“Remainders of KM” plot for polymers using msRepeatFinder: Intuitive display of High energy collision induced dissociation mass spectra acquired by SpiralTOF™/TOF

Product used：Mass spectrometer (MS)

Tandem mass spectrometry of polymer ions provides valuable information about the nature of individual end-groups, chain architecture (linear / cyclic / branched) or copolymeric microstructure. A high energy collision-induced dissociation (HE-CID) tandem time-of-flight analysis (TOF/TOF) advantageously follows a matrix-assisted laser desorption ionization (MALDI) TOF analysis. However, the interpretation of the resulting mass spectrum is not obvious with numerous ion series and signals of low intensity. A “remainders of Kendrick mass” analysis (RKM) is proposed as a rapid post-acquisition data processing of TOF/TOF mass spectra to visualize and filter the ion series instantly via intuitive point alignments.

Experimental

Poly(propylene oxide) (PPO 1000 g mol^{-1}) was used for an analyte. Product ion spectra were recorded with a JMS-S3000 SpiralTOF™ mass spectrometer (CHCA 10 mg mL^{-1}, PPO 10 mg mL^{-1}, NaTFA 1 mg mL^{-1}, 10:1:1 in MeOH). KMD and RKM plots were computed using msRepeatFinder 3.0.

HE-CID mass spectrum

A typical HE-CID mass spectrum of a (OH, H)-ended PPO 30-mer with isotopic selection of the precursor ion at *m/z* 1782 displays two main product ion series detected with low intensity (**Fig. 1**) while several minor series are also barely observed in the background. Visualizing and interpreting such type of mass spectral data remains inconvenient and time-consuming as a manual assignment of each peak one by one as well as a tedious artwork are necessary to label all the product ions in a quite unclear figure.

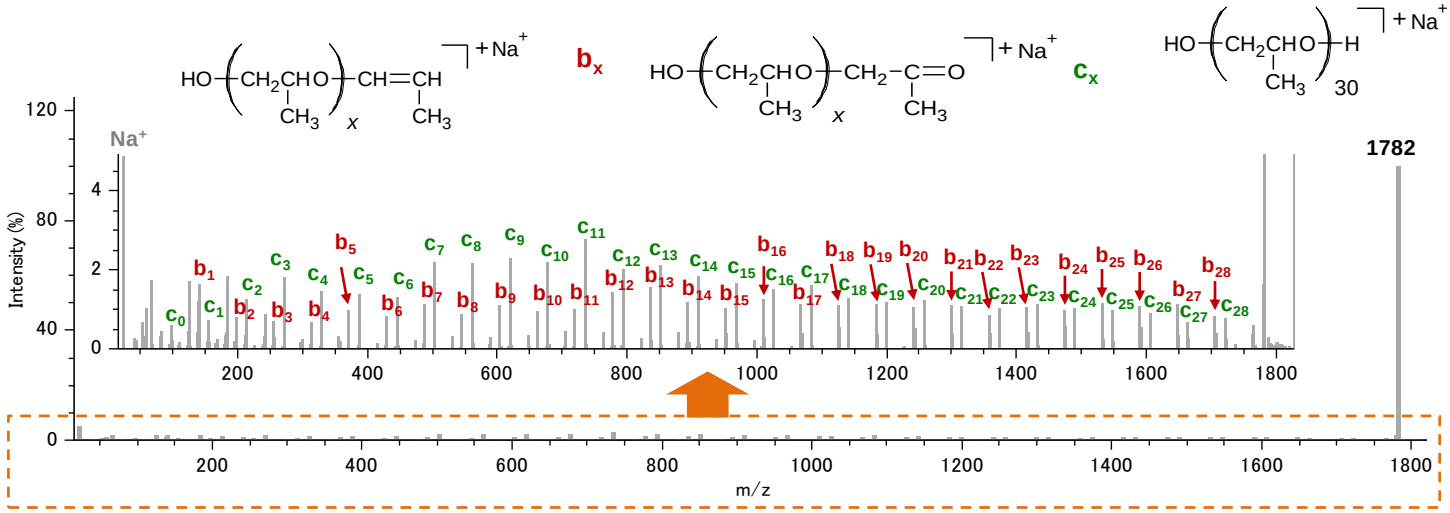

Fig. 1. HE-CID mass spectrum with two main product ion series noted b_x and c_x (adapted from Wesdemiotis et al [1] – structures in inset).

