

Instrument: Pegasus® BTX

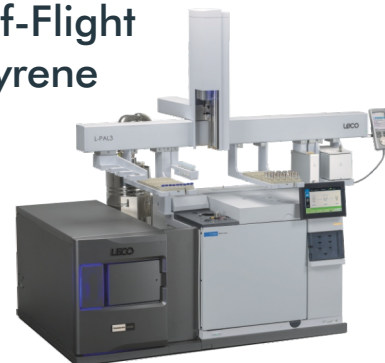
The Utility of Pyrolysis–Gas Chromatography–Time-of-Flight Mass Spectrometry for the Characterization of Polystyrene

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Introduction

Pyrolysis–gas chromatography–time-of-flight mass spectrometry (Py-GC-TOFMS) is a powerful technique for characterizing polymers that are difficult to analyze directly due to their high molecular weight or limited volatility. By thermally decomposing the polymer into smaller, volatile fragments, Py-GC-TOFMS generates reproducible chromatographic “fingerprints” that enable identification, quality control, and detection of additives or contaminants. For example, polystyrene produces characteristic pyrolysis products such as styrene monomer, dimer, and trimer, along with alkyl-substituted styrenes, providing a highly diagnostic pattern for material confirmation or differentiation among grades. Similarly, polymers such as polyethylene, PVC, or polyesters yield distinctive fragment distributions that reflect their backbone structure and substituents. Because it requires minimal sample preparation and provides rapid, structure-specific information, Py-GC-TOFMS is widely applied in plastics analysis, forensic materials testing, and degradation studies. In this application note, we used Py-GC-TOFMS for the analysis of polystyrene (Figure 1).



Polystyrene

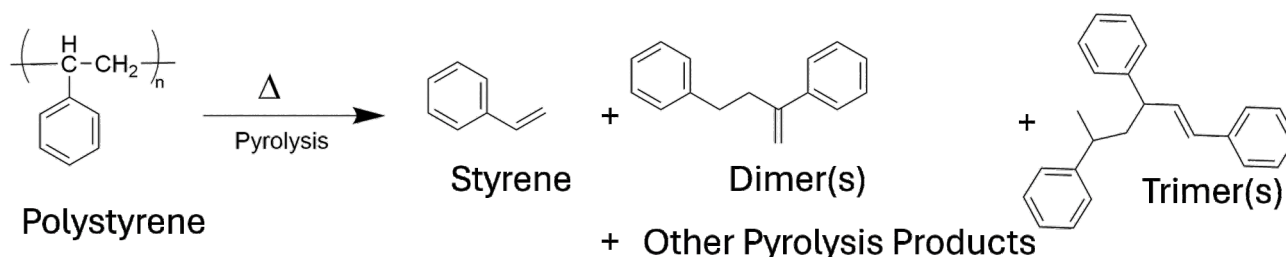


Figure 1. Polystyrene products (top). Pyrolysis products of polystyrene (bottom).

Experimental

Pyrolysis was performed using a Pegasus BTX GC-TOFMS instrument equipped with a GL Sciences Optic-4 inlet.¹ A 2 μ L aliquot of a polystyrene standard solution (2.5 mg in 0.5 mL dichloromethane)² was pipetted into a 30 mL microtube and then transferred to a quartz liner for analysis. Data was acquired using the instrumental parameters listed in Table 1. GC-TOFMS data were processed using ChromaTOF[®] with automated peak finding and deconvolution for untargeted workflows, incorporating spectral similarity searches against large reference libraries and mass delta (ΔM) calculations for molecular ion evaluation.

Table 1. Instruments Parameters

Gas Chromatograph	Agilent 8890 with GL Sciences Optic-4 Inlet
Inlet	Pyrolysis, 45 °C to 600 °C at 60 °C/s
Carrier Gas	He @ 1.0 mL/min, Constant Flow
Primary Column	Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 μ m
Temperature Program	45 °C (1.5 min) ramp to 300 °C at 10 °C/min (Hold 13 min)
Transfer Line Temperature	320 °C
Mass Spectrometer	LECO Pegasus BTX
Source Temperature	250 °C
Ionization	El
Mass Range (m/z)	35-1000
Acquisition Rate	10 sps

Results and Discussion

Polystyrene undergoes thermal depolymerization during pyrolysis, generating a characteristic suite of volatile and semi-volatile products that provide a highly reproducible analytical fingerprint for techniques such as Py-GC-MS. The major and minor pyrolysis products have been extensively documented and are routinely used to confirm the presence of polystyrene in complex matrices. The primary pyrolysis products include styrene, styrene dimers ($C_{16}H_{16}$), and styrene trimers ($C_{24}H_{24}$). Secondary products consist of alkylated styrenes (e.g., α -methylstyrene), vinyl toluene isomers, and additional aromatic species such as toluene and ethylbenzene (Table 2).

