

TOF-SIMS Parallel Imaging MS/MS of PET Crystalline Oligomers

Introduction

TOF-SIMS has been used for a quarter century for identifying chemistries present on the outermost surfaces of samples. Recent advances in cluster ion beam technology, e.g. Au and Bi cluster LMIG, C_{60} and Ar-GCIB, has further advanced the technique by increasing secondary ion yields for high mass fragments (>200 Da), thus, providing even better chemical speciation. However, with the increased production of high mass fragments comes the difficulty of identifying the composition or structure of these fragments. Due to the large number of elemental combinations possible to produce a given nominal mass, even milli-mass unit mass accuracy is often insufficient to positively identify the elemental composition of a high mass peak. To overcome this obstacle, Physical Electronics (PHI) is in the process of developing a TOF-SIMS tandem mass spectrometry instrument (MS/MS) [1] which allows secondary ions of choice (precursor ions) to be selected for further study and identification (See Figure 1).

Experimental

In a traditional TOF-SIMS analysis, the secondary ions generated from the sample surface are extracted and mass (time-of-flight) separated as they traverse through the spectrometer. A pulse counting detector is used to count these secondary ions (MS1 detector), and a full mass spectrum is collected for each image pixel. In the MS/MS mode, the precursor ion of choice is deflected into a high energy collision induced dissociation (CID) cell. In the CID cell, the precursor ions collide with neutral gas molecules (e.g. Ar) which results in fragmentation of the precursor ions. The resulting fragment ions are mass separated in a linear TOF and counted at a second pulse counting detector (MS2 detector) while the rest of the ions are collected as usual with the MS1 detector. Again, with the MS2 detector, a full mass spectrum is collected for each image pixel. The resulting MS/MS fragmentation spectrum is used to identify the composition of the precursor ion by either identification of the fragmented ions or, potentially, comparison to spectra contained in on-line databases. Operating the TOF-SIMS in the MS/MS mode can also improve the sensitivity for species in which the peak of interest has mass interferences with other compounds. By detection of a unique MS/MS fragment ion originating from the species of interest, the limit of detection can be greatly improved.

To exemplify the use of high spatial resolution parallel imaging MS/MS on a polymer surface, a piece of polyethylene terephthalate (PET) was heated to 150-170°C for two hours and analyzed using a Bi_3^+ primary ion source. It is known that during heat-treatment of PET very small thin crystals can be formed on the sample surfaces and are thought to be comprised of cyclic ethylene terephthalate trimer [2]. Analysis of these crystals with TOF-SIMS produces a characteristic fragmentation pattern with a strong peak at 577 m/z in the positive ion spectrum. The 577 m/z peak is believed to have a composition of $[3M+H]^+$ ($C_{30}H_{25}O_{12}^+$), where M is the ethylene terephthalate repeat unit of the polymer.

Results

Figure 2 shows a set of 40 μm field-of-view secondary ion images for several peaks identified in the positive ion mass spectrum of the crystal-laden heat-treated PET surface. The total ion image, as well as each of the organic fragment images, highlight the crystals, while the Na and K contaminants are localized on the PET substrate.

