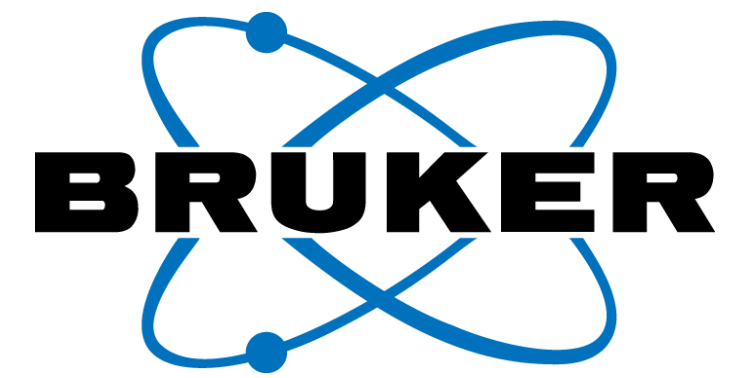


# Isomer structural elucidation of plastic materials caused by thermal degradation using LC-ESI-Ion mobility-MS/MS and MetaboScape™ software

Yoshifumi Mori<sup>1</sup>, Toshiji Kudo<sup>1</sup>,

Bruker Japan K.K.

## Typically, plastic materials are mixtures containing additives and

starting materials in addition to the main component to maintain the quality of the products. Furthermore, in case of degradation analysis, the composition would be complicated due to the reactions of each component. Therefore, an analytical workflow that can detect components comprehensively including trace ones, and can analyze molecular structure at the same time, is required.

In this research, thermally degraded polystyrene material was investigated using LC-ESI-Trapped Ion Mobility (TIMS)-MS/MS. The combination of HPLC, Trapped Ion Mobility and high accuracy MS system has excellent separation and qualitative analytical capabilities. Additionally, the ion mobility separation could provide the data for confirmation of decomposition products.

## Methods

Commercially available polystyrene foam produced with the bead method was heated in an oven at 120 degrees C and 180 degrees C for the duration up to 24 hours. The polymer component was removed from them using the reprecipitation method (THF/acetonitrile), and the supernatant was analyzed by the system consisting of LC (1290 Infinity, Agilent) and Trapped Ion Mobility qTOF-MS (timsTOF pro2, Bruker) with Parallel Accumulation Serial Fragmentation (PASEF) data acquisition equipped with ESI ion source. The acquired data were analyzed with DataAnalysis 5.3 (Bruker) and MetaboScape™2021 (Bruker).

## Results

The data acquired from the supernatant shows that many small molecules were detected. Data analysis and peak picking were performed in MetaboScape™2021. The ion mobility ( $1/k_0$ ) and collision cross section (CCS) of each compound were calculated and listed in table (Fig.1 a). In this method, 1,468 cations and 103 anions were detected. The result was verified using mass accuracy, isotope pattern matching and MS/MS fragmentation analysis. The candidate compound structures were confirmed further, by in-silico fragment matching using MetaboScape™2021 (Fig.2). The identified components were categorized into five main types: polystyrene oligomers, pigments, dispersants, antioxidant oxides and glidants.