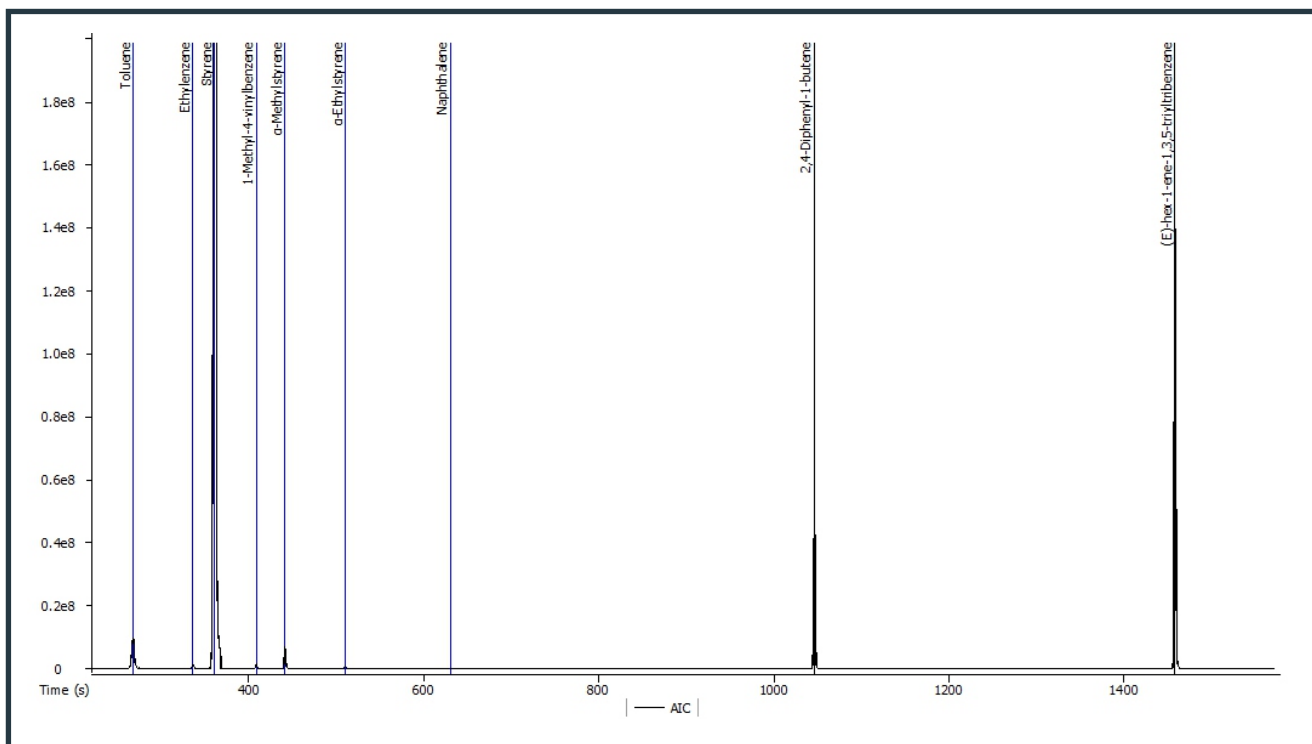


Figure 2. Analytical ion chromatogram (AIC) showing select primary pyrolytic markers for polystyrene.

Table 2. Primary and secondary polystyrene pyrolysis products.

Name (Primary Marker)	Formula	R.T. (s)
Styrene	C ₈ H ₈	360
2,4-Diphenyl-1-butene (Dimer)	C ₁₆ H ₁₆	1046
(E)-hex-1-ene-1,3,5-triyltribenzene (Trimer)	C ₂₄ H ₂₄	1459
Name (Secondary Marker)	Formula	R.T. (s)
Toluene	C ₇ H ₈	268
Ethylbenzene	C ₈ H ₁₀	336
4-Vinyltoluene	C ₉ H ₁₀	408
α-Methylstyrene	C ₉ H ₁₀	441
α-Ethylstyrene	C ₁₀ H ₁₂	510
Naphthalene	C ₁₀ H ₈	630

Peak True (deconvoluted) spectra for styrene and 4-vinyl toluene (1-methyl-4-vinylbenzene) are shown in Figure 3. The spectral similarity scores for styrene and 4-vinyltoluene were 959 and 920, respectively. The corresponding molecular ion mass delta values were 0.03 Da for both markers.

