

Polymer Analysis by MS/MS Measurement - Polymethyl Methacrylate Fragmentation -

MS/MS measurement is effective in the analysis of synthetic polymers. We introduce here an example of the structural analysis of polymethyl methacrylate (PMMA) using the AXIMA-QIT time-of-flight ion trap mass spectrometer. The PMMA used was commercially available with an average molecular weight of approximately 4000 Da. Before performing MALDI, we added dithranol as a matrix and trifluoroacetic acid sodium salt (TFA-Na) as a cationization agent. It is believed that under these conditions the PMMA compound readily ionizes as the $[M+Na]^+$ form.

Fig. 1 shows the results of the MS analyses. The ion group evident at 100 Da intervals, corresponding to the PMMA repeating unit ($C_5H_8O_2$), was detected from m/z 2000 to m/z 6000.

Fig. 2 shows the MS/MS spectra obtained from the measurement of the m/z 2326 ($n=23$) and m/z 4027 ($n=40$) precursor ions from the ion group shown in Fig. 1. In the AXIMA-QIT MS/MS measurement, precursor ions are held in the ion trap where they repeatedly collide with should this be diluted gas molecules to induce ion dissociation (collision induced dissociation, CID). As a result, high-fragmentation efficiency is achieved, enabling MS/MS measurement of precursor ions consisting of high-mass ions in excess of m/z 4000.

