“Remainders of KM” plot for polymers using msRepeatFinder: compositional mapping over a broad mass range

Product used：MS

Mass Spectrometry (MS) with soft ionization such as matrix-assisted laser desorption ionization (MALDI) allows the compositional analysis of polymers (repeating units, chain terminations) of low dispersity. Combining a size exclusion chromatography (SEC) fractionation with a high-resolution MALDI SpiralTOF™ MS analysis enables the evaluation of the composition of polydisperse polymeric samples over a broad mass range (high-resolution/high-accuracy mass measurements in the low mass range <4 kDa, isotopic resolution in higher mass range < 30kDa). However, the higher the resolution the more the peaks detected in the mass spectrum with one spectrum per fraction, making the interpretation of mass spectral data the rate-limiting step of the whole analytical procedure. A “remainders of Kendrick mass” analysis (RKM) is proposed as a rapid post-acquisition data processing using visual maps from concatenated low/high-accuracy and low/high mass range data.

Experimental

A 1 mg mL^{-1} solution of poly(ε-caprolactone) (PCL, Polymer Source, P1302-CL) in $CHCl_3$ was fractionated by SEC (HLC8220 GPC system, Tosoh, TSKgel multipore HXL-M columns, flow rate: 1 mL min^{-1}, 0.5 mL per fraction). Mass spectra were recorded with a JMS-S3000 SpiralTOF™ mass spectrometer (matrix: DCTB, no salt added). Plots were computed using msRepeatFinder 3.0.

SEC-MALDI-MS

Five fractions are collected from the SEC elution turning the PCL sample into aliquots of low dispersity (Fig. 1A). The main distributions in the last fraction (*m/z* 2000 to 5000, Fig. 1B) are assigned to sodiated (H, OH)-ended PCL (red circles) and (H, C_3H_7O)-ended PCL (blue triangle) taking full advantage of the high resolution of the analyzer. The SpiralTOF™ analyzer is still capable of producing mass spectra for the four other fractions of increasing molecular weight up to 20000 Da with a neat isotopic resolution (Fig. 2A). Mass spectra are concatenated using msRepeatFinder3.0 to display the full mass spectral data in one graph (Fig. 2B).

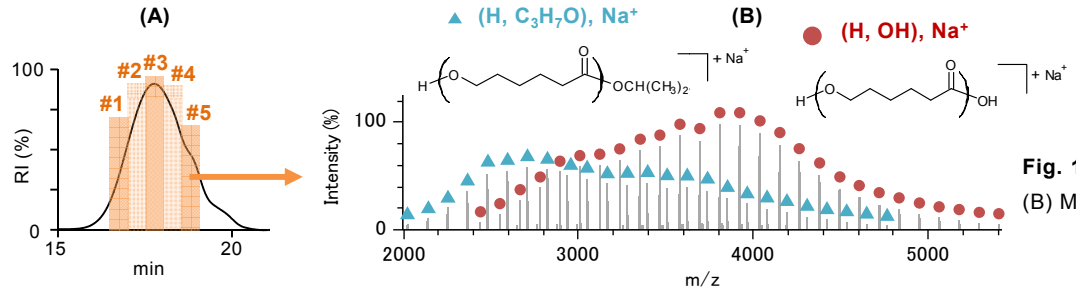


Fig. 1. (A) SEC chromatogram. (B) Mass spectrum of fraction 5.

