\text{CH}^+$
104	1000	20	99	$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2^+$
105	—	64	25	$\text{C}_7\text{H}_6\text{CH}_3^+$
106	—	65	4	$\text{CH}_3-\text{C}_6\text{H}_4-\text{CH}_3^+$ ; $\text{C}_6\text{H}_5\text{C}_2\text{H}_5^+$
115	—	319	279	
117	—	1000	872	$\text{C}_7\text{H}_6\text{CH}=\text{CH}^+$
118	—	764	1000	

throughout the direct-pyrolysis experiments to minimize possible contamination of the spectrometer.

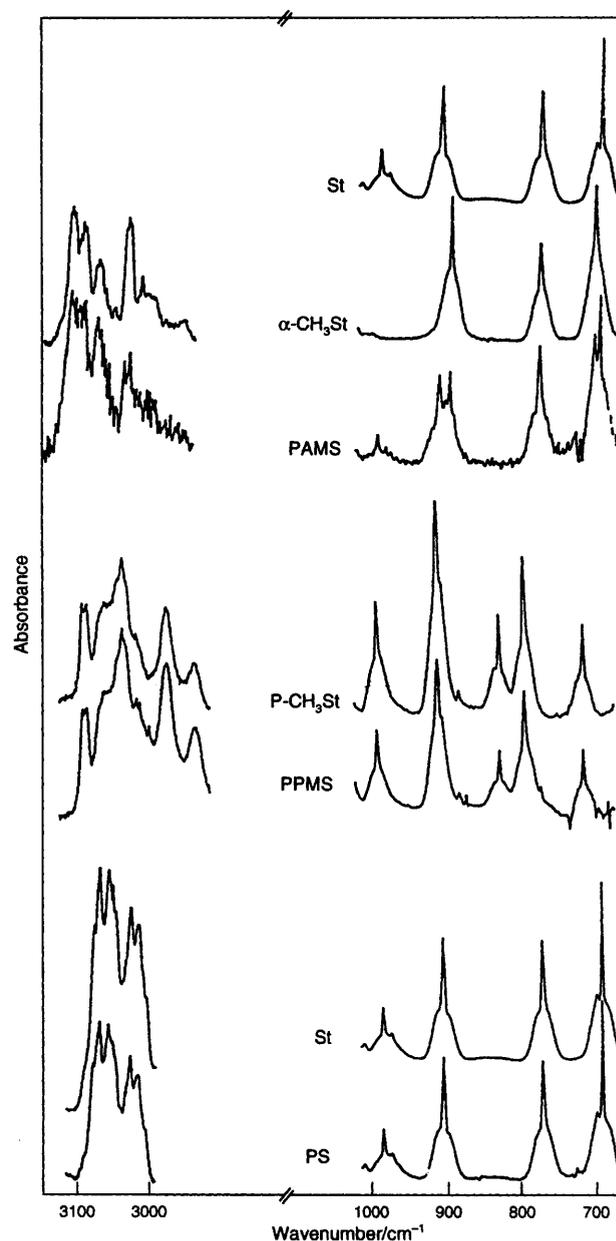
### Polymer samples

Monodispersed PS samples (number average molecular mass, 300 000) supplied by Aldrich (Milwaukee, USA) were used without further purification. Poly(*p*-methylstyrene) and poly( $\alpha$ -methylstyrene) were prepared as described previously.<sup>21,25</sup>

## Results and Discussions

### Evolved-gas Analysis by MS

None of the polymers under investigation produced ion peaks at higher  $m/z$  than the monomer peaks. Intense peaks below



**Fig. 2** IR spectra of evolved gases from the pyrolysis of PS, PPMS, and PAMS, and the corresponding monomers: St, styrene; P-CH<sub>3</sub>St, *p*-methylstyrene; and  $\alpha$ -CH<sub>3</sub>St,  $\alpha$ -methylstyrene. Only part of the spectrum is displayed in each instance as the full spectra reveal features due to CO<sub>2</sub>, H<sub>2</sub>O, etc., which could cause unnecessary confusion