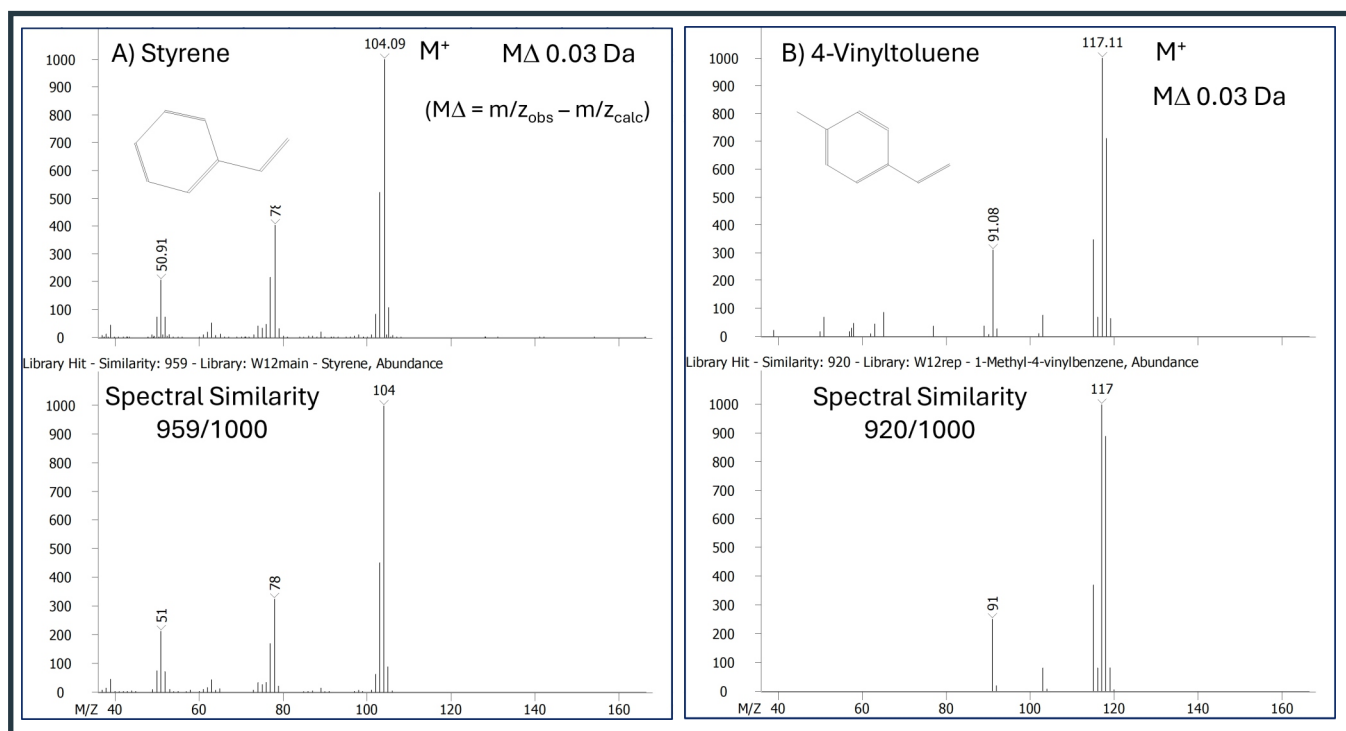


Figure 3. A) Peak True Deconvoluted (top) and library (bottom) mass spectra for styrene. B) Peak True Deconvoluted (top) and library (bottom) mass spectra for 4-Vinyltoluene.

Conclusion

The spectral data generated through pyrolysis provides distinct molecular markers that can be effectively analyzed using the LECO Pegasus BTX GC-TOFMS for the characterization of polymers such as polystyrene. High-confidence annotation of these markers is achieved through the combined use of spectral-similarity matching against established, commercial mass spectral libraries and mass-delta calculations for molecular-ion confirmation.

References

- ¹GL Sciences Optic-4: <https://www.glsciences.eu/html/intro-optic-4.html>
- ²Frontier Lab Polystyrene Standard: <https://store.lqa.com/product/polystyrene-sample-for-pyrolyzer-performance-evaluation/>