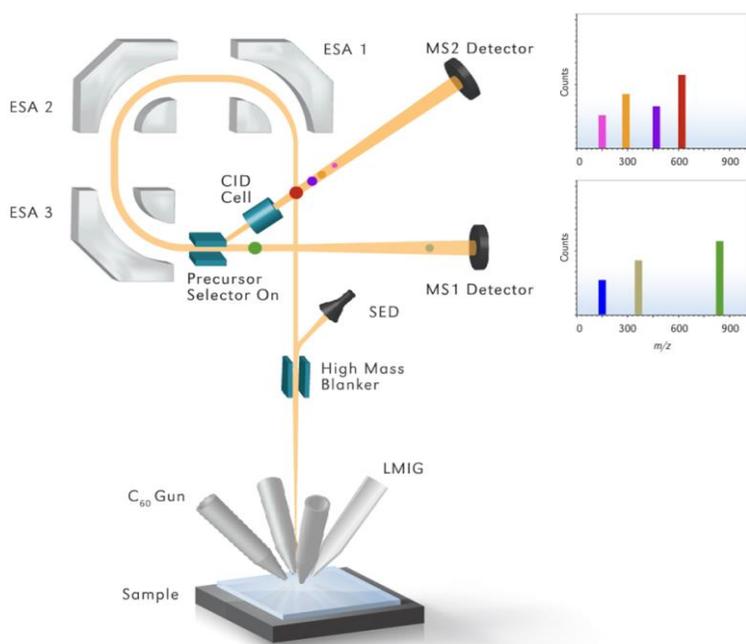


Figure 1. Diagram of Parallel Imaging MS/MS Instrument

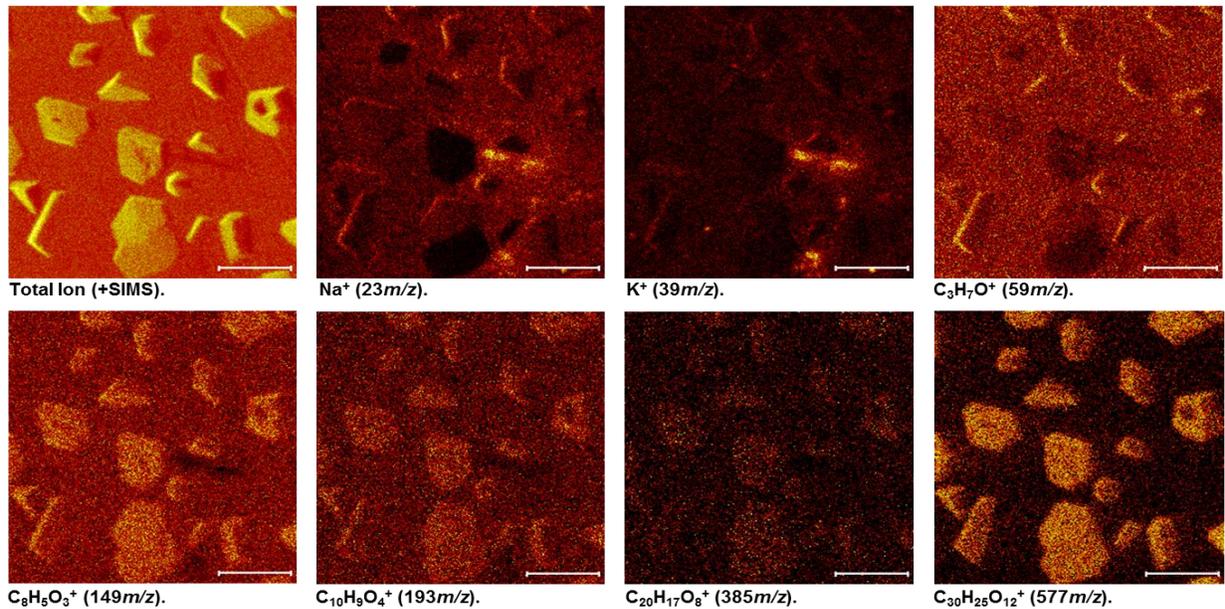


Figure 2. TOF-SIMS secondary ion images (MS^1) obtained from the surface of a heat-treated sample of PET. Positive secondary ion images, 40 μm field-of-view, 10 μm scale bar, 256 x 256 pixels, 6nA Bi_3^+ .

To confirm the chemical composition of the 577 m/z peak, this mass was selected as the precursor ion and deflected into the CID cell. The mass spectra obtained at the MS^1 detector, with and without the precursor selector in operation, are shown in Figure 3. Note that the 577 m/z peak is totally absent in the lower spectrum as it is efficiently deflected into the CID cell.