$m/z$  40 were observed during the initial stages of pyrolysis below 350 °C, indicating the formation of low relative molecular mass volatile compounds such as ethylene and acetylene. The main decomposition started above 400 °C for the polymer samples studied in this work. The relative intensities of the most characteristic ions observed during the direct pyrolysis of PS, PPMS, and PAMS, and the assigned chemical formulae are given in Table 2. The base peak is the monomer at  $m/z$  104 for PS and  $m/z$  118 for PAMS, whereas for PPMS, the base peak is at  $m/z$  117. As the mass spectra of the gases, *e.g.*, of the corresponding monomers, toluene and styrene, also yield identical peaks due to ionization and/or fragmentation within the ion source of the mass spectrometer, it is extremely difficult to assign with high certainty all the fragments produced.

### Evolved-gas Analysis by IR

The IR spectra recorded during the pyrolysis of polystyrenes indicate that the polymers mainly depolymerize to the corresponding monomers. The relevant parts of the IR spectra of the gases evolved during the pyrolysis of PS, PPMS, and PAMS, and of the related monomers are shown in Fig. 2. The spectrum of the evolved gases from PS matches exactly the spectrum of the monomer (St). Similarly, the spectrum of the evolved gases from PPMS is the same as that of its monomer, *p*-methylstyrene (P-CH<sub>3</sub>St). Only for PAMS, is there an indication of styrene (St) formation in addition to the presence of the monomer ( $\alpha$ -CH<sub>3</sub>St). No other thermal degradation product can be identified from the IR data for any of the polymers under study. Weak peaks due to the solvents used in sample preparation are present in the PPMS spectrum.

### Direct-pyrolysis by MS

The mass spectra recorded at different temperatures during the direct pyrolysis of PS are shown in Fig. 3. Analysis of such data requires a considerable amount of effort. Fig. 4 displays the mass spectra obtained during the direct pyrolysis of PS, PPMS, and PAMS at 230, 217, and 197 °C, corresponding to their respective maximum decomposition temperatures.

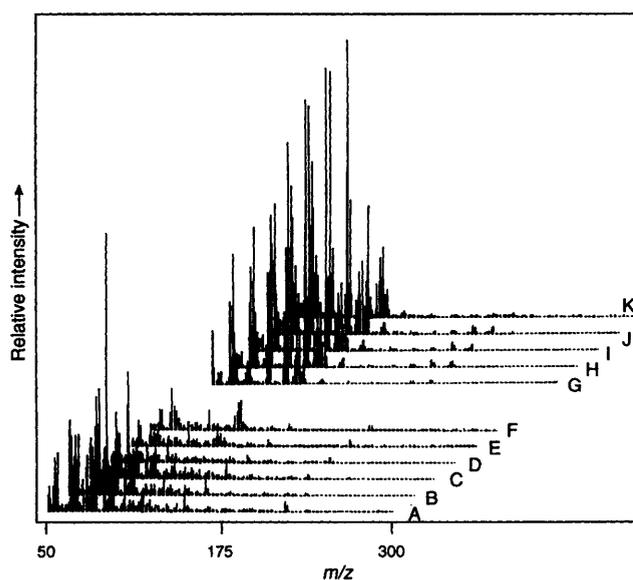


Fig. 3 Mass spectra of PS recorded at various temperatures: A, 50; B, 60; C, 70; D, 80; E, 90; F, 100; G, 200; H, 210; I, 220; J, 230; and K, 240 °C

All the polymers under investigation yield mainly their corresponding monomers, similar to the situation with indirect pyrolysis. However, peaks corresponding to dimer ions (at  $m/z$  208 for PS,  $m/z$  236 for PAMS, and  $m/z$  235 for PPMS) are also detectable. Other high mass fragments around  $m/z$  131, 167, 178, 194, 221, and 250 can also be detected. In all three instances, the intensities of the higher mass peaks are less than 5% of the monomer ion intensities. However, it must be remembered that the peaks observed in the mass spectra cannot be directly attributed to sample-degradation products, as further fragmentation by electron impact occurs in the ion source. It is also known that under vacuum or in an oxygen atmosphere, thermal degradation of PS at elevated temperatures (below 300 °C) is initiated by random scission of the main

