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AppNote 14/2012

Thermal Gravimetric Analysis/Mass Spectrometry Simulation using the GERSTEL Automated Pyrolyzer

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KEYWORDS

Pyrolysis, thermogravimetric analysis, gas chromatography, mass spectrometry, evolved gas analysis

ABSTRACT

This study shows the use of the GERSTEL MPS 2/TDU/CIS with pyrolysis module for generating simulated thermal gravimetric-mass spectrometry data (TGA-MS) of polymer samples. This mode of operation is also referred to as evolved gas analysis (EGA).

For EGA analysis, a short piece of uncoated capillary is attached from the GC inlet to the mass spectrometer. A relatively slow temperature ramp is run similar to that used for actual TGA analysis. The total ion chromatogram can be plotted as a function of temperature to produce simulated TGA-MS data. The mass spectral data is used to identify degradation products at various temperatures.

Several types of polymers are examined in this study. Simulated TGA-MS data is compared with actual TGA data.

INTRODUCTION

The GERSTEL MultiPurpose Sampler (MPS) in combination with the GERSTEL Thermal Desorption Unit (TDU) and Cooled Injection System (CIS 4), PTV-type inlet, provides the user with a multitude of analytical options to utilize for sample analysis. A pyrolysis insert, GERSTEL PYRO, is also available for the TDU. Combined with the MPS, the TDU PYRO offers efficient automation (up to 2 x 98 samples) and a variety of pyrolysis modes including standard pulsed, sequential, and fractionated pyrolysis. The CIS 4 can be used to cryofocus analytes in the inlet or as a hot split interface for direct transfer to the column.

This study describes the use of the GERSTEL MPS with CIS, TDU, and PYRO module for simulation of thermogravimetric (TGA)/MS analysis. The EGA mode relies on a relatively slow temperature ramp for the TDU and Pyrolysis units, and a short piece of deactivated fused silica to connect the CIS to the mass spectrometer.

The thermogravimetric data was collected on a TA Instruments Model Q5000 thermogravimetric analyzer.

Several polymer types were analyzed in order to demonstrate this mode with the TDU PYRO unit.

EXPERIMENTAL

Instrumentation. Analyses were performed on a 7890 equipped with a 5975C Inert XL MSD with triple axis detector (Agilent Technologies), PTV inlet (CIS 4, GERSTEL), Thermal desorber (TDU, GERSTEL), TDUPyrolysis Insert (GERSTEL) and MPS robotic sampler (GERSTEL).

Sample Preparation - Pyrolysis. Approximately one to three milligrams of sample were weighed into a short, quartz test-tube shaped pyrolysis vessel. The quartz tubes were connected to pyrolysis adapters and placed into a 98 position pyrolysis tray in the MPS.

Sample Preparation - TGA Analysis. Approximately 20 mg of sample was placed in the TGA pan.

Analysis conditions.

Pyrolysis:	Lead Time 0.10 min Follow up Time 0.50 min Initial Time 1.5 min 80°C (1.0 min), 0.17°C/s, 600°C (1.0 min)
TDU:	splitless 70°C (1 min); 10°C/min; 350°C (25 min)
PTV:	solvent vent (50 mL/min) -120°C; 12°C/min; 280°C (3 min)
Column:	1 m Deactivated Fused Silica (Restek) $d_i = 0.1$ mm
Pneumatics:	He, constant flow = 1 mL/min $p_i = 7.1$ psi
Oven:	250°C (isothermal)
TGA:	50°C, 20°C/min, 700°C, 100°C/min, 1000°C

RESULTS AND DISCUSSION

Four polymer samples were used to demonstrate the TDU PYRO unit used in EGA mode. Two Kraton® polymers (styrenic block copolymers consisting of polystyrene and rubber blocks), a urethane elastomer, and an acrylonitrile-styrene-acrylate co-polymer.