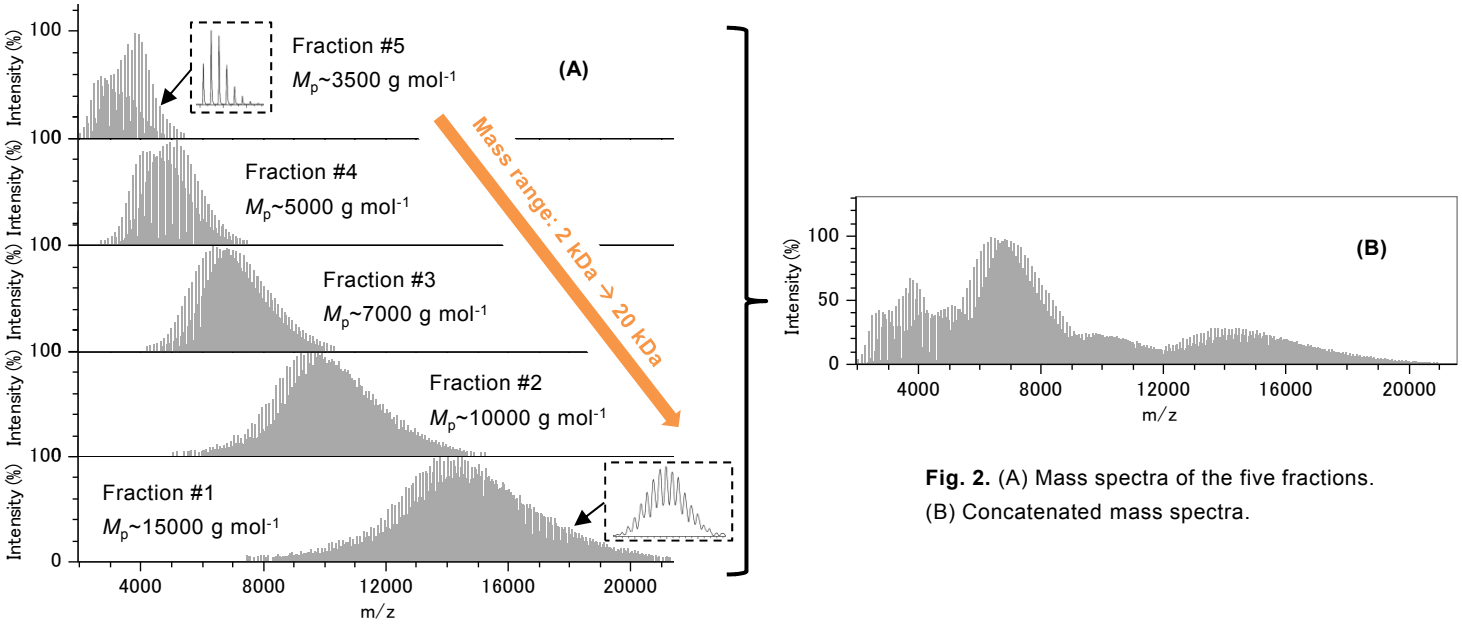
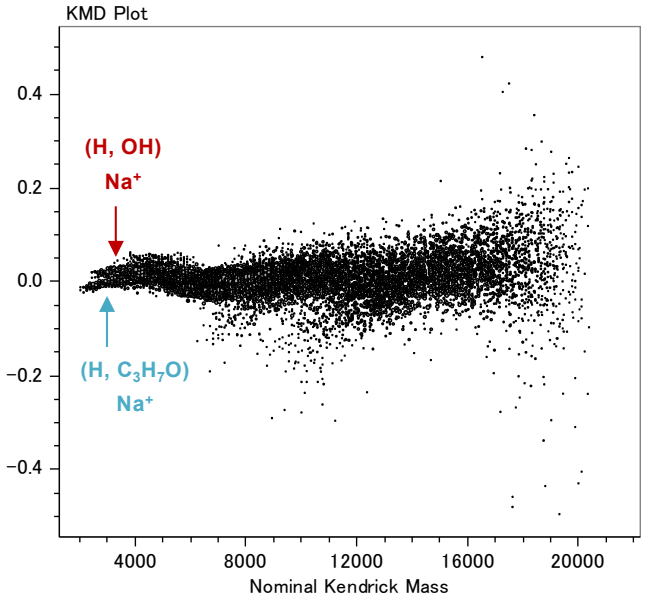


Fig. 2. (A) Mass spectra of the five fractions. (B) Concatenated mass spectra.

Kendrick mass defect (KMD) plots

The regular KMD plot from the concatenated mass spectra barely separates the sodiated (H, OH)- and (H, C_3H_7O)-ended oligomers in the lowest mass range but the plot becomes unresolved while increasing the chain length (Fig. 3). In spite of the isotopic resolution reached by the SpiralTOF™ analyzer, the mass accuracy is not high enough for a regular KMD analysis. The resolution-enhanced KMD plot using a fractional base unit CL/113 (Fig. 4) successfully separates the four main distributions (sodiated and potassiated (H, OH)- and (H, C_3H_7O)-ended oligomers) over the whole mass range. The separating power is nevertheless decreasing while the molecular weight is increasing and the plot becomes fuzzy with a low quality of point alignment.



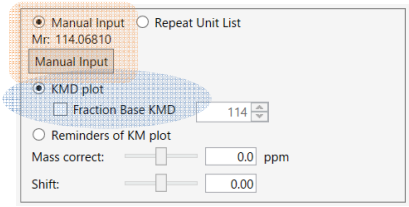


Fig. 3. Regular KMD plot [1] from the concatenated mass spectra of the five fractions (base unit: CL, $C_6H_{10}O_2$, 114.0681).

