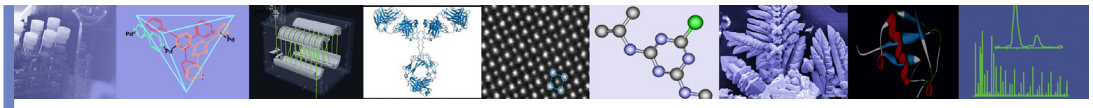

Applications Note

SpiralTOF-TOF

MALDI for Polymer Analysis: Synthetic Polymers and Additives

Introduction:

A high-resolution MALDI/TOF-TOF system with unique ion optics is applied to the identification of polymers and polymer additives. Exact mass measurements and isotopic abundances were used to identify elemental compositions. High-energy collision-induced dissociation with monoisotopic precursor selection provided structural information for additives and polymers. The mass accuracy for the sodiated molecule of Irganox 1010 in polymethyl methacrylate (PMMA) was within 1ppm of the calculated *m/z* (*m/z* 1199.7733, $C_{73}H_{108}O_{12}Na^+$). The high-energy CID product-ion mass spectrum for sodiated Irganox 1010 shows bond cleavage with little or no rearrangement. Four types of product ions are identified for the high-energy CID product-ion mass spectra of sodiated PMMA ions.

Experimental:

Samples were analyzed by using a MALDI/TOF-TOF (JEOL JMS-S3000 "Spiral TOF™ MS") mass spectrometer with multi-turn ion optics that fit a 17-meter flight path within a 1 meter space. Electrostatic sectors are used to continuously refocus the ion beam to minimize ion losses.

The MS-I resolving power is sufficiently high (60,000 FWHM) that monoisotopic precursor selection can be achieved by using a simple deflector. Ions with 20 keV kinetic energies undergo collisions with helium and a 9 keV post-acceleration combined with an offset parabolic reflector provides a wide energy acceptance for product ions.

Irganox1010 added to PMMA solution was used as a model sample, which included 5000 ppm as concentration of Irganox1010. 2,5-Dihydroxybenzoic acid (DHB) was used as the MALDI matrix and sodium iodide (NaI) was used as cationization agent.

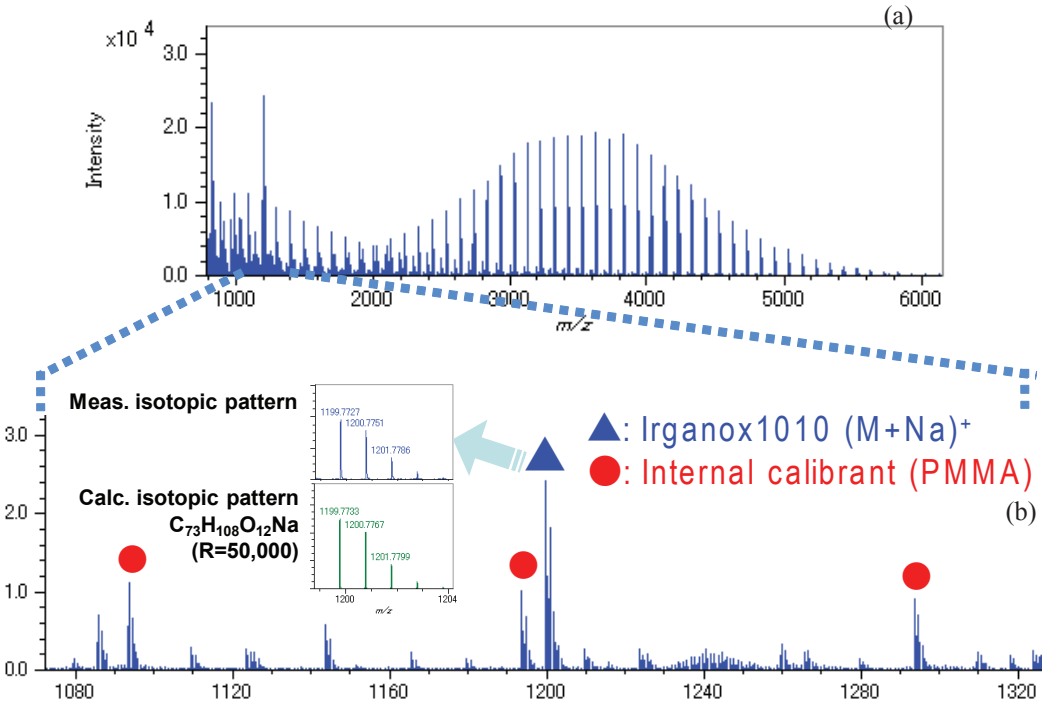

Figure 1. MALDI mass spectra of Irganox 1010 in PMMA solution (a) over all, (b) enlarged.