Figure 1 shows the TGA and first derivative curves for a Kraton® D1161 sample. The curve shows rapid weight loss starting at 325°C and continuing up to 400°C. A second transition is seen in the first derivative curve from 415°C to 470°C. Spikes seen in the TGA curves from 370-400°C, are caused by balance being perturbed by the rapid weight loss of the sample during this time frame.

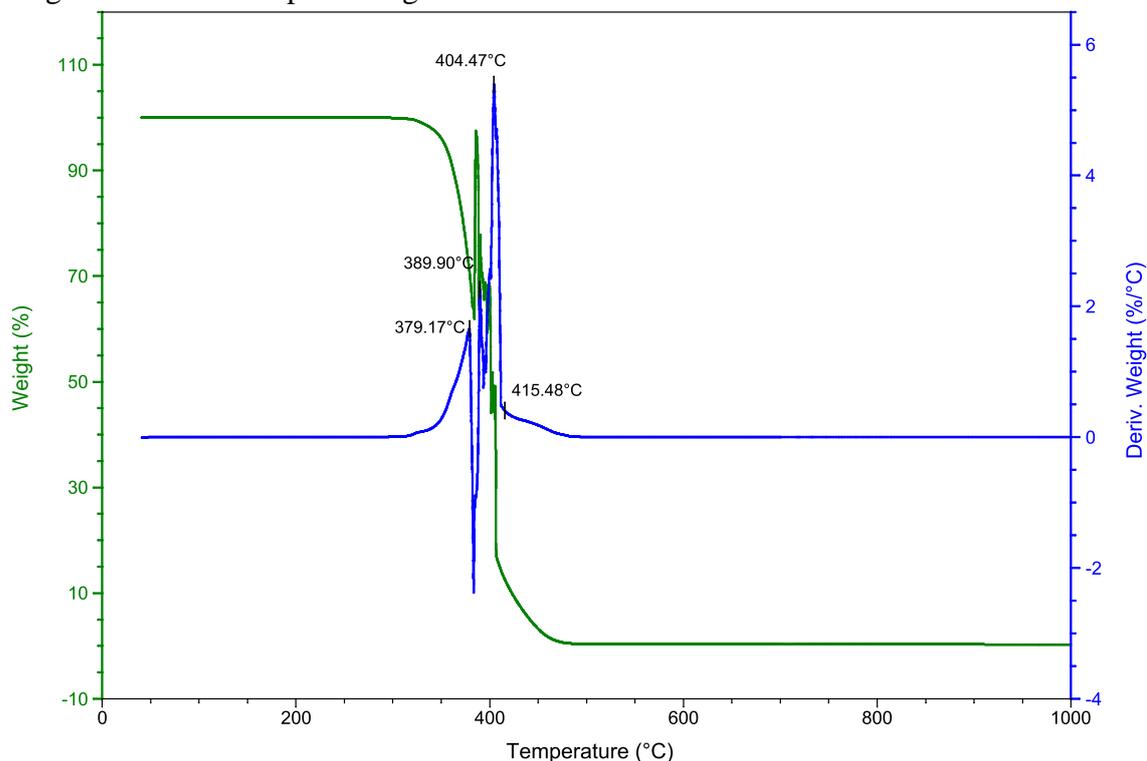


Figure 1. TGA and first derivative curve for Kraton® D1161.

Figure 2 shows the TGA-MS data collected using the TGA PYRO unit. The shape is similar to that seen in the first derivative TGA curve. The spectral information obtained shows that the major, first, transition is mainly from loss of the natural rubber component of the polymer. The second smaller transition, 415-500°C, is mainly from loss of the polystyrene.