Kendrick mass defect (KMD) plot

The KMD plot [2] computed from the HE-CID mass spectrum displays a cloud of points barely aligned horizontally (**Fig. 2**). As the resolution of a TOF/TOF mass spectrum is unitary with limited mass accuracy for the mass measurements of the product ions, accurate mass defects cannot be evaluated and the resulting KMD plot is unresolved with no separation of the product ion series.

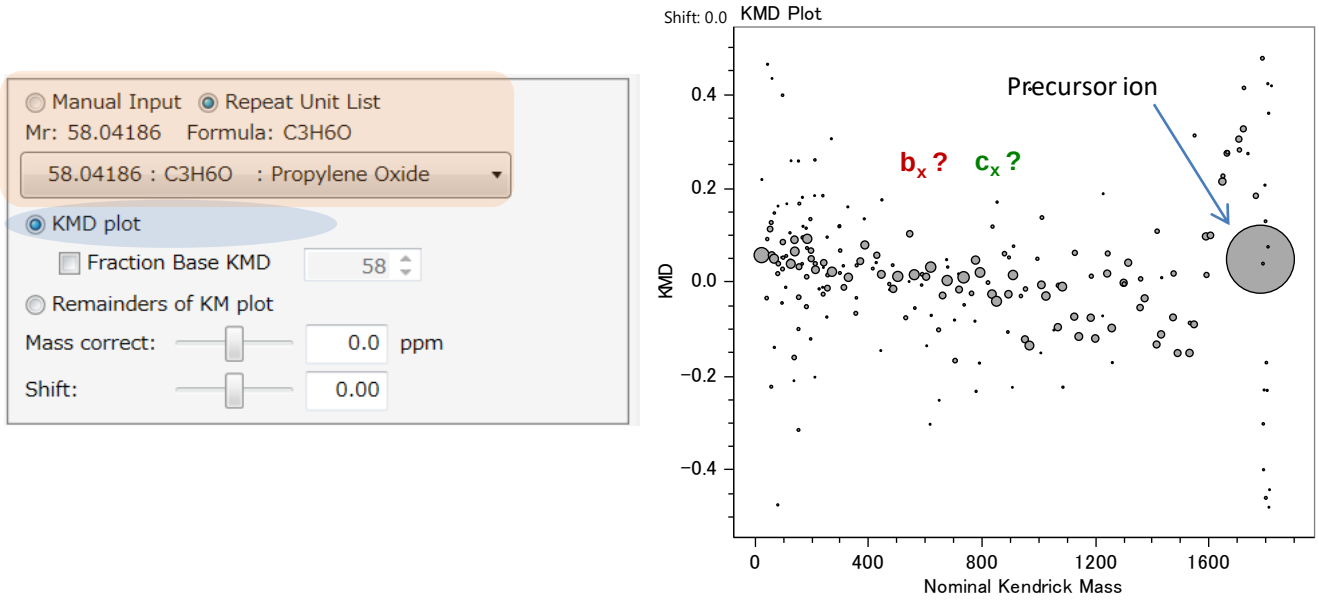

Fig. 2. "Regular" KMD plot (base unit: propylene oxide C_3H_6O from the repeat unit list) using msRepeatFinder.

Remainders of KM (RKM) plot

A "remainders of KM" plot [3] (base unit: C_3H_6O, PO repeating unit) is readily computed by checking the corresponding option in msRepeatFinder (**Fig. 3**). Instead of the unresolved cloud of points in the KMD plot, several series of points are clearly visualized in the RKM plot which does not require high-accuracy mass measurement to display horizontal alignments. Each line is instantly assigned to the main product ion series (c_x: green dots; b_x: red dots) and the minor series barely seen in the HE-CID mass spectrum.