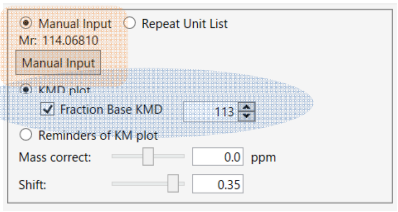
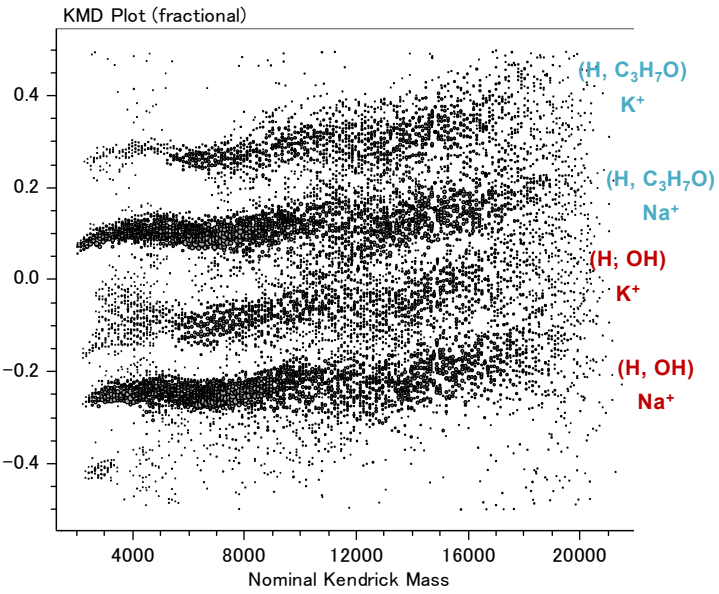


Fig. 4. Resolution-enhanced KMD plot [2] from the concatenated mass spectra of the five fractions using the “fraction base KMD” option (base unit: CL/113).



Remainders of KM (RKM) plot

The RKM plot of the concatenated mass spectra reveals a great compositional homogeneity of PCL throughout a broad 20 kDa mass range with (H, OH)- and (H, C_3H_7O)-ended chains (sodium and potassium adduction, Fig. 5A). An additional cyclic ion series is observed in the lowest mass range (fraction #5, blue square) typical of ring-opening and polycondensation synthesis routes. The detection of (H, ONa)-ended oligomers seen in the fraction #5 (violet square) further validates the presence of a COOH acidic end-group and confirms the (H, OH) assignment. As compared to the unresolved or fuzzy KMD plots, points are perfectly aligned in the RKM plot throughout the whole mass range in spite of using different external calibrants (one per fraction). The isotopic shift ($^{12}C \rightarrow {}^{13}C$) is clearly seen while increasing the chain length (from ^{12}C to $^{13}C_{16}$ for the largest chains, Fig. 5B). The high separating power of the RKM plot allows a rapid filtering of a given ion series (full series or fixed isotopic composition) over the whole mass range using the “Grouping Mode” of msRepeatFinder (Fig. 6, red bars assigned to (H, OH)-ended PCL from 2 kDa to 20 kDa).

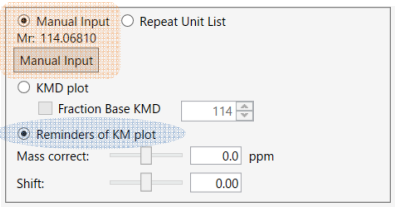
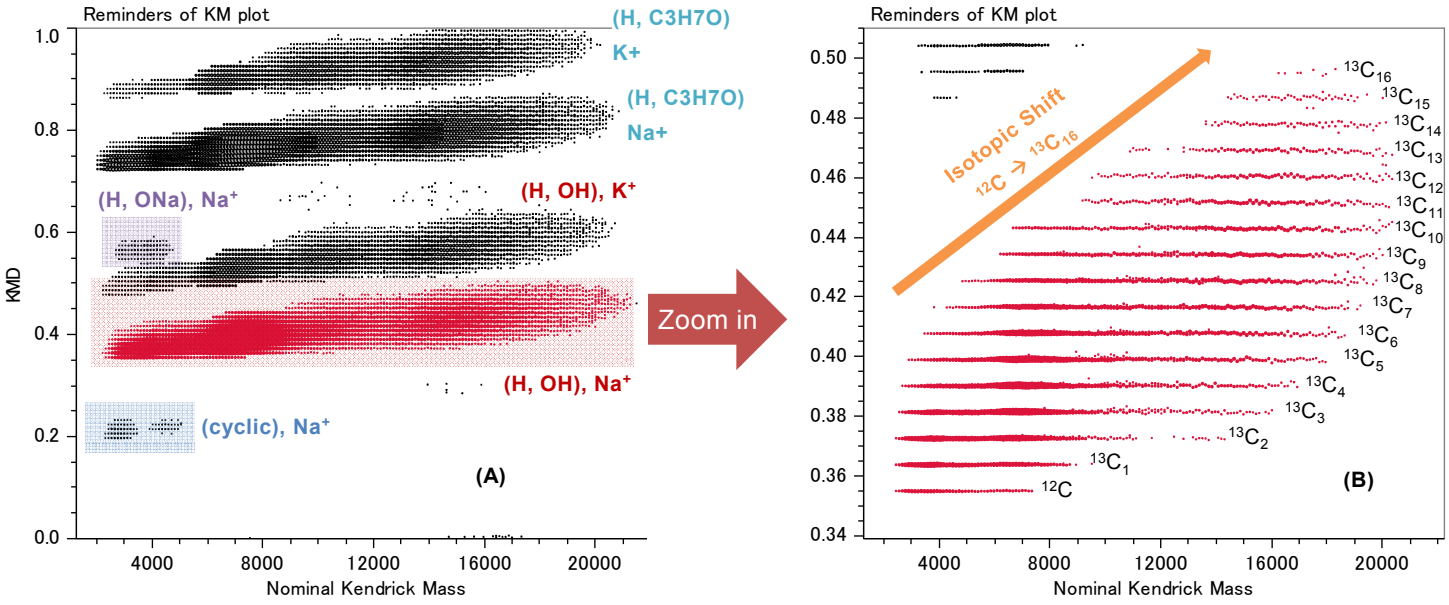