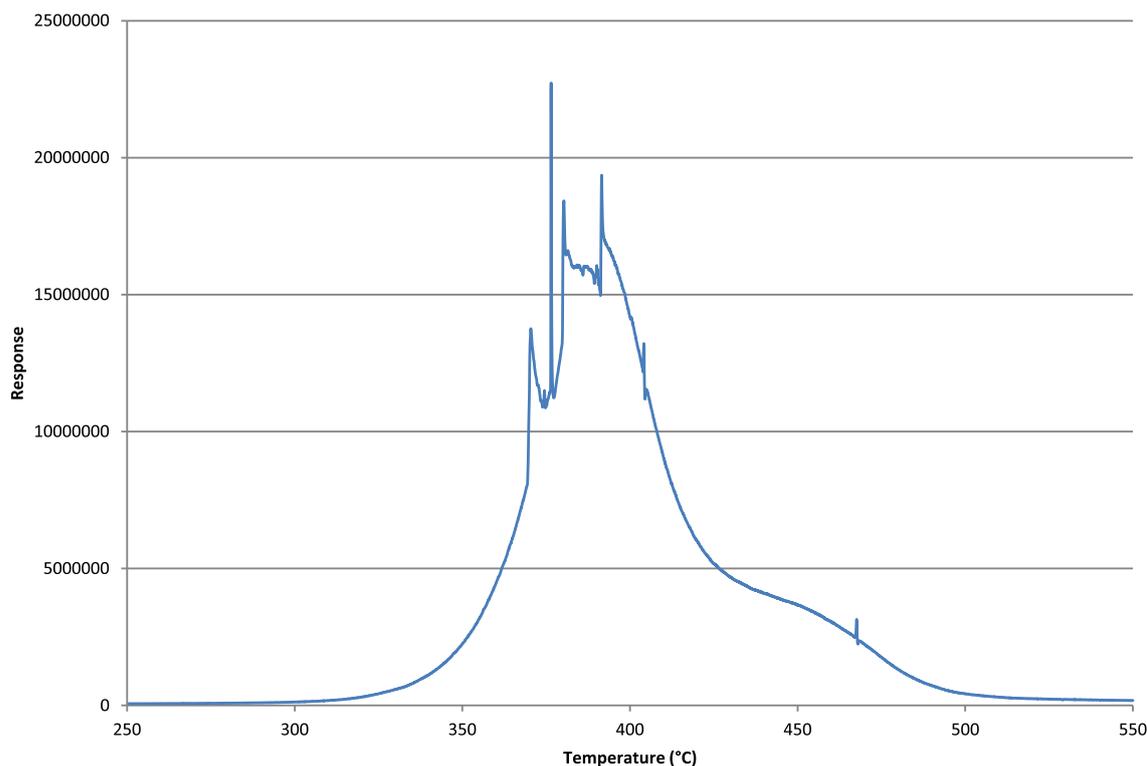


Figure 2. TGA-MS data for Kraton® D1161.

Figure 3 shows the TGA and first derivative curves for a Kraton® D1111 sample. The curve shows rapid weight loss starting at 325°C and continuing up to 387°C. A second transition is seen in the first derivative curve at 434°C. In comparison to the other Kraton® sample (Figure 1), the main transition peaks at a lower temperature and the second transition is a larger percentage of the overall weight.