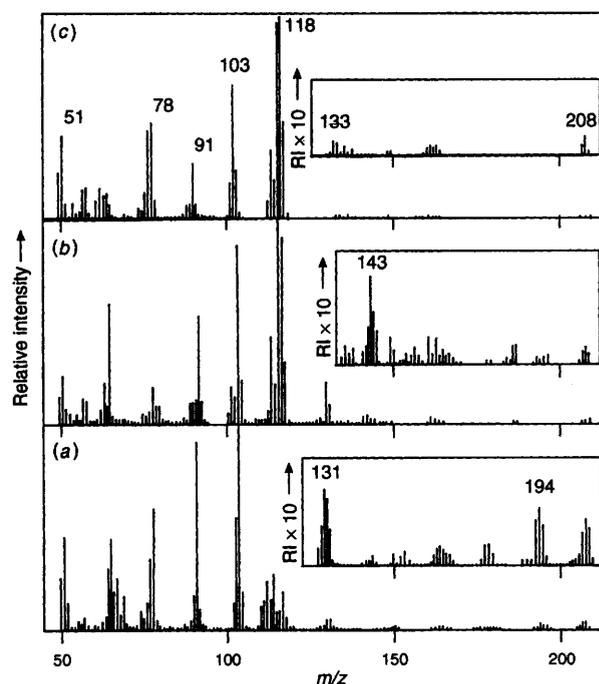


Fig. 4 Direct-pyrolysis mass spectra of (a) PS, (b) PPMS, and (c) PAMS at their maximum decomposition temperatures (230, 217 and 197 °C, respectively). RI, Relative intensity

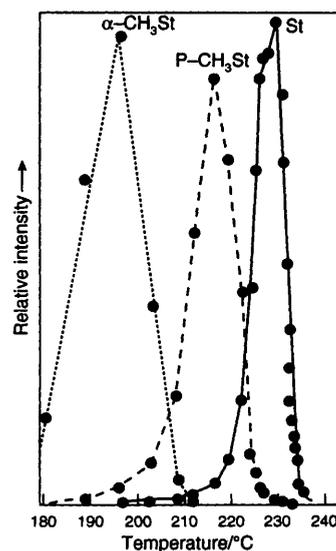


Fig. 5 Ion-temperature profiles of the monomers corresponding to PS (St), PPMS (P-CH<sub>3</sub>St), and PAMS ( $\alpha$ -CH<sub>3</sub>St)

chain, without evolution of low relative molecular mass volatile products to give primary and secondary macroradicals, which depolymerize to the monomer.<sup>15-17,24</sup> Hence a radical depolymerization mechanism, initiated by random scission of the main chain followed by unzipping reactions, can be assigned for the thermal degradation of these polymers under direct-pyrolysis conditions, in agreement with other findings.<sup>14-20</sup> Owing to similarities between the ions that would be produced from all possible products, complete identification of the decomposition products is not possible.

Some information concerning the thermal stability of the polymers can also be inferred from the data. The ion-temperature profiles of the monomers corresponding to the polymers studied exhibit different maxima for each polymer (Fig. 5). Accordingly, the thermal stability of these polymers is seen to follow the trend, PS > PPMS > PAMS, as expected.

### Conclusions

It has been shown that of the three systems studied direct-pyrolysis MS provides the most reliable information for structural analysis and/or the determination of the degradation mechanism. Only stable degradation products can be detected by evolved-gas analysis. Mass spectrometric techniques yield more complicated data than evolved-gas analysis by IR, however, the much lower sensitivity of IR spectrometers must be taken into account.

We acknowledge the financial support provided by METU through research grant No. AFP-92-01-03-01, and one of us (M. M. F.) acknowledges the TUBITAK fellowship.

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Paper 3/04193J

Received July 19, 1993

Accepted September 7, 1993