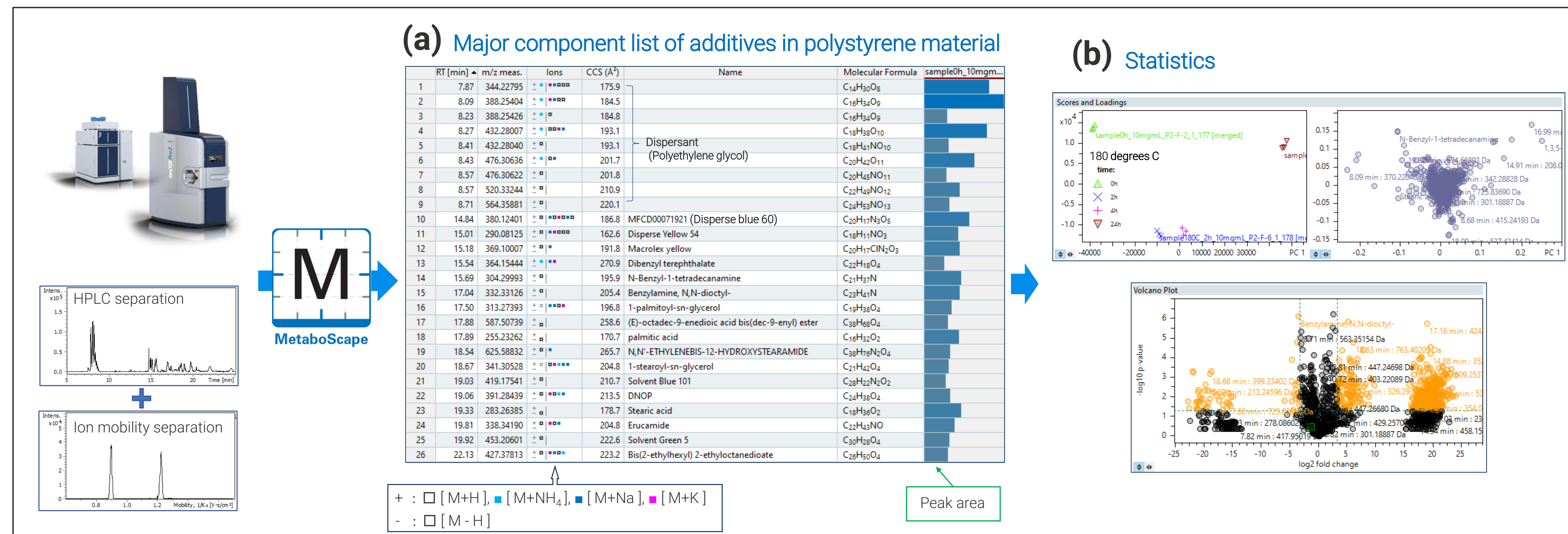


Fig. 1 Analytical workflow of polymer additives using LC-ESI-TIMS-MS/MS measurements and software.

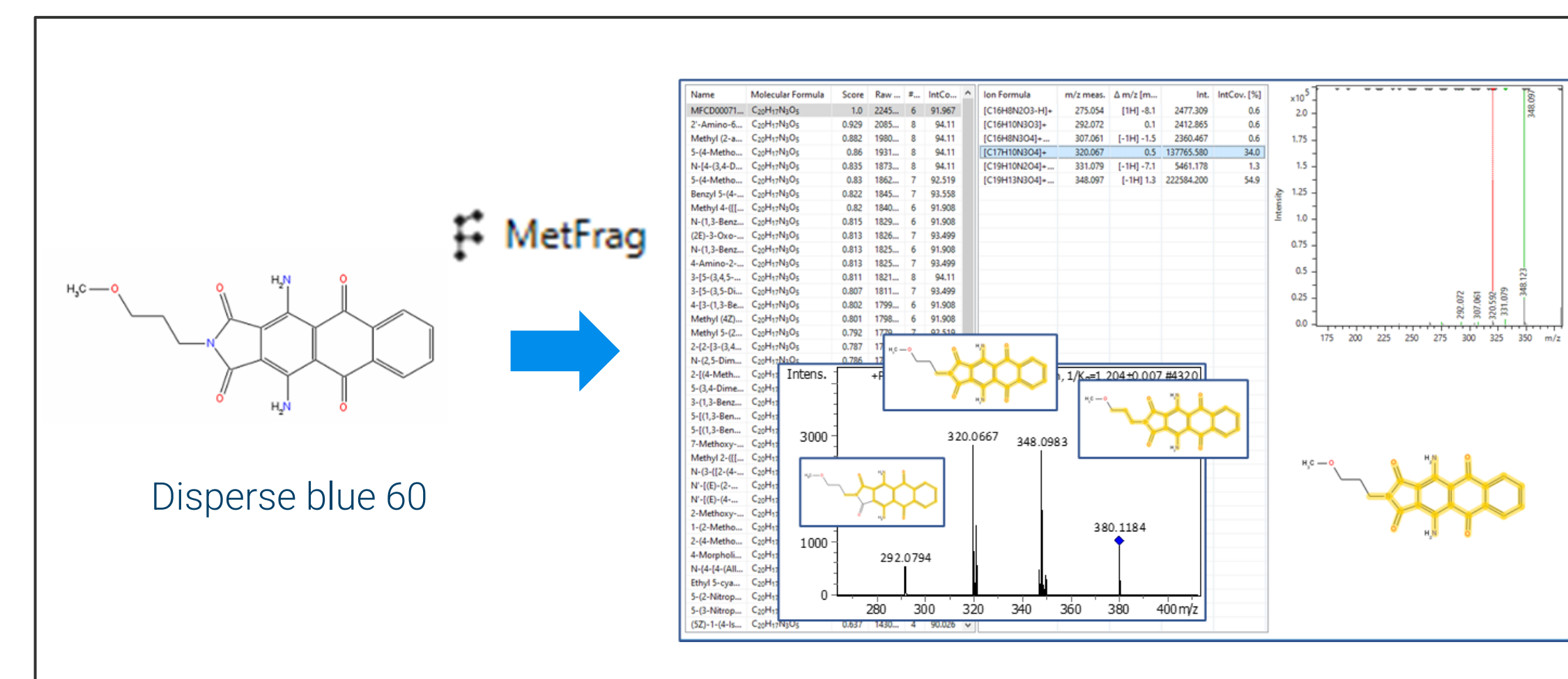


Fig. 2 Example of structural deamination by in-silico fragmentation matching.