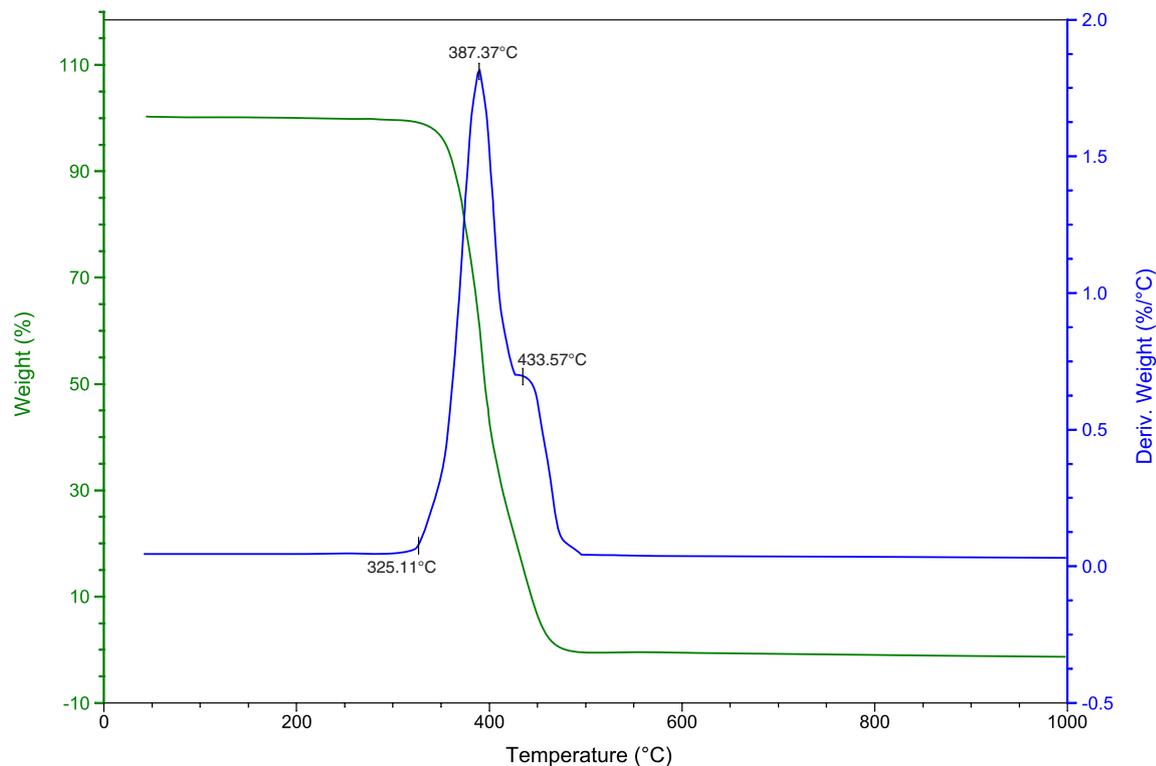


Figure 3. TGA and first derivative curve for Kraton® D1111.

The TGA-MS data, Figure 4, shows that the decomposition products for the two transitions are similar. The spectral information obtained shows that the major, first, transition is mainly from loss of the natural rubber component of the polymer. The second smaller transition is mainly from loss of the polystyrene.

