"Remainders of KM" plot for polymers using msRepeatFinder: compositional mapping over a broad mass range
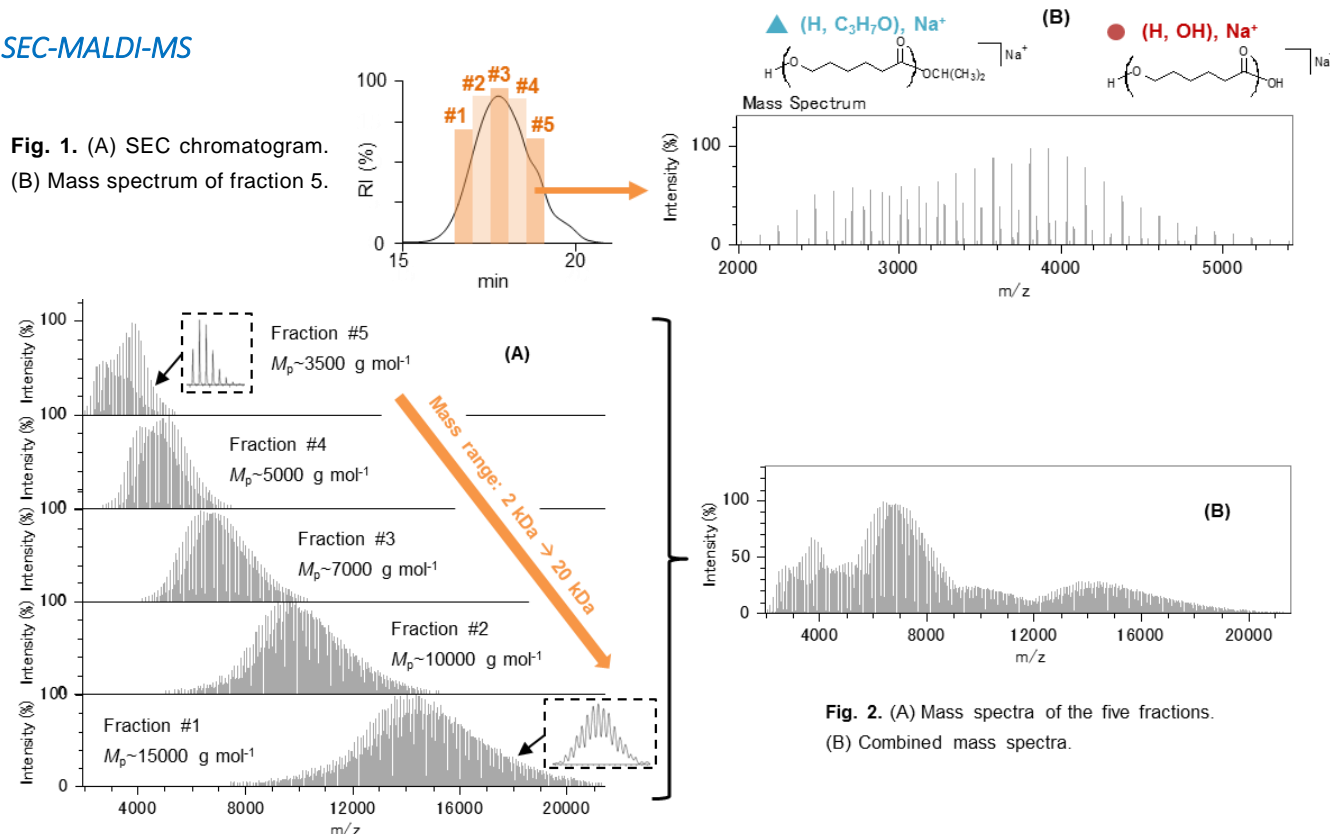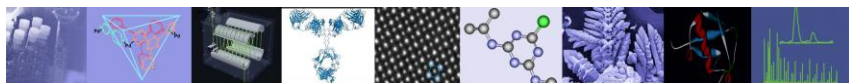
Product: JMS-S3000

Introduction

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, as the resolution gets higher, more peaks are detected in the mass spectrum for each fraction, making the interpretation of the mass spectral data the rate-limiting step for the whole analytical procedure. In this work, a "remainders of Kendrick mass" (RKM) analysis is used as a rapid post-acquisition data processing tool that uses visual maps from combined 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 by using a JEOL JMS-S3000 SpiralTOF™ mass spectrometer (matrix: DCTB, no salt added). The plots were computed by using msRepeatFinder 3.0 (JEOL Ltd.).

