

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

Product: JMS-S3000

## Introduction

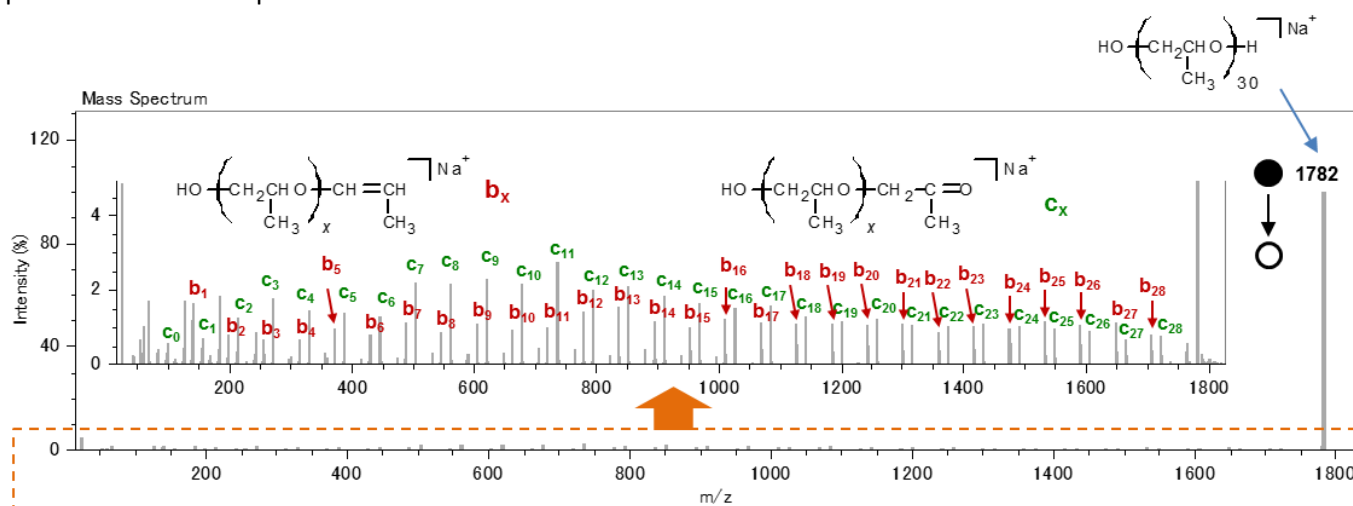
Tandem mass spectrometry of polymer ions provides valuable information about the nature of individual end-groups, chain architecture (linear / cyclic / branched) and copolymeric microstructure. Using matrix-assisted laser desorption ionization (MALDI) with high energy collision-induced dissociation (HE-CID) tandem time-of-flight analysis (TOF/TOF) can be advantageous for MS/MS polymer analysis. However, the interpretation of the resulting mass spectrum may not be obvious when a number of ion series with low intensity signals are present. In this work, a “remainders of Kendrick mass” (RKM) analysis is used as a rapid post-acquisition data processing tool for TOF/TOF mass spectra in order to visualize and filter the ion series instantly via intuitive point alignments.

## Experimental

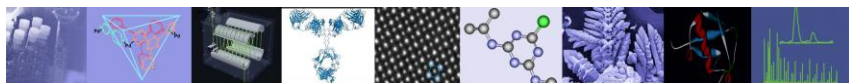
Poly(propylene oxide) (PPO 1000 g mol<sup>-1</sup>) was used for an analyte. Product ion spectra were recorded with a JEOL JMS-S3000 SpiralTOF™ mass spectrometer (CHCA 10 mg mL<sup>-1</sup>, PPO 10 mg mL<sup>-1</sup>, NaTFA 1 mg mL<sup>-1</sup>, 10:1:1 in MeOH). The plots were computed by using msRepeatFinder 3.0 (JEOL Ltd.).

## HE-CID mass spectrum

A typical HE-CID mass spectrum for a (OH, H)-terminated PPO 30-mer with isotopic selection of the precursor ion at  $m/z$  1782 showed two main product ion series with low intensity (**Fig. 1**) along with several minor series observed just above the background. Visualizing and interpreting this type of mass spectral data remains inconvenient and time-consuming as the manual assignment of each peak one-by-one as well as labeling all of the product ions can be quite tedious.