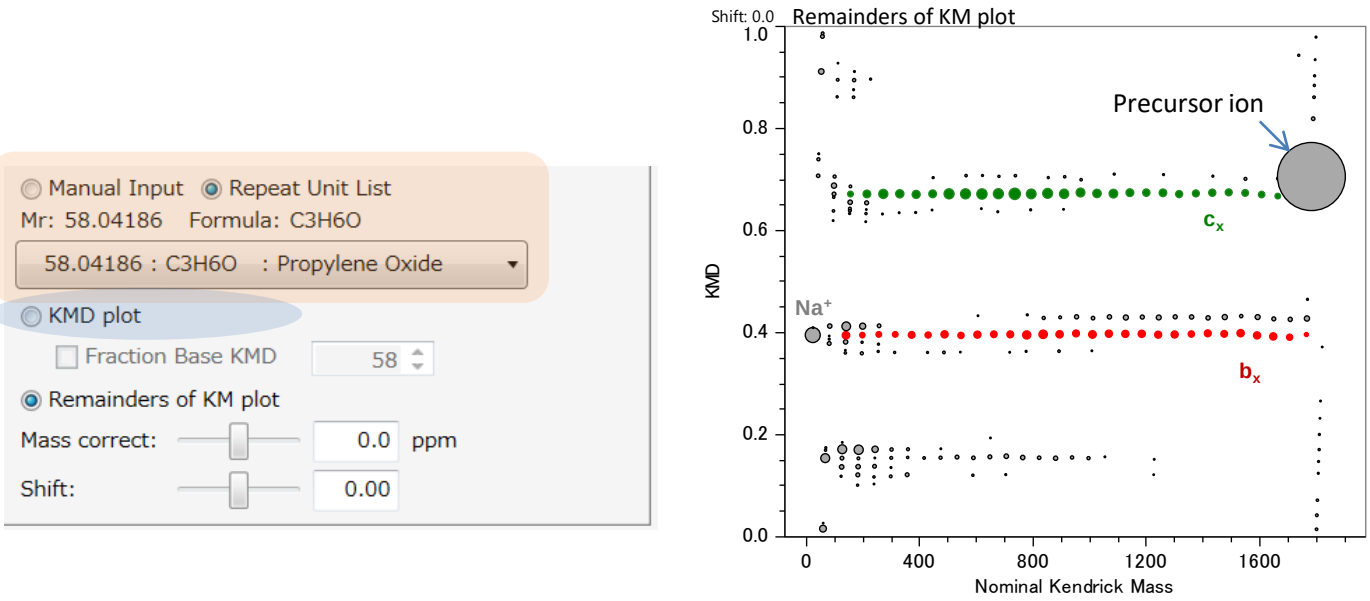

Fig. 3. RKM plot (base unit: propylene oxide C_3H_6O from the repeat unit list) using msRepeatFinder.

The “grouping mode” in msRepeatFinder further allows each ion series to be instantly label in the HE-CID mass spectrum with visual color coding by a simple selection of a given point series horizontally aligned in the RKM plot (**Fig. 4**). Unselected ion series can be hidden for an ever more visual mapping of complex mass spectral data (**Fig. 5**).