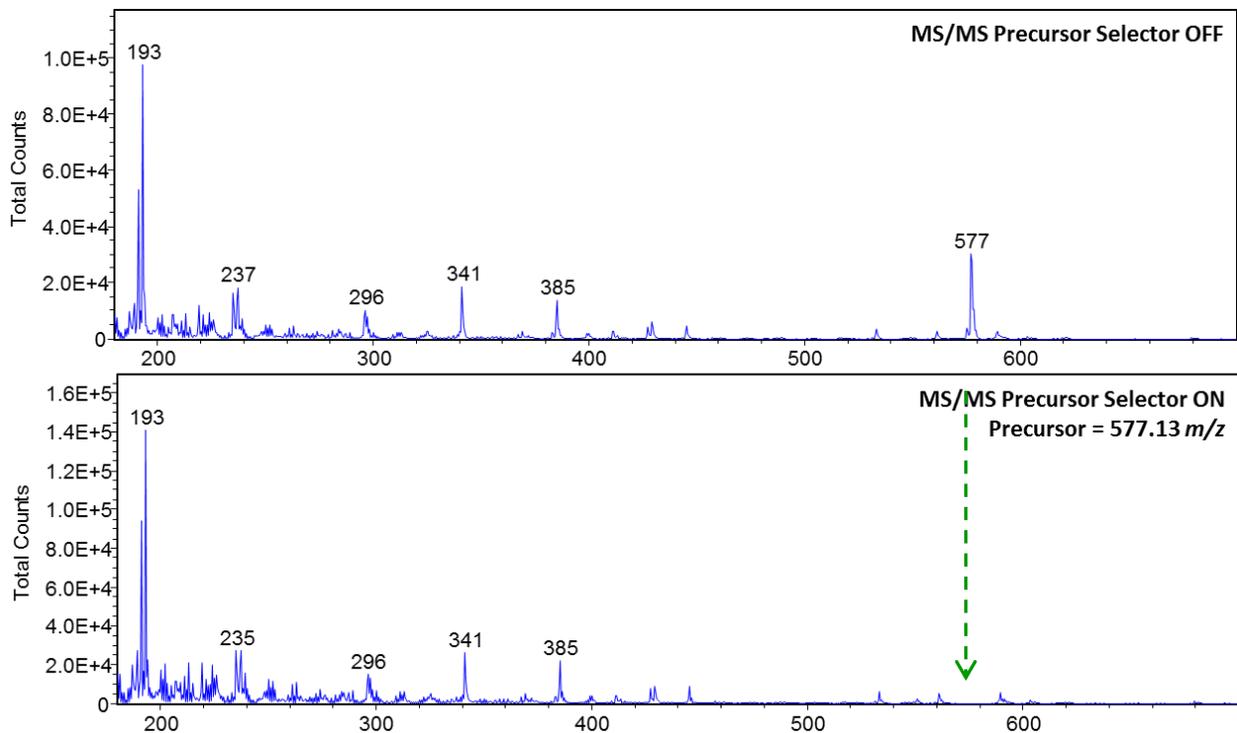


Figure 3. MS^1 spectra. Positive secondary ion mass spectra obtained at MS^1 with the precursor selector off (upper spectrum), and with the precursor selector set to mass 577 (lower graph).

Figure 4 shows the mass spectrum of the ions exiting the CID cell and collected at the MS2 detector. The top spectrum is displayed in mass-to-charge ratio (m/z) while the bottom spectrum shows the mass loss of each ion relative to the precursor ion. A number of peaks are observed in the MS² spectrum, but the spectrum is relatively simple as the chemical background has been removed. After making the obvious peak assignments, usually beginning at lower mass, the spectral mass calibration is updated and additional peak assignments are made. The composition assignments for the various masses observed in the MS² spectrum are shown in Figure 5. Peaks for both $[M+H]^+$ and $[2M+H]^+$ are identified, and the 577 m/z peak is indeed confirmed to be $[3M+H]^+$. Note that the instrument is a parallel imaging system [3], thus allowing secondary ion imaging to be performed simultaneously in a single acquisition.