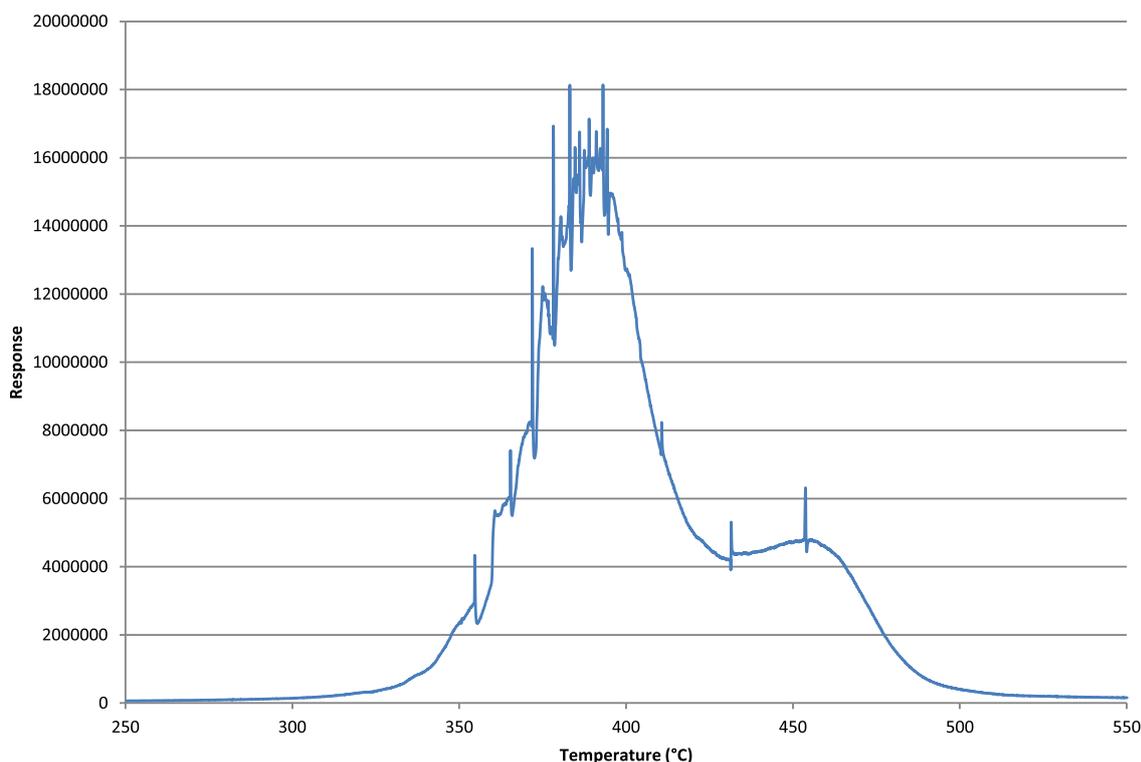


Figure 4. TGA-MS data for Kraton® D1111.

Figure 5 shows the TGA and first derivative curves for a urethane elastomer. The first derivative curve shows two maxima at 389°C and 432°C. The TGA-MS total ion chromatogram (not shown) shows the same two peaks.