In the qualitative analysis, several isomers were detected by ion mobility separation.

Thermal degradation mechanism was discussed using time-series in 120 degrees C and 180 degrees C heating experiments. Multivariate analysis (Fig.1 b) was used to search for key components of degradation. From these results, we concluded that oxidation at double bonds or hydrolysis of ester type compounds yielding fatty acids (FAs) occurs at the first step of the degradation. That reaction gradually starts even at 120 degrees C (Fig.3 a). Then, the amount of esters between polyethylene glycol (PEG) and FAs increases with increasing reaction time (data not shown).

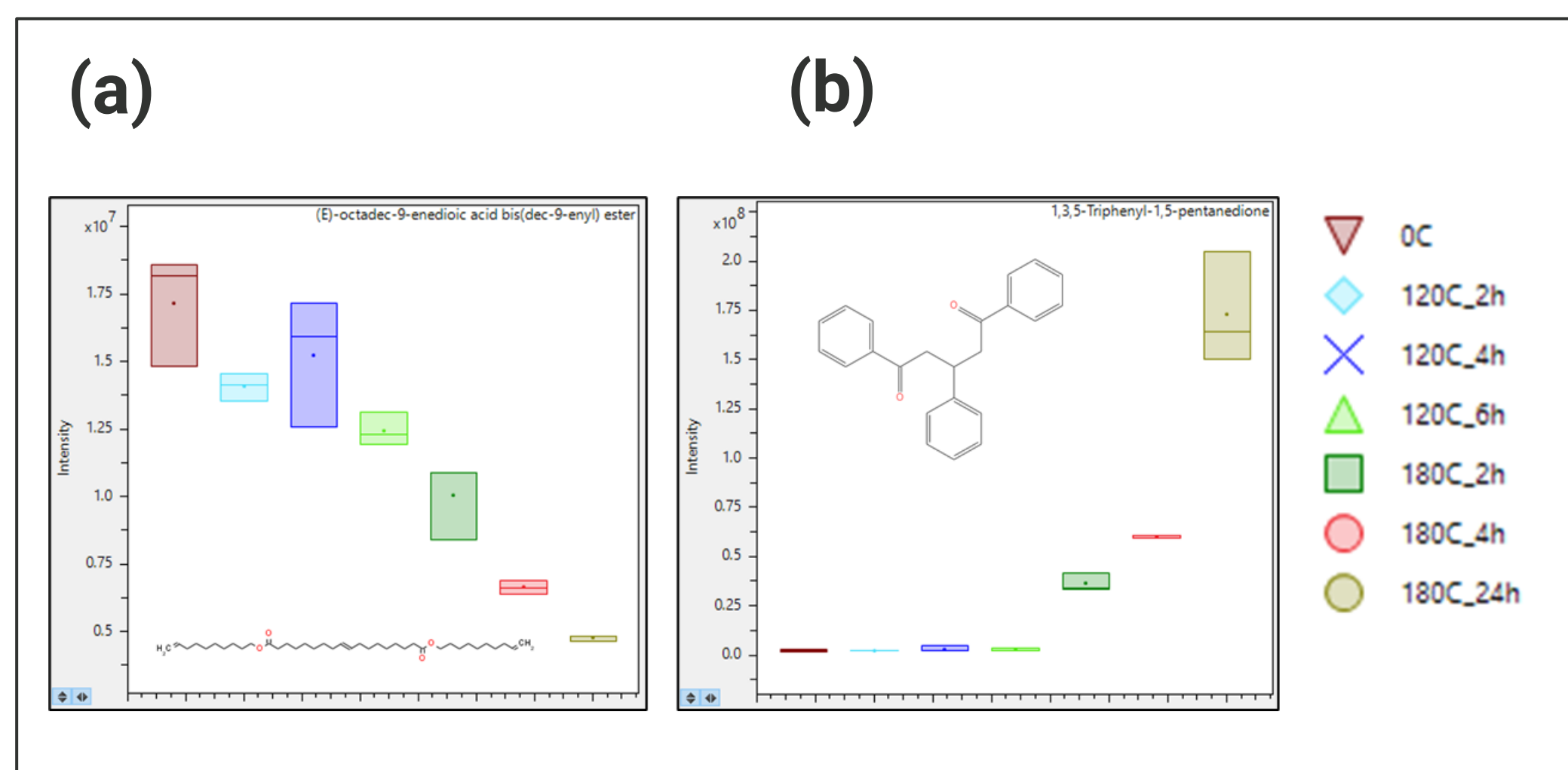


Fig. 3 Results of time series plot of (a) ester type lubricant and (b) oxidized fragment component from polystyrene main chain.