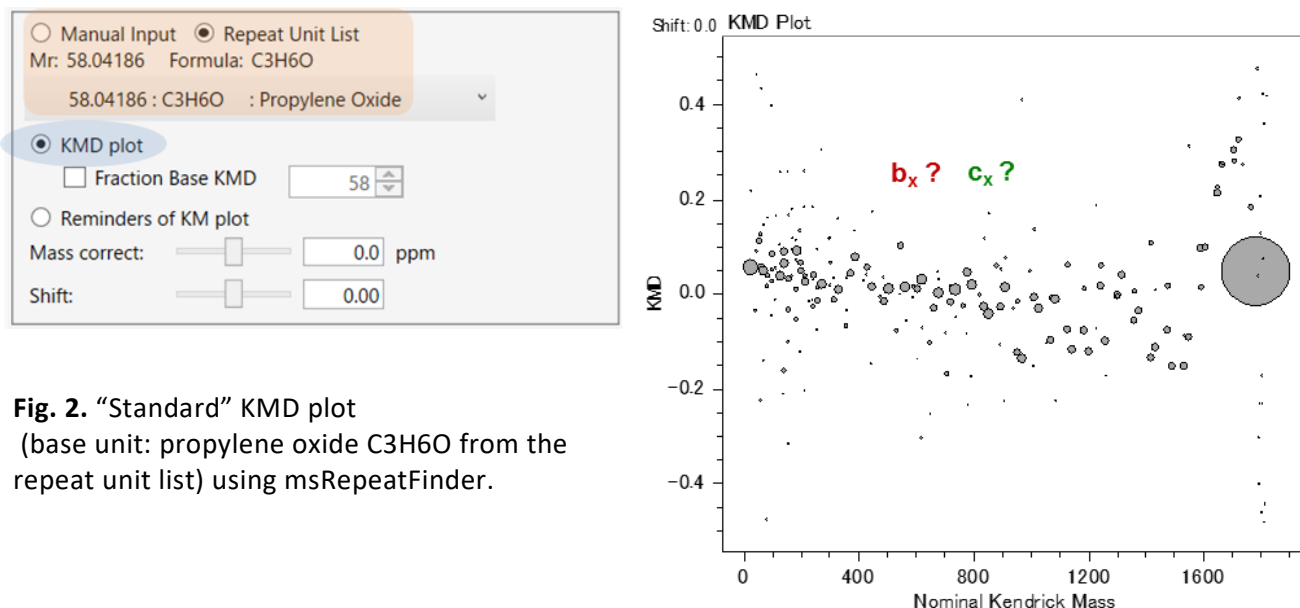


**Fig. 1.** HE-CID mass spectrum with two main product ion series noted  $b_x$  and  $c_x$  (adapted from Wesdemiotis et al [1] – structures in inset).



### Kendrick mass defect (KMD) plot

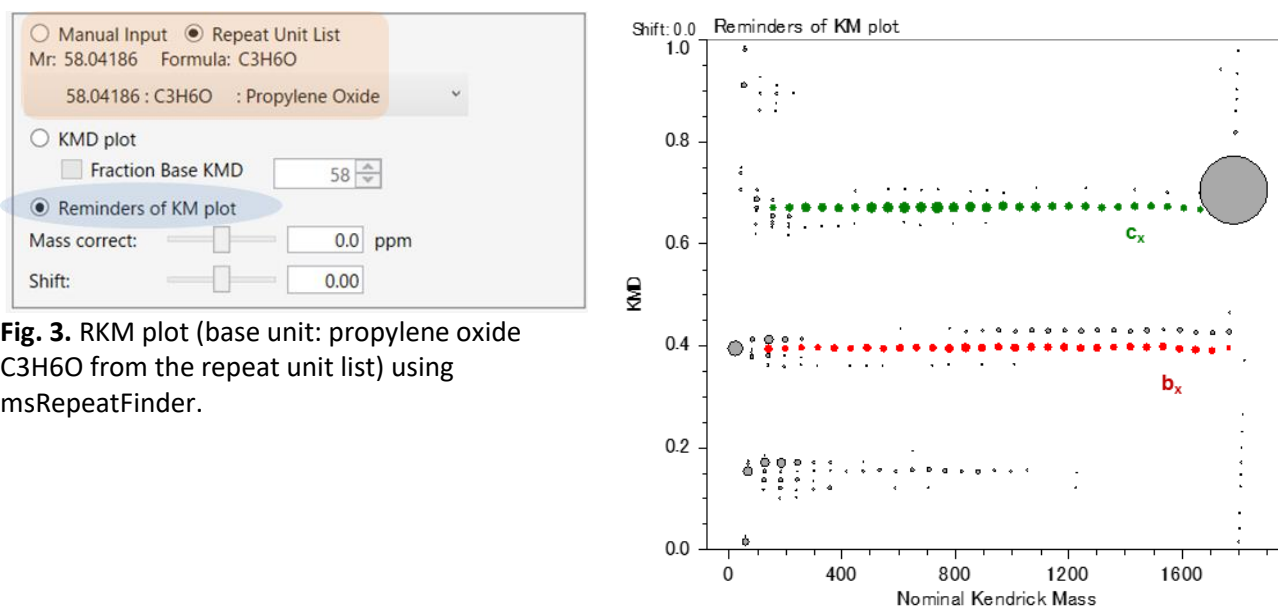
The KMD plot [2] computed from the HE-CID mass spectrum showed a cloud of points that barely aligned horizontally (**Fig. 2**). As the resolution of a TOF/TOF mass spectrum is unitary with limited mass accuracy for the mass measurements of the product ions, accurate mass defects cannot be evaluated thus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



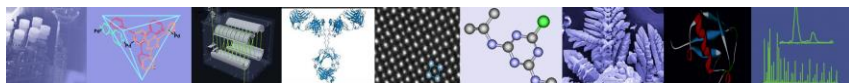
**Fig. 2.** “Standard” KMD plot  
(base unit: propylene oxide  $C_3H_6O$  from the repeat unit list) using msRepeatFinder.