Fig. 5. RKM plots from the concatenated mass spectra. (A) Full plot with assignments of end-groups. (B) Detail of the sodiated (H, OH) ion series.



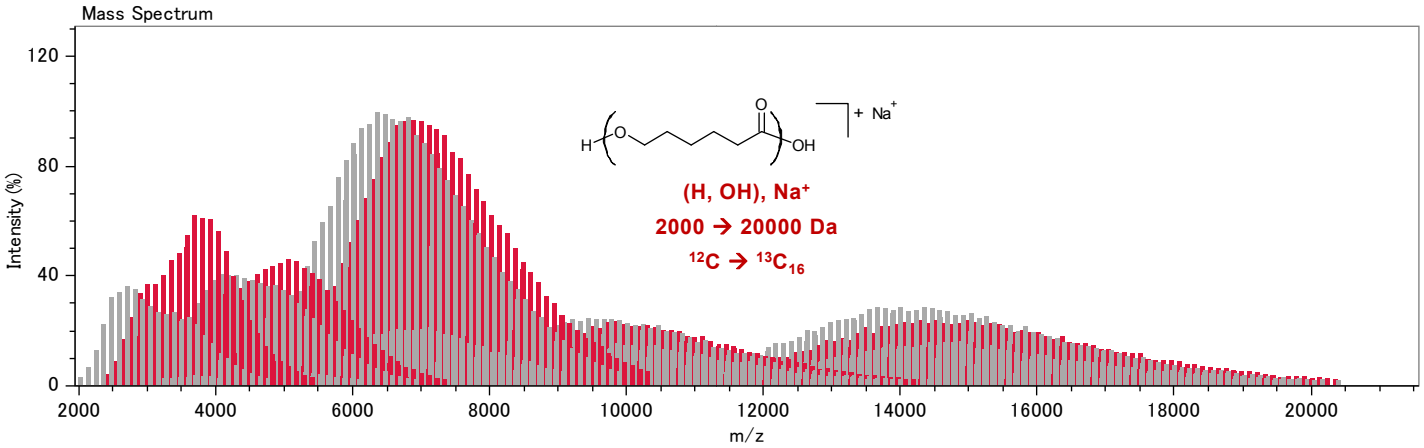


Fig. 6. Instant selection of the whole sodiated (H, OH)-PCL series throughout the 20kDa mass range (five fractions at once) using the "grouping mode" of msRepeatFinder.

Prospects

The RKM plots are compatible with high-accuracy and low-accuracy mass spectral data from the SpiralTOF™ analyzer (isotopic resolution) and the linear TOF analyzer (oligomeric resolution) of the JMS-S3000 mass spectrometer [3]. It is also compatible with multiple charging potentially observed in the MALDI-MS analysis of high molecular weight polymers [4].

Acknowledgment

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References

[1] H. Sato, S. Nakamura, K. Teramoto, T. Sato. *J. Am. Soc. Mass Spectrom.* **2014**, *25*, 1346–1355.
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[3] T. Fouquet, T. Satoh, H. Sato. *Anal. Chem.* **2018**, *90*, 2404–2408.
[4] T. Fouquet, R. B. Cody, Y. Ozeki, S. Kitagawa, H. Ohtani, H. Sato. *J. Am. Soc. Mass Spectrom.* **2018**, 29, 1611-1626.

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