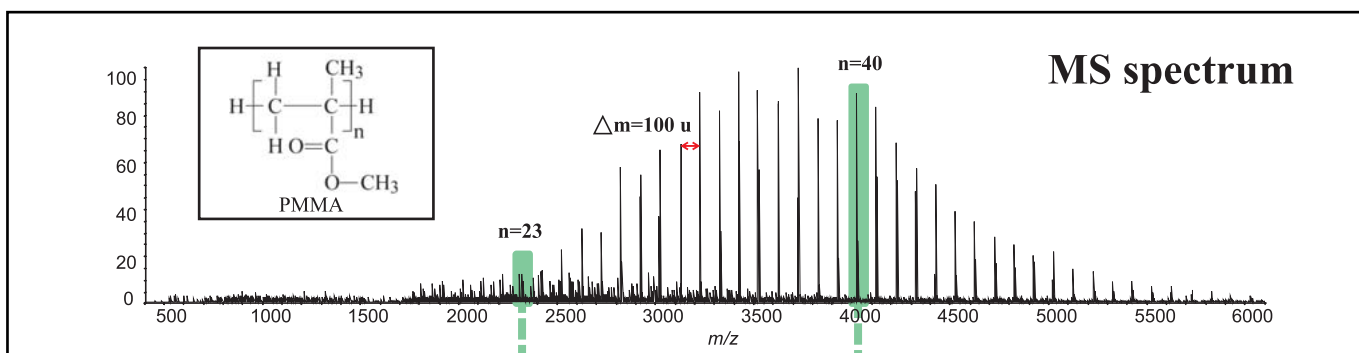


Fig. 1: PMMA Mass Spectrum

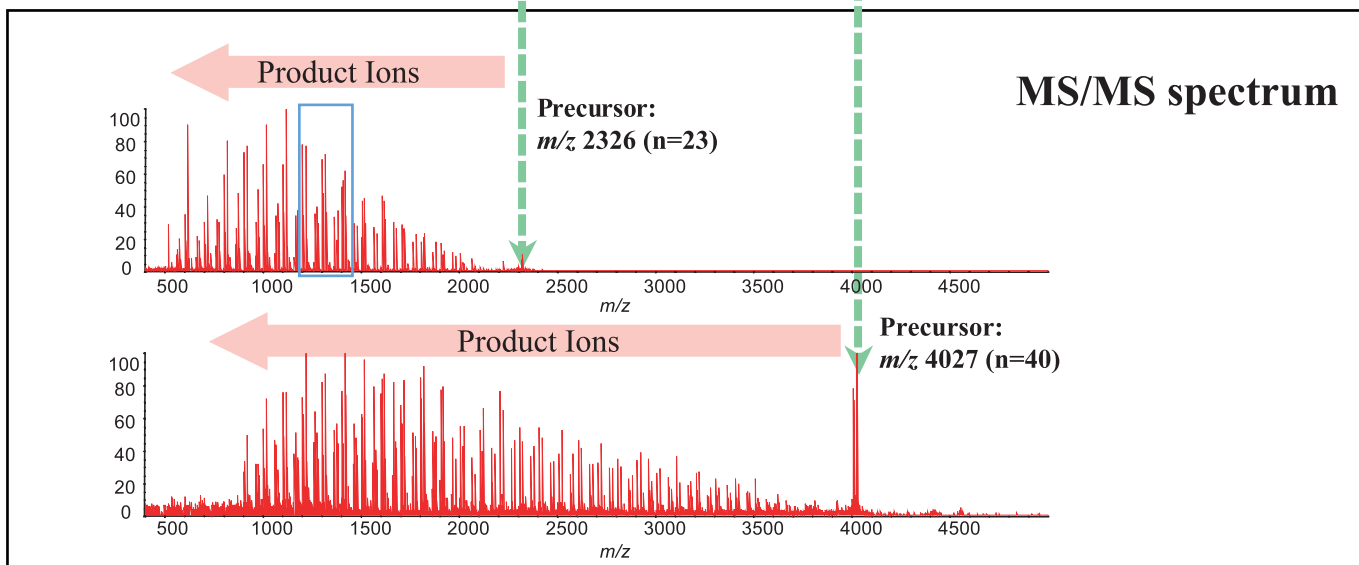


Fig. 2: PMMS MS/MS Spectra

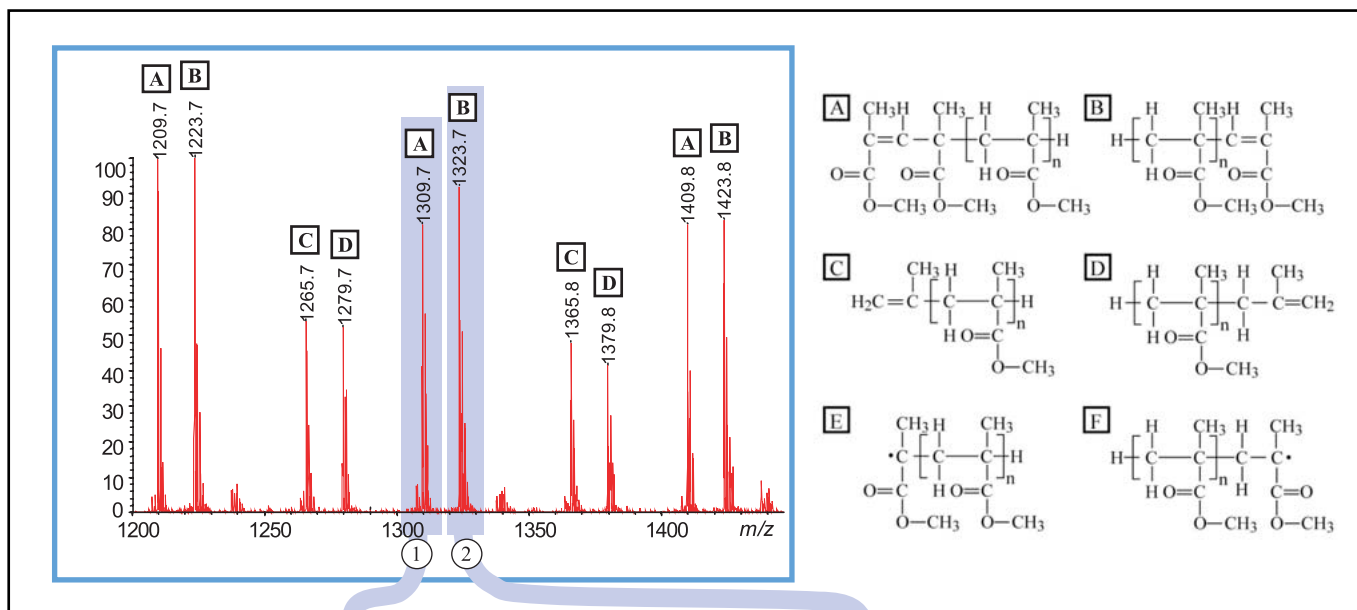


Fig. 3: Product Ion Classification and their Structures According to Terminus Structure