### Reminders of KM (RKM) plot

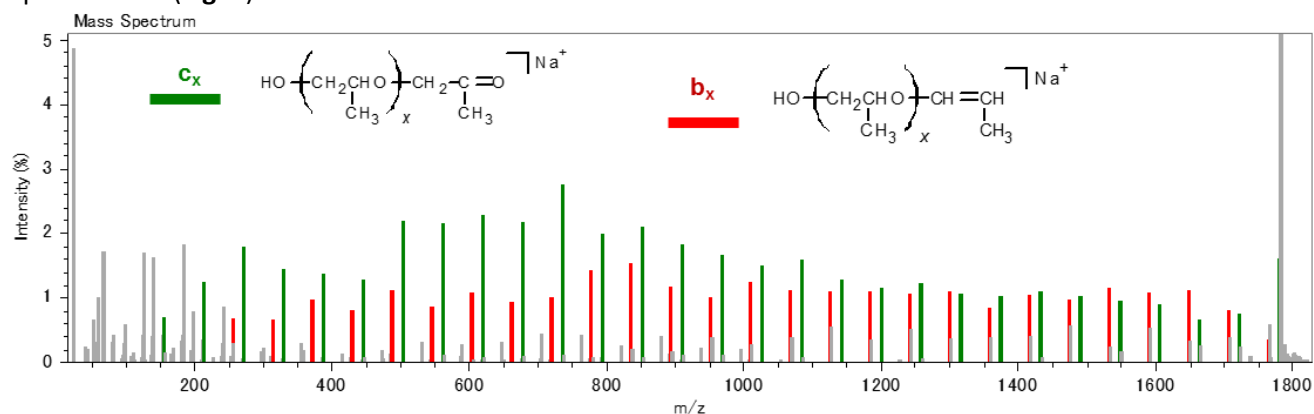
A “remainders of KM” plot [3] (base unit:  $C_3H_6O$ , PO repeating unit) was easily computed by checking the corresponding option in the msRepeatFinder software (**Fig. 3**). Instead of the unresolved cloud of points in the KMD plot, several series of points were clearly visualized in the RKM plot which does not require high-accuracy mass measurements to display horizontal alignments. Each line is instantly assigned to the main product ion series ( $c_x$ : green dots;  $b_x$ : red dots) along with the minor series (aligned dots above and below the main series) that are barely observed in the HE-CID mass spectrum.



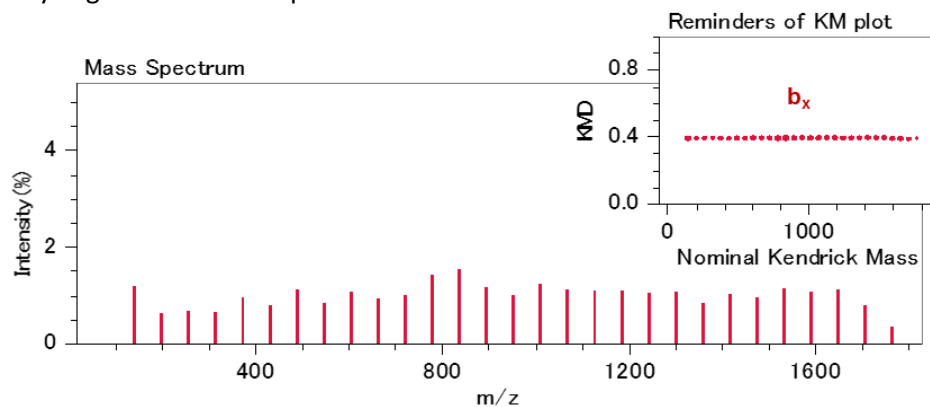
**Fig. 3.** RKM plot (base unit: propylene oxide  $C_3H_6O$  from the repeat unit list) using msRepeatFinder.



The “grouping mode” within msRepeatFinder further allowed 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 to help visualize the mapping of complex mass spectral data (**Fig. 5**).



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



**Fig. 5.** Visualization of a single ion series 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 ion series end-groups and/or architecture block/random) or the expelled neutrals (filiations) [4].

### 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.