SpiralTOF-TOF

Synthetic Polymer Structure Analysis
Poly Methal Methacrylate (PMMA)

Introduction:
The JMS-S3000 "SpiralTOF™" is a MALDI-TOFMS that incorporates an innovative SpiralTOF ion optics system. This system is available with a TOF-TOF option that can acquire high-energy collision-induced dissociation (CID) product ion spectra for monoisotopically selected precursor ions.

In this work, we analyzed Poly Methyl Methacrylate (PMMA) shown in Fig. 1 by using the JMS-S3000 SpiralTOF with the TOF-TOF option. The resulting high-energy CID data was then processed using the Polymerix™ (Sierra Analytics, Inc., http://massspec.com/) analysis software.

Samples:
Polymer: PMMA
Matrix agent: 2,5-Dihydroxybenzoic acid (DHB)
Cationization agent: NaI

Results and Discussion:
The MALDI mass spectrum of PMMA and the product ion spectra for *m/z* 1525.8 (n=15, $[M+Na]^+$) and *m/z* 2326.2 (n=23, $[M+Na]^+$) are shown in Fig. 2. These product ion spectra show the full range of ions from *m/z* 23.0 for $[Na^+]$ to the precursor ion *m/z* 1027.7 and *m/z* 2326.2, respectively. Also worth noting, these product ions are all monoisotopic because the precursor ion was monoisotopically selected, which greatly simplified the resulting MS-MS spectrum.

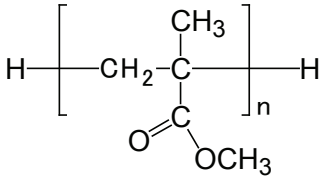

Figure 1. Structural formula of PMMA.

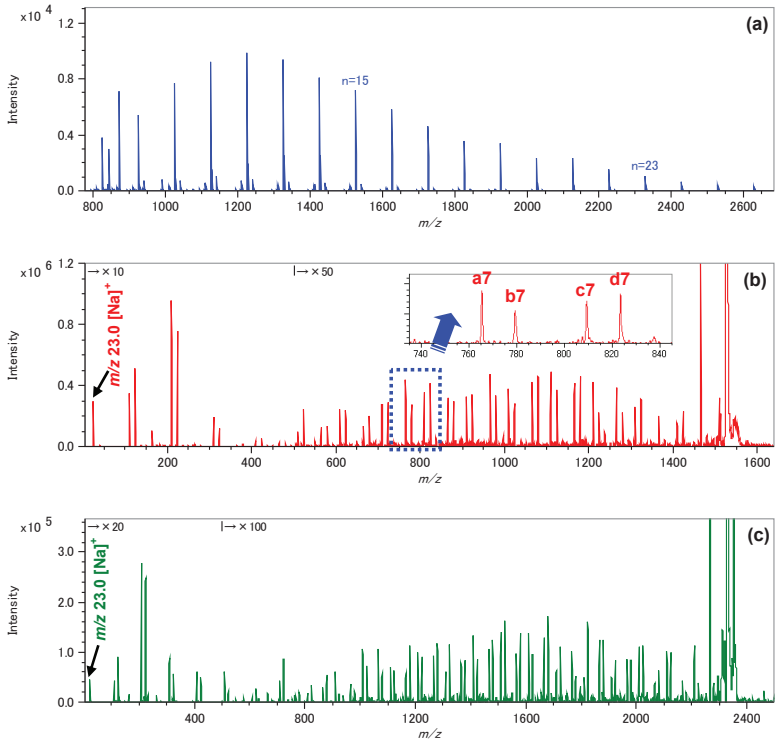

Figure 2. MALDI mass spectrum of a) PMMA, b) product ion spectrum of *m/z* 1525.8 (n=15, $[M+Na]^+$), and c) product ion spectrum of *m/z* 2326.2 (n=23, $[M+Na]^+$).

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The enlarged region (*m/z* 730-850) in Fig. 2b shows that there are at least four different product ions present that could result from the monomer repeat unit (100u, $C_5H_8O_2$). Therefore, this high-energy CID data for PMMA suggests that there are four possible fragmentation pathways.

Based on previously published work[1], we hypothesized that the structural formulas for these different product ion series were most likely the structures shown in Fig. 3a-d. These formulas were then used in the Polymerix™ software which resulted in the product ion series assignments shown in Fig. 5. These results supported our hypothesis for each structure and showed that the JMS-S3000 high-energy CID data fully represents the structural fragmentation expected for PMMA.

