

SpiralTOF-TOF Synthetic Polymer Structure Analysis Poly Propylene Glycol (PPG)

Introduction:

The JMS-S3000 "SpiralTOFTM" is a MALDI-TOFMS that incorporates an innovative SpiralTOF ion optics system (Fig.1). The JMS-S3000 is available with a TOF-TOF option that can acquire high-energy collision-induced dissociation (CID) product ion spectra for monoisotopically selected precursor ions. This monoiso-topic precursor selection is made possible by the fact that the distance to the ion gate is 15 m, which is more than one order of magnitude longer than that of conventional MALDI TOF-TOF instruments. Additionally, the second TOF MS incorporates a re-acceleration mechanism and an offset parabolic reflectron, another innovative ion optical design developed by JEOL. This unique design enables seamless observation of product ions ranging from very low m/z up to that of the precursor ion.



Figure 1. JMS-S3000 "SpiralTOF" with TOF-TOF attachment.

In this work, we analyzed Polypropylene Glycol (PPG) 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:PPOMatrix agent:α-C(CHCA)Cationization agent: NaI

PPG α-Cyano-4-hydroxycinnamic acid



Figure 2. Structural formula of PPG.

Results and Discussion:

The MALDI mass spectrum of PPG and the m/z 1027.7 (n=17, [M+Na]⁺) product ion spectrum are shown in Fig. 3. The MS-MS spectrum shows the full range of ions from m/z 23.0 for [Na⁺] to m/z 1027.7 for the precursor ion. Also worth noting, these product ions are all monoisotopic because the precursor ion was monoisotopically selected, which greatly simplified the resulting MS-MS spectrum.

The enlarged region (m/z 580-630) in Fig. 3 shows that there are five different product ions present that could result from the monomer repeat unit (58u, C₃H₆O). Therefore, this high-energy CID data for PPG suggests that there are five possible fragmentation pathways.

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Based on previously published work¹, we hypothesized that the structural formulas for these different product ion series were most likely the structures shown in Fig. 4a-e. 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 PPG.

Conclusions:

Structural analysis of synthetic polymers such as PPG 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. MALDI mass spectrum of PPG (upper) and product ion spectrum of m/z 1027.7 (n=17, [M+Na]⁺) (lower).



Figure 4. Structural formula of product ions series.

Figure 5. PolymerixTM analysis result of m/z 1027.7 (n=17, [M+Na]⁺).

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