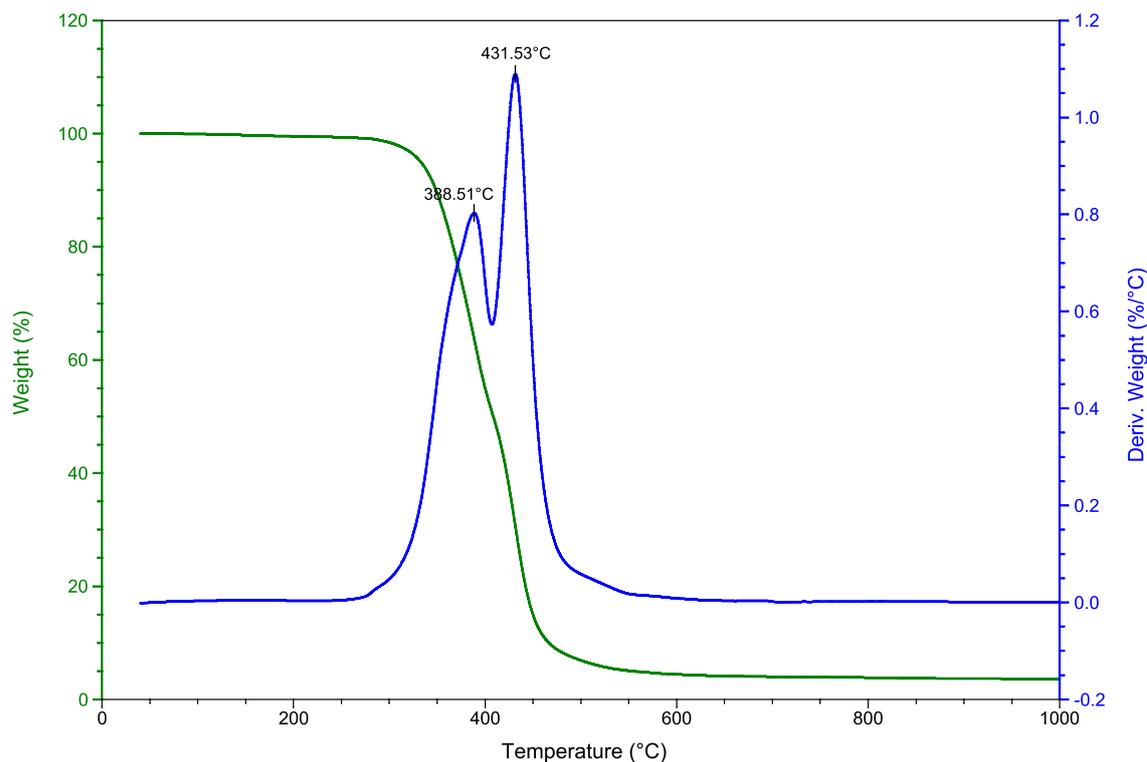


Figure 5. TGA and first derivative curve for a urethane elastomer.

Figure 6 shows Extracted Ion Chromatograms (EICs) for the urethane elastomer. The EICs show that the initial loss is due to loss of the monomer, diphenylmethane diisocyanate ((MDI), $m/z=250$) and the linking agent butanediol ($m/z=42$). The second maximum is caused by loss of MDI-butanediol ($m/z=129$).

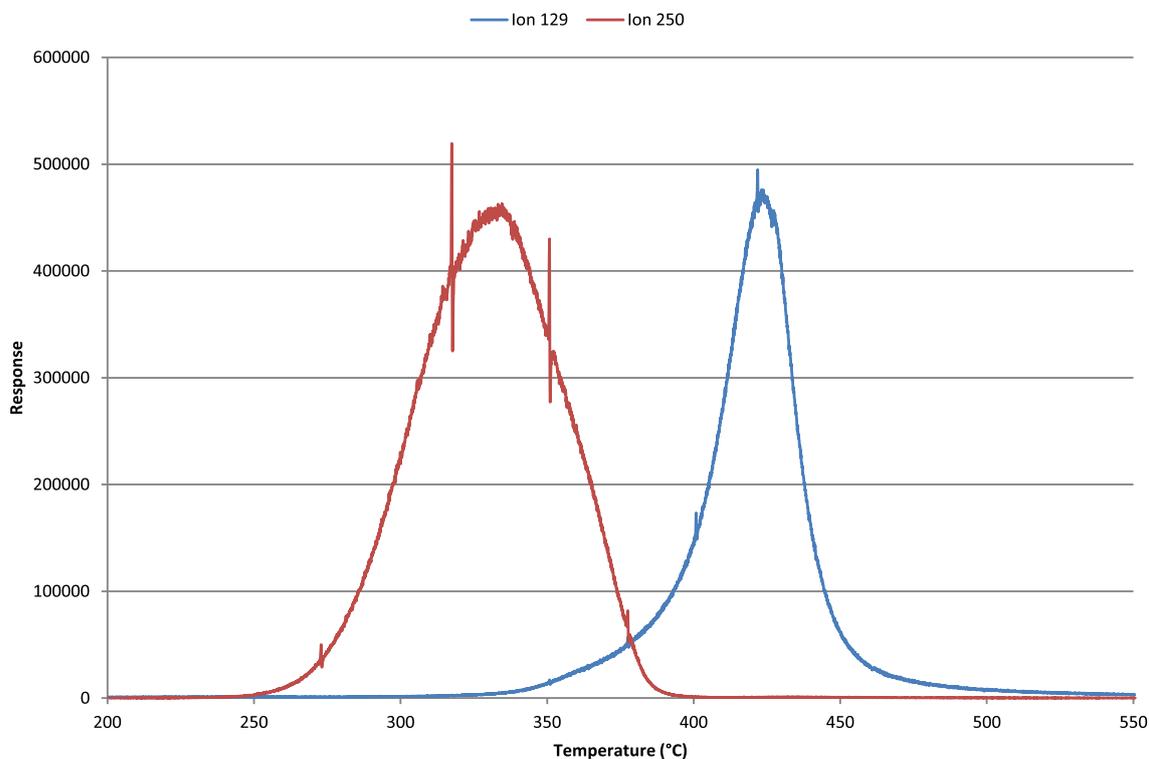


Figure 6. TGA-MS EICs for a urethane elastomer.