From this result, it is considered that the dehydration condensation of dispersants (PEG) and glidants (contains FA related structure) occur as the second step. Finally, all additives break down and then oxidative decomposition of the main chain of polystyrene starts. Regarding decomposition of the main chain, two kinds of polystyrene oligomer oxide could be assigned by ion mobility separation and MS/MS spectra (Fig.4).

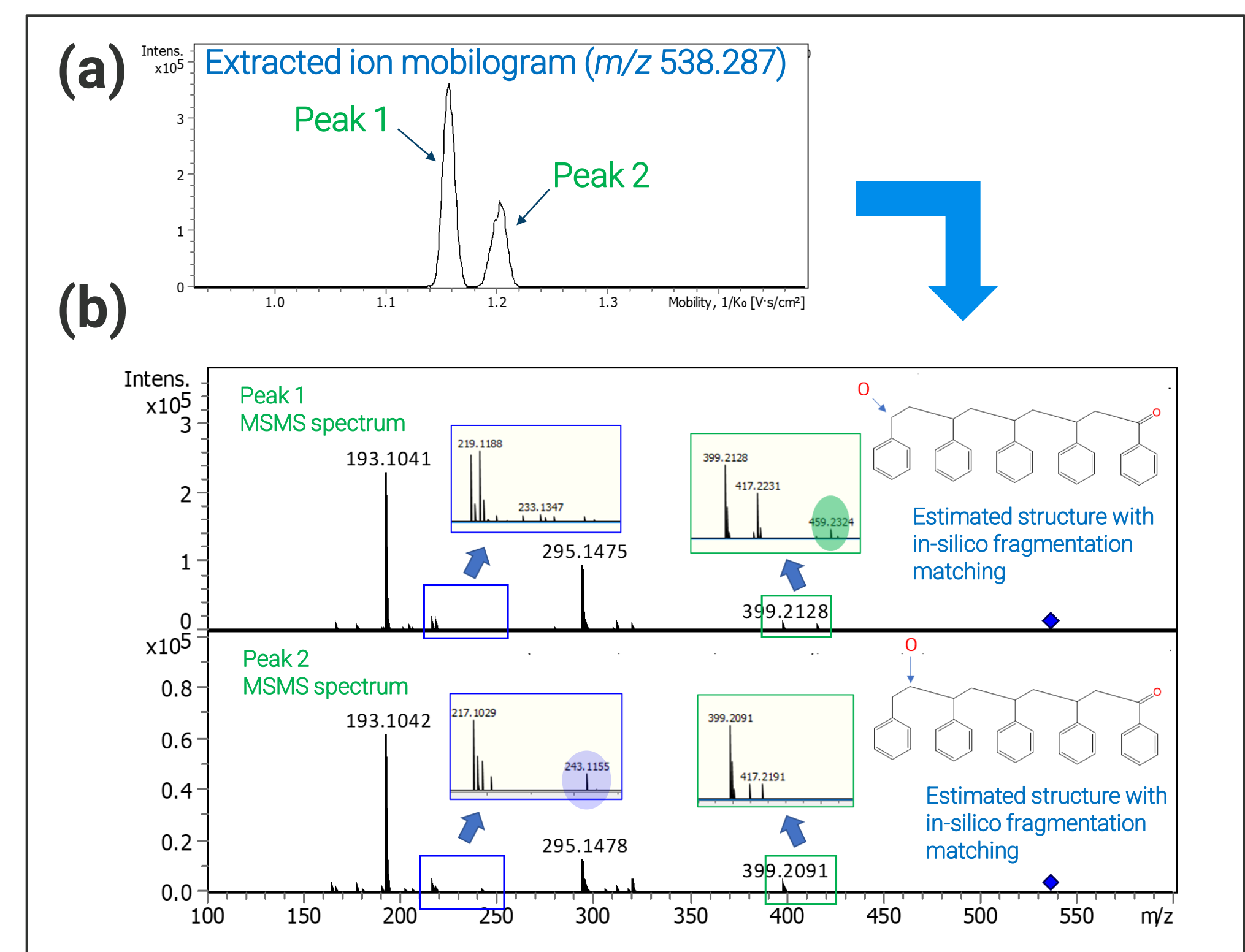


Fig. 4 (a) Extracted ion mobilogram of oxidative fragment (pentamer oxide) of polystyrene. (b) MS/MS spectra of two peaks in mobilogram (a).

These isomers could not be separated in commonly used conditions without ion mobility spectrometer. In-silico fragmentation matching method, suggested that the difference between two peaks in the mobilogram is their site of oxidation.

These results provide us clues to understand the degradation of polystyrene.

## Conclusion

- LC-ESI-TIMS-MS/MS and MetaboScape™2021 workflow allowed us to more easily analyze the structures of more ions.
- Commercial polystyrene materials contained five different types of additive component.
- Trapped ion mobility was successfully used to detected oxidative fragments of polystyrene and other isomers.

LC-ESI-TIMS-MS/MS