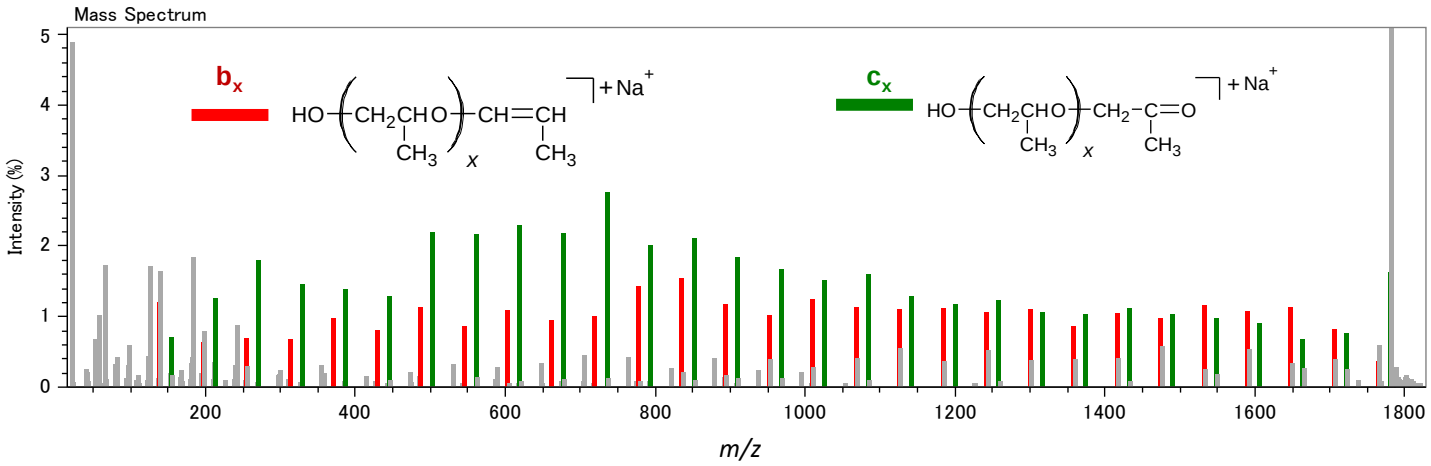

Fig. 4. Visualization of the two main product ion series (green bars: c_x; red bars: b_x) by grouping points horizontally aligned in the RKM plot.

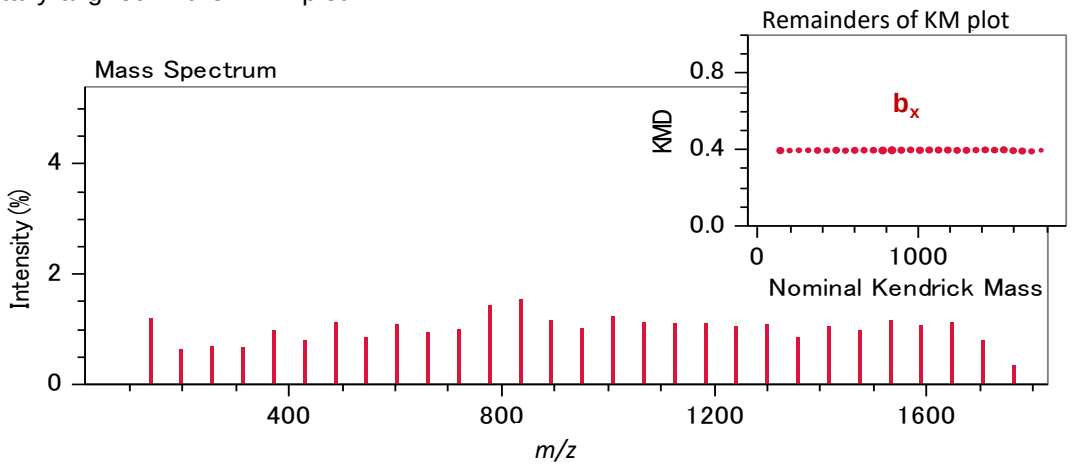

Fig. 5. Visualization of one ion series only by hiding the unselected points.

Prospects

The RKM plots are compatible with HE-CID mass spectra of homopolymers and copolymers using one of the repeating units (different end-groups of ion series and/or architecture block/random) or the expelled neutrals (filiations) [4].

Acknowledgment

This application note is written based on the results of a joint research project with Dr. Hiroaki Sato and Dr. Thierry Fouquet in Research Institute for Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST).

References

[1] C. Wesdemiotis, N. Solak, M. J. Polce, D. E. Dabney, K. Chaicharoen, B. C. Katzenmeyer. *Mass Spec. Rev.* **2011**, *30*, 523-559.

[2] H. Sato, S. Nakamura, K. Teramoto, T. Sato. *J. Am. Soc. Mass Spectrom.* **2014**, *25,* 1346–1355.

[3] T. Fouquet, T. Satoh, H. Sato. *Anal. Chem.* **2018**, *90,* 2404–2408.

[4] T. Fouquet, H. Sato. *Rapid Commun. Mass Spectrom.* **2016**, *30*, 1361–1364.

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