Figure 7 shows the TGA and first derivative curves for an acrylonitrile-styrene-acrylate copolymer. The first derivative curve shows a single maximum at 442°C. The TGA-MS total ion chromatogram (not shown) also shows a single peak.

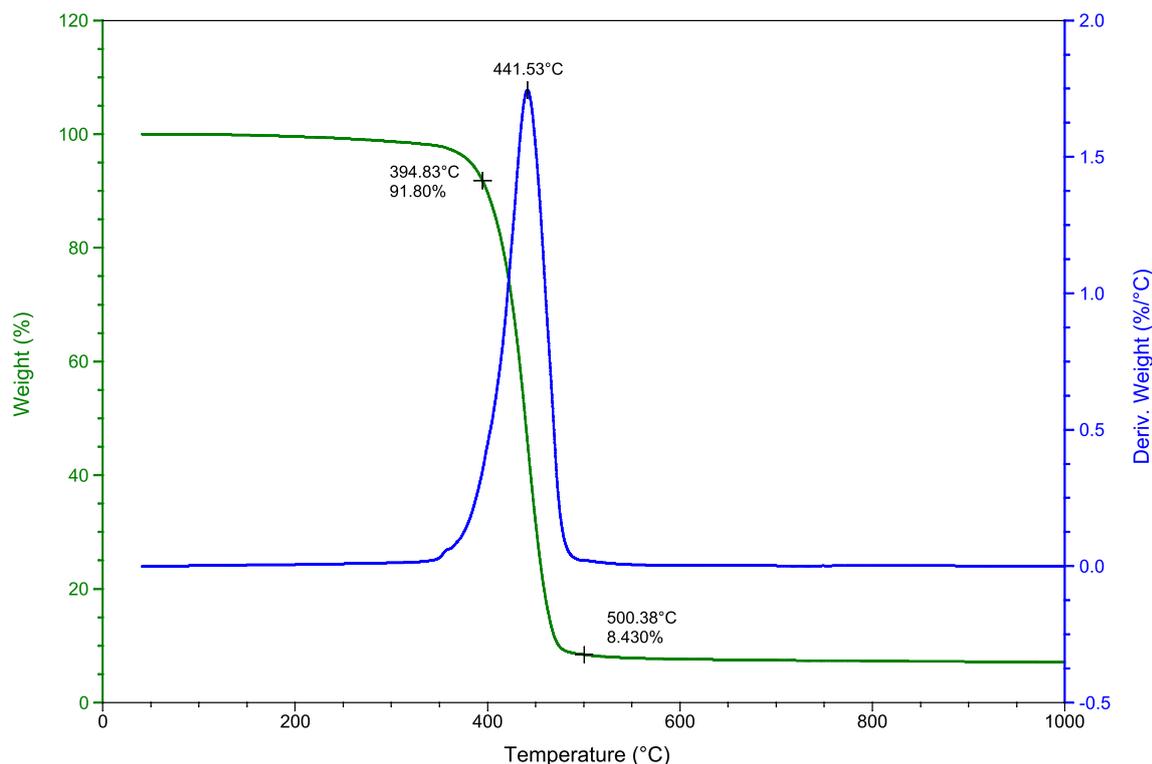


Figure 7. TGA and first derivative curve for an acrylonitrile-styrene-acrylate copolymer.

When specific ion chromatograms are extracted from the TIC, as shown in figure 8, a clearer picture of the polymer degradation develops. The EICs show that around 325°C, the ions for styrene ($m/z=104$) and butanol ($m/z=56$) appear. The butanol loss reaches a maximum at 400°C, and ends around 425°C. The styrene loss reaches a maximum around 430°C along with the ion for the acrylonitrile monomer ($m/z=53$) and the ion for butylmethacrylate ($m/z=73$).