SEC-MALDI-MS

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

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

Five fractions were collected from the SEC elution turning the PCL sample into aliquots with low dispersity (Fig. 1A). The main distributions in the last fraction (*m/z* 2000 to 5000, Fig. 1B) were assigned to sodiated (H, OH)-terminated PCL (red circles) and (H, C_3H_7O)-terminated PCL (blue triangle) taking full advantage of the analyzer's high resolution capability. The SpiralTOF™ analyzer was also able to produce mass spectra for the four other fractions with increasing molecular weights up to 20000 Da with isotopic resolution (Fig. 2A). The mass spectra were then combined using msRepeatFinder to display the full mass spectral data in one graph (Fig. 2B).

Kendrick mass defect (KMD) plots

The standard KMD plot from the concatenated mass spectra barely separates the sodiated (H, OH)- and (H, C_3H_7O)-terminated oligomers in the lowest mass range, but the plot becomes unresolved as the chain lengths increased (Fig. 3). In spite of the isotopic resolution reached by the SpiralTOF™ analyzer, the mass accuracy was not high enough for a standard KMD analysis. The resolution-enhanced KMD plot using a fractional base unit CL/113 (Fig. 4) successfully separated the four main distributions (sodiated and potassiated (H, OH)- and (H, C_3H_7O)-terminated oligomers) over the whole mass range. Nevertheless, the separating power decreased as the molecular weight increased, resulting in the plot becoming fuzzy with low quality point alignment.
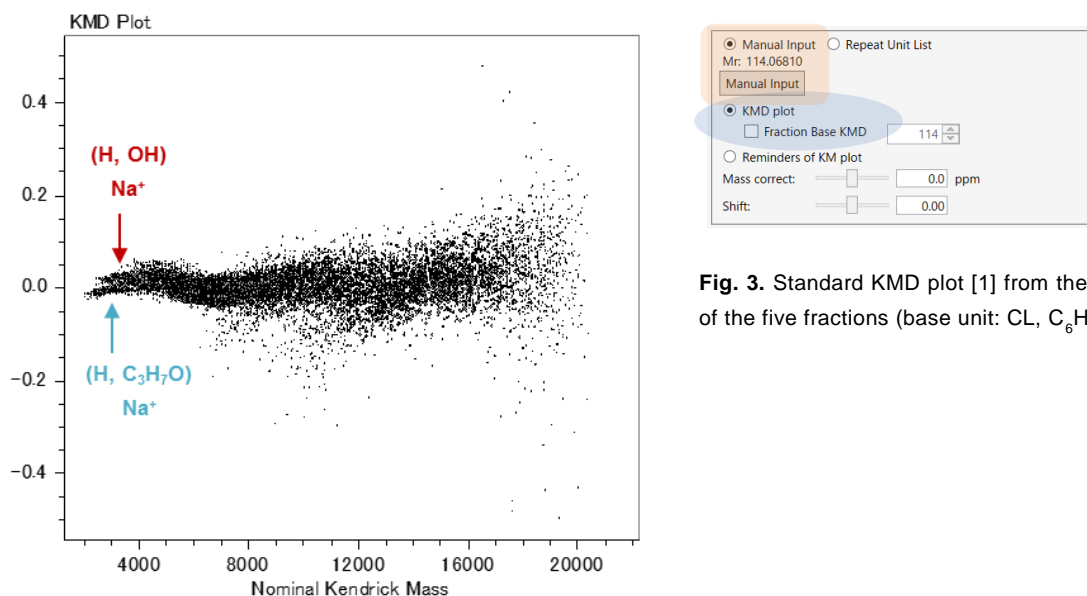