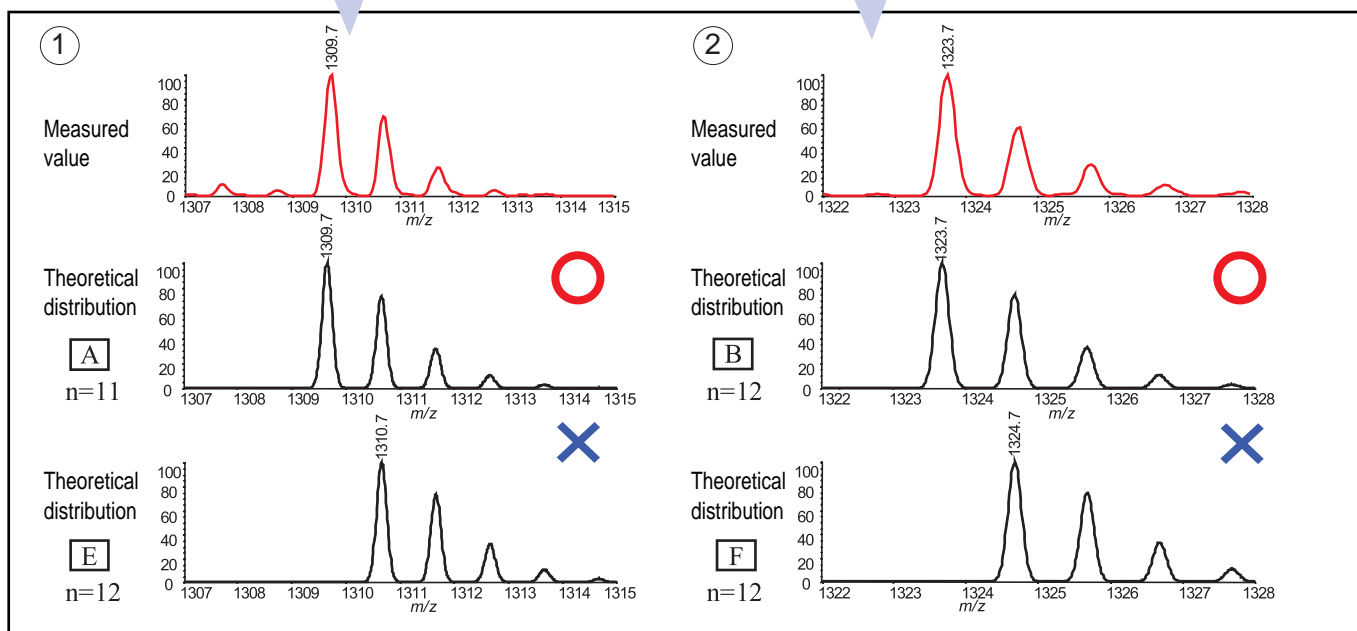


Fig. 4: Product Ion Attributes Based on Comparison of Measured and Theoretical Spectra

The product ions obtained in the MS/MS measurement were classified into 4 different groups as reflected in their respective characteristic terminal structures (□ of Fig. 2, spectra of Fig. 3). Of the 6 types of structures (products A, B, C, D, E, F) proposed as the product ion structures formed from PMMA, ions corresponding to the products A, B, C and D were detected in this measurement (Fig. 3).

Although there is no more than a 1 Da mass difference between product A and E and product B and F, respectively, the analysis using the AXIMA-QIT clearly indicated that products A and B were formed, as shown in Fig. 4.

From the above, it was demonstrated that MS/MS using the AXIMA-QIT is effective for the analysis of synthetic polymers, based on its high mass resolution, mass accuracy and fragmentation efficiency.

Literature cited: 1) O. Laine *et al.*, *Eur. J. Mass Spectrom.* **9**, 195-201, 2003.



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