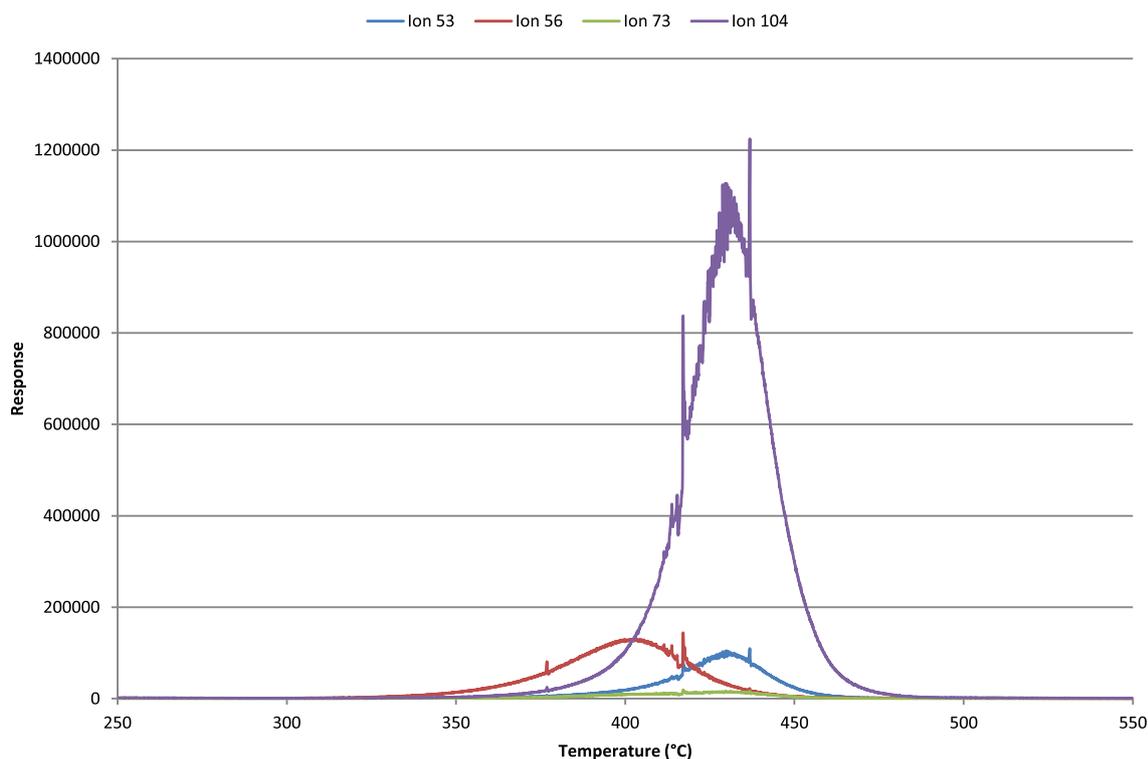
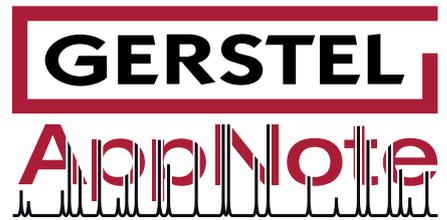


Figure 8. TGA-MS EICs for an acrylonitrile-styrene-acrylate copolymer.

CONCLUSIONS

The GERSTEL MPS/PYRO/TDU/CIS system can be used for evolved gas analysis, producing data similar to thermal gravimetric analysis-mass spectrometry. This type of data in conjunction with standard TGA analysis can provide useful information regarding the thermal stability and degradation pathway for polymers as well as subtle differences between polymers of similar composition. This type of data can also be used to determine appropriate polymer pyrolysis temperatures.



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