Table 1. Accurate mass measurement results for sodium-cationized molecule of Irganox1010.

No.	Resolution @ *m/z* 1199.7733	Mass error (ppm)	
		Internal calib.	External calib.
1	52,762	-0.31	-1.23
2	48,061	-0.71	-0.72
3	49,726	-0.54	-1.20
4	51,716	-0.61	-2.10
5	50,911	-1.02	5.46
6	47,648	-0.16	5.41
7	49,394	0.13	3.19
8	51,403	0.35	3.62
9	53,594	-0.47	5.64
10	46,463	-0.28	2.13
Ave.	50,635	0.46	3.07

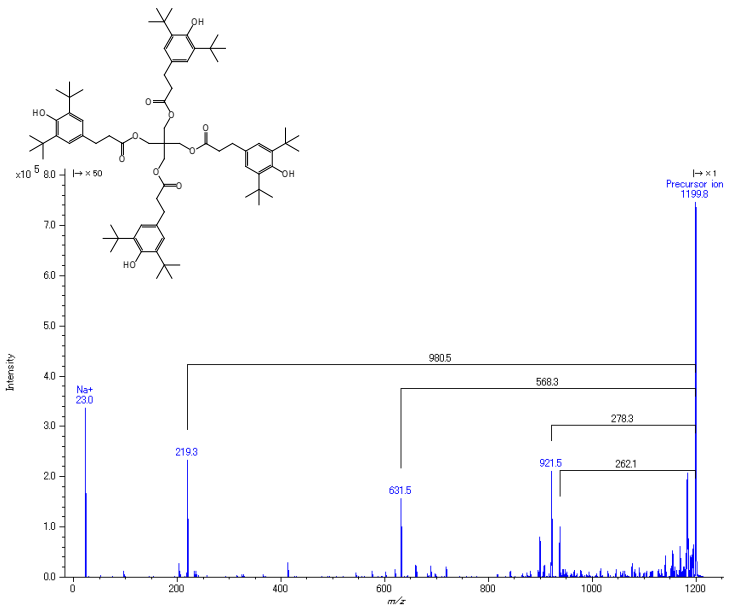

Figure 2. Product-ion spectrum and fragment ions of Irganox1010 in model sample (m/z 1199.8 ($[M+Na]^+$)).

Results:

(1) Additives

The phenolic antioxidant Irganox 1010 was detected as the sodiated molecule (*m/z* 1199.7733, $C_{73}H_{108}O_{12}Na^+$) in the model sample. The resolving power (FWHM) was approximately 50,000 for the $[M + Na]^+$ peak, well in excess of that needed to separate isotope peaks.

Accurate mass values of the monoisotopic ion of the sodiated molecule of Irganox 1010 were determined by using PMMA as either internal or external calibrant. The average mass errors were 0.46 ppm using internal calibration and 3.07 ppm using external calibration, respectively. Mass accuracy and isotopic abundances were sufficient to confirm the elemental composition of a sodiated molecule as $C_{73}H_{108}O_{12}Na$.

High-energy CID product-ion mass spectra were obtained with monoisotopic precursor selection for sodiated Irganox in the PMMA mass spectrum. All product ions were monoisotopic. The product-ion mass spectrum of sodiated Irganox 1010 was relatively simple due to the symmetric structure of the molecule.

(2) PMMA

High-energy CID product-ion mass spectra were obtained with monoisotopic precursor selection for the sodiated n=15 and n=23 species in the PMMA mass spectrum. All product ions were monoisotopic. Product-ion assignments corresponded to direct bond cleavage with minimal rearrangement. Four major fragment classes were observed in the high-energy CID product-ion mass spectra of sodiated PMMA (Fig,5). The *m/z* range for the product-ion mass spectra extended from the precursor *m/z* to *m/z* 23 (Na^+).