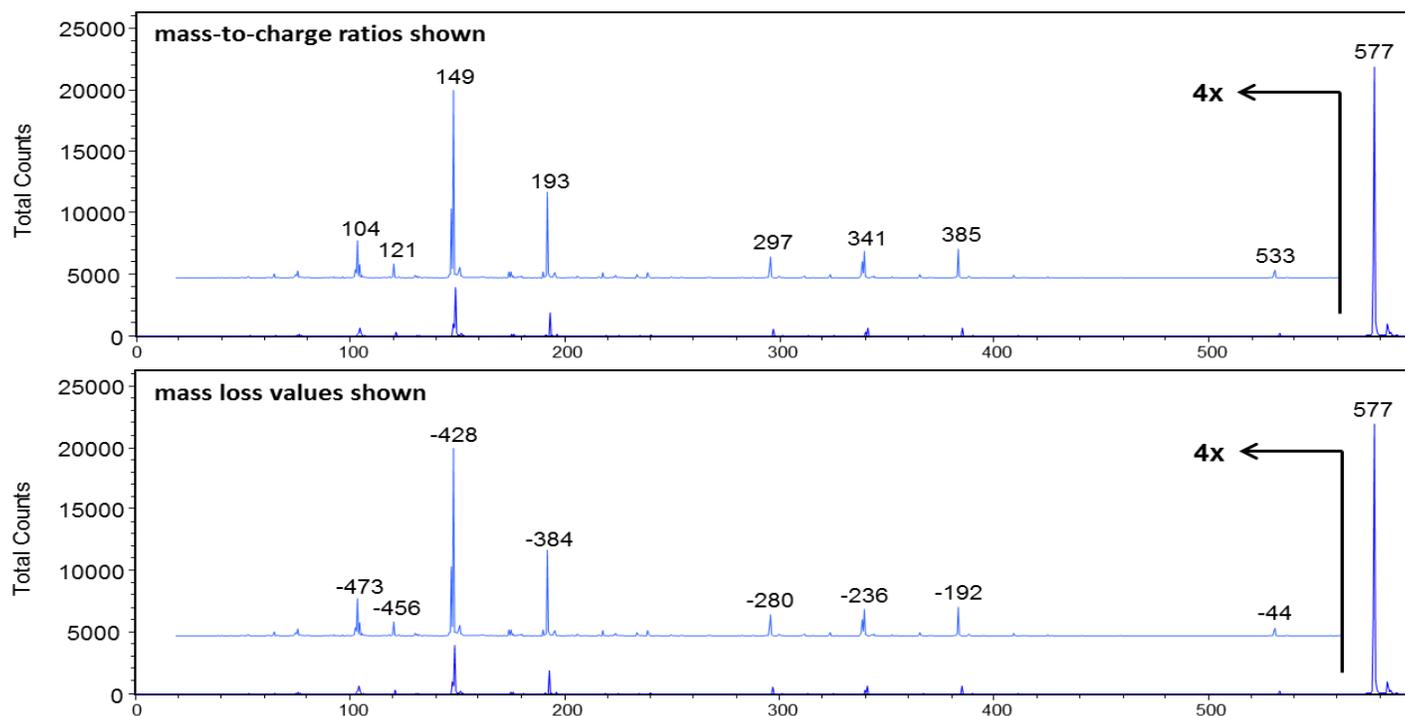


Figure 4. MS² spectrum. Positive secondary ion mass spectrum of ions exiting the CID cell (precursor selector set to 577 m/z) and collected at the MS2 detector. The top spectrum has the peaks labeled in daltons (m/z) while the bottom spectrum shows the mass loss of each ion, relative to the precursor ion.

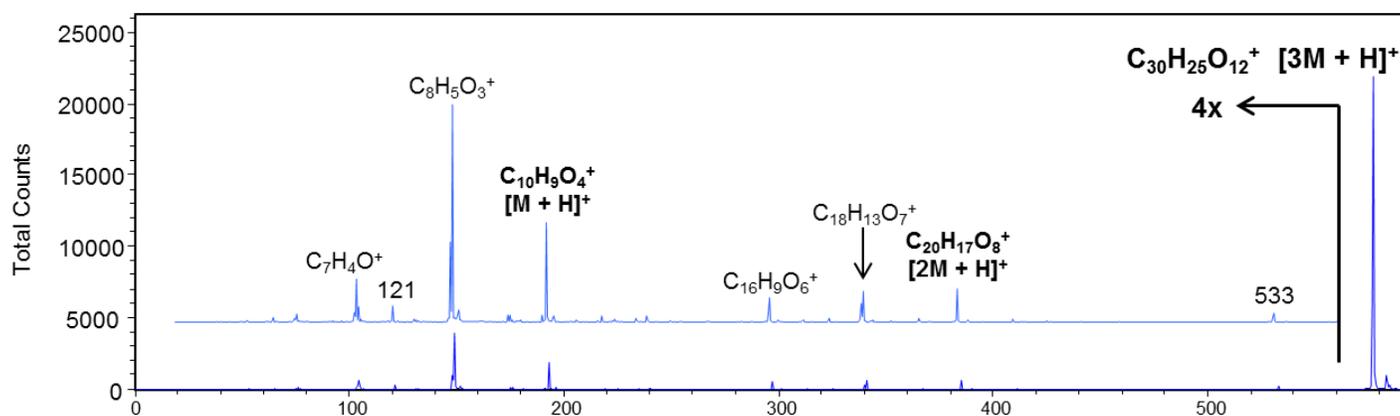


Figure 5. Composition assignments for the MS² spectrum obtained from CID fragmentation of the mass 577 precursor ion.