Fig. 3. Standard KMD plot [1] from the combined mass spectra of the five fractions (base unit: CL, $C_6H_{10}O_2$, 114.0681).
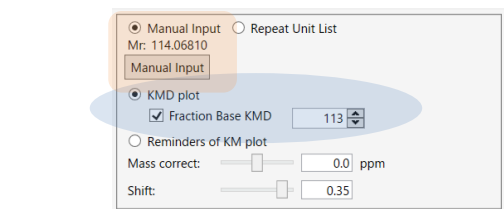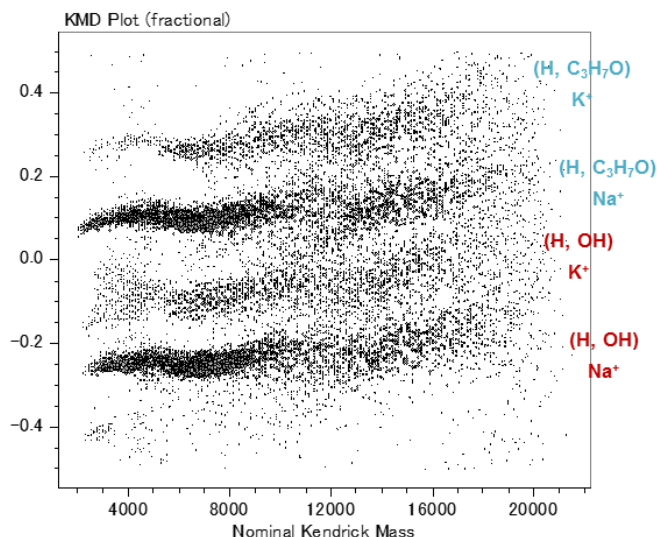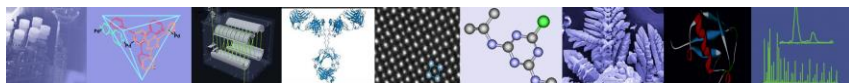

Fig. 4. Resolution-enhanced KMD plot [2] from the combined mass spectra for the five fractions using the "fraction base KMD" option (base unit: CL/113).

Remainders of KM (RKM) plot

The RKM plot for the combined mass spectra revealed a great compositional homogeneity of PCL throughout a broad 20 kDa mass range for (H, OH)- and (H, C_3H_7O)-terminated chains (sodium and potassium adducts, Fig. 5A). An additional cyclic ion series was observed in the lowest mass range (fraction #5, blue square), which is typical for ring-opening and polycondensation synthesis routes. The detection of (H, ONa)-terminated oligomers seen in fraction #5 (violet square) further validated the presence of a COOH acidic end-group, thus confirming the (H, OH) assignment. As compared to the unresolved fuzzy KMD plots, the points are perfectly aligned in the RKM plot throughout the whole mass range in spite the fact that different external calibrants were used (one per fraction). The isotopic shift ($^{12}C \rightarrow {}^{13}C$) is clearly seen as the chain length increased (from ^{12}C to $^{13}C_{16}$ for the largest chains, Fig. 5B). The high separating power of the RKM plot allowed for a rapid filtering of each ion series (full series or fixed isotopic composition) over the whole mass range using msRepeatFinder "Grouping Mode" (Fig. 6, red bars assigned to (H, OH)-terminated PCL from 2 kDa to 20 kDa).
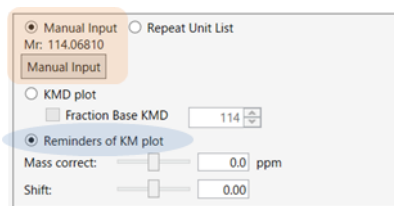