Conclusions:

Structural analysis of synthetic polymers such as PMMA can easily be done by using the JMS-S3000 TOF-TOF method (high-energy CID, monoisotopic precursor selection) with the Polymerix™ analysis software.

Reference:

(1) Liang Li, "MALDI Mass Spectrometry for Synthetic Polymer Analysis", John Wiley & Sons, Inc., United States of America (2010).

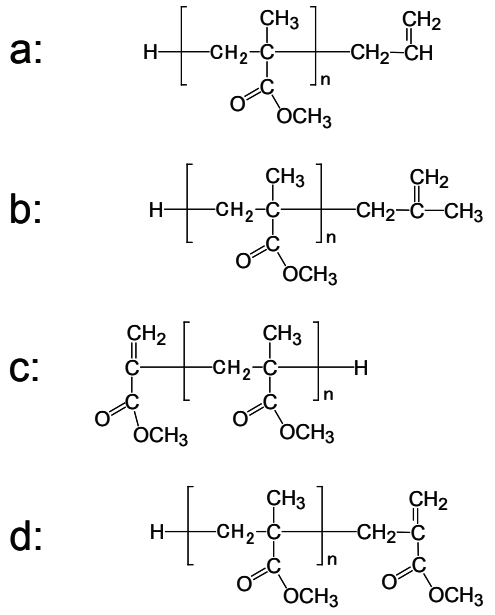

Figure 3. Structural formula of product ions series.

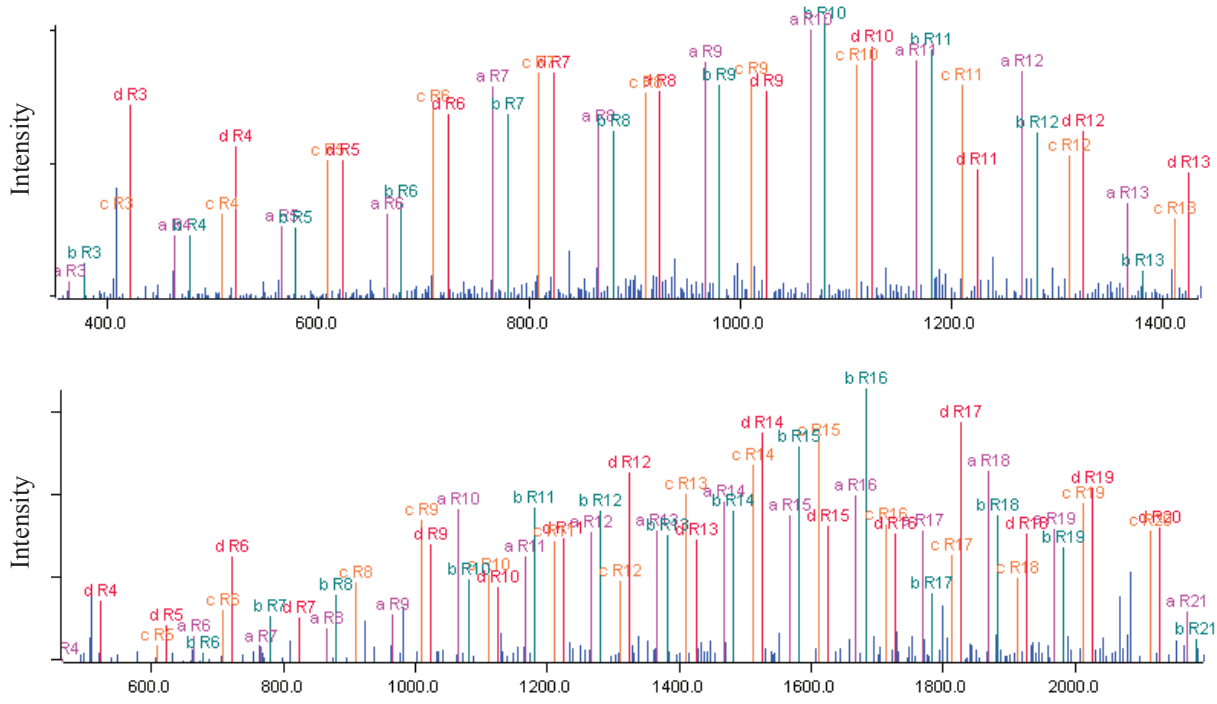

Figure 4. Polymerix analysis results of *m/z* 1525.8 (n=15, $[M+Na]^+$) (upper) and *m/z* 2326.2 (n=23, $[M+Na]^+$) (lower).

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