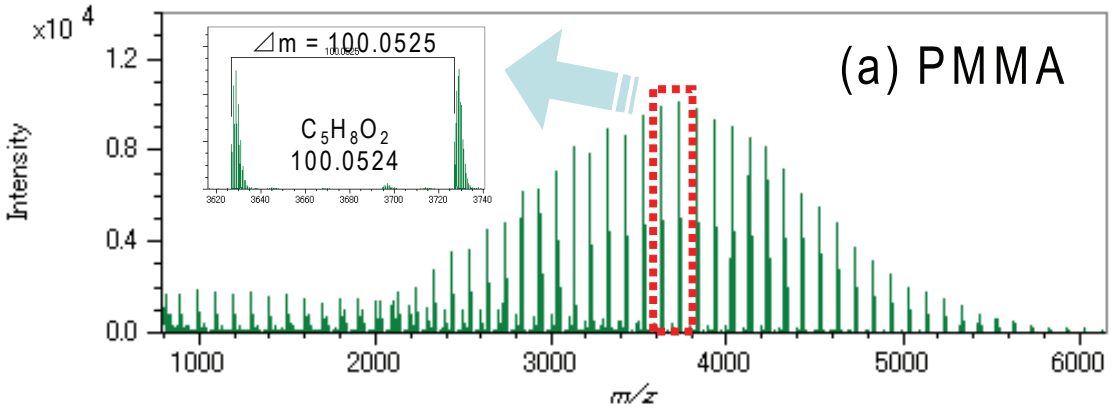

Figure 3. MALDI mass spectrum of PMMA.

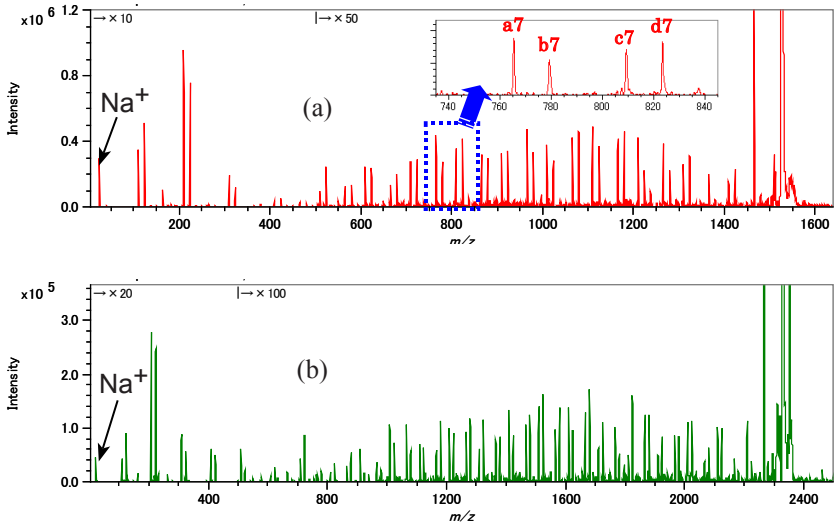

Figure 4. Product-ion spectra of PMMA,
(a) m/z 1525.8 (n=15, $[M+Na]^+$), (b) m/z 2326.2 (n=23, $[M+Na]^+$).

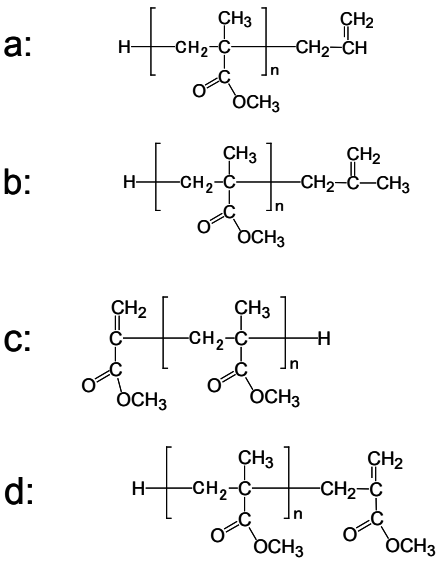

Figure 5. Structural formula of four major fragment classes.

Conclusion:

In this study we demonstrate accurate mass measurement for the polymer additive Irganox 1010 and structural analysis for PMMA and Irganox 1010.

- The SpiralTOF system provides ultra high resolution and high mass accuracy. It is very easy to perform accurate mass measurements. The sodium-cationized molecule of Irganox 1010 was detected with a mass accuracy of less than 1 ppm.

- MS/MS spectra were obtained by using the TOF-TOF option to provide structural information for PMMA