Fig. 5. RKM plots for the combined mass spectra. (A) Full plot with assignments of end-groups. (B) Details for the sodiated (H, OH) ion series.
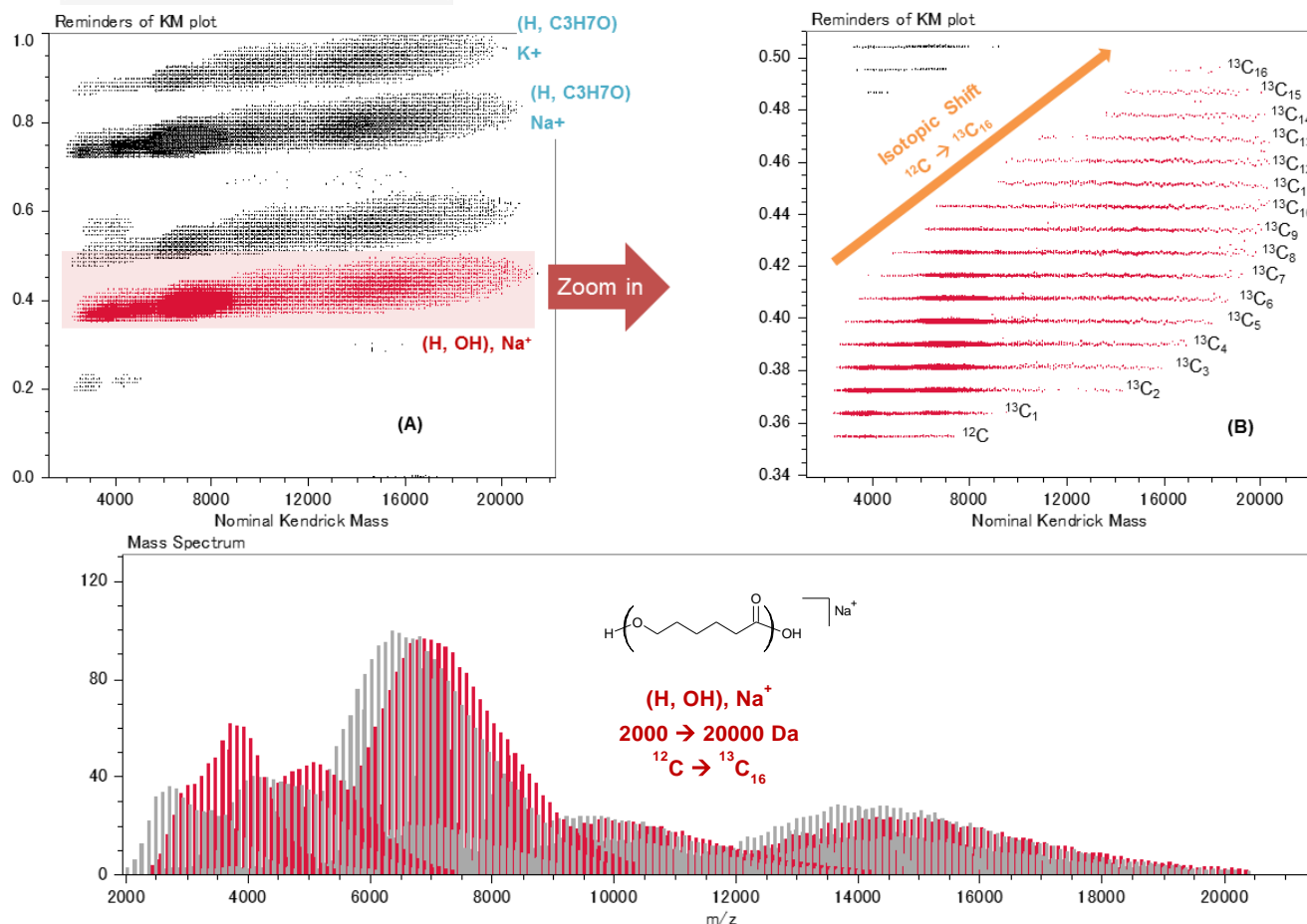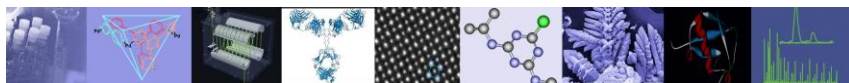

Figure 6. Instant selection of the whole sodiated (H, OH)-PCL series throughout the 20kDa mass range (five fractions at once) using the "grouping mode" of msRepeatFinder.

Prospects

The RKM plots worked well for the high-accuracy and low-accuracy mass spectral data from the SpiralTOF™ analyzer (isotopic resolution) and the linear TOF analyzer (oligomeric resolution) measured on the JMS-S3000 MS system [3]. It is also useful for multiply charged ions that can be potentially observed during MALDI-MS analysis of high molecular weight polymers [4].

References

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

[2] T. Fouquet, H. Sato. *Anal. Chem.* **2017**, *89*, 2682–2686.

[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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