Figure 6 shows the total ion, 149 m/z and 104 m/z images from both MS¹ and MS², showing that identical areas are analyzed simultaneously with the two spectrometers. The MS² images, originating from the 577 m/z precursor peak, indicate that the PET trimer is localized to the crystals. Parallel Imaging MS/MS is especially important for organic materials that are susceptible to ion beam damage. The instrument is also capable of high lateral resolution. Line scans across the PET trimer crystals consistently showed lateral beam resolutions of less than 0.2 μm (80/20% measurement).

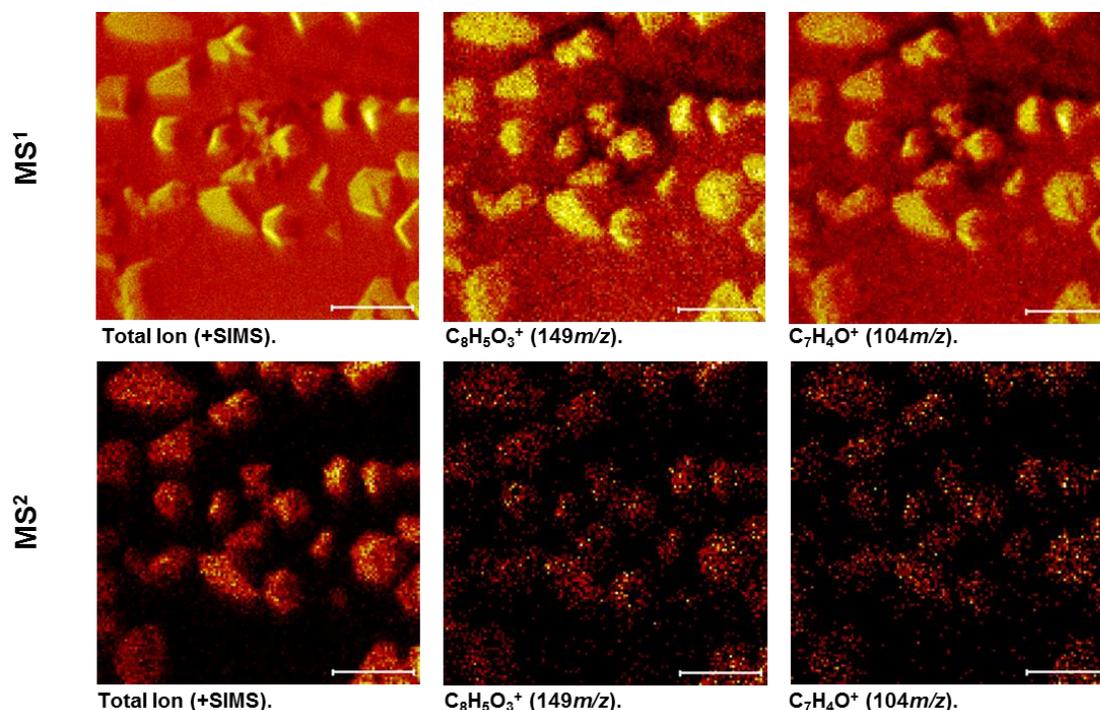


Figure 6. Parallel imaging of MS¹ and MS² peaks, showing that identical areas were analyzed at the two detectors and confirming that the PET trimer is localized to the crystals. Positive secondary ion images, 40 μm field-of-view, 10 μm scale bar, 256 x 256 pixels, 6nA Bi₃⁺.

Summary

Using the capability of a TOF-SIMS parallel imaging MS/MS instrument containing a high energy collision induced dissociation (CID) cell, it was possible to positively identify a high-mass fragment at 577 m/z , originating from the surface of heat-treated PET, as [3M+H]⁺ (C₃₀H₂₅O₁₂⁺). Without the advantages of MS/MS technology, the exact composition of high mass peaks is often left a mystery.

References

1. Bryan, S., Fisher, G., Hammond, J., Larson, P., (2015, September), *New Instrument with Parallel TOF-SIMS and MS/MS Data Acquisition*, Paper presented at the SIMS XX meeting, Seattle, WA.
2. Reichlmaier, S., Bryan, S.R., Briggs, D., (1995, June). Surface Trimer Crystallization on Poly (ethylene terephthalate) Studied by Time-of-Flight Secondary Ion Mass Spectrometry. *Journal of Vacuum Science & Technology A Vacuum Surfaces and Films*, 13 (3-13) pp. 1217 - 1223.
3. US patent granted (2015/0090874 A1); Japan and EU patents pending.



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