

Improving the resolution of Kendrick mass defect analysis for polymer ions with fractional base units

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1) Values of the divisor X for a horizontal alignment

According to the basic KMD analysis, two oligomers of a same distribution have the same KMD value if calculated with the repeat unit of the distribution.¹⁾ In other words and using EO as the base unit, the *difference* of the KMD values for two PEO congeners (same distribution) is 0. Owing to the presence of round functions in the calculation of KM, NKM and KMD values, the influence of the use of the newly introduced fractional base units on those values is hard to predict and deserve to be plotted. The differences of the KMD values (noted Δ KMD) of simulated POE oligomers calculated with EO/X as the base unit are plotted in **Fig. S1** (A) with X as a natural number (positive integer) ranging from 1 to 10, (B) with X as a decimal number {1.0, 1.1, 1.2...} over the same range and C) as a continuous function. At first sight, all the values of the divisor X which lead to a non-null value for Δ KMD should be dismissed since they will not lead to the expected horizontal alignments in the KMD plots. Several values of X cancel out the difference of KMD (i.e. the two oligomers would be horizontally aligned in the associated KMD plot) but it is remarkable to notice all the natural numbers allow Δ KMD to be 0 (**Fig. S1A**). The associated fractional values of the repeat unit (i.e. EO/2, EO/3, EO/4...) will thus be the only values considered in this preliminary study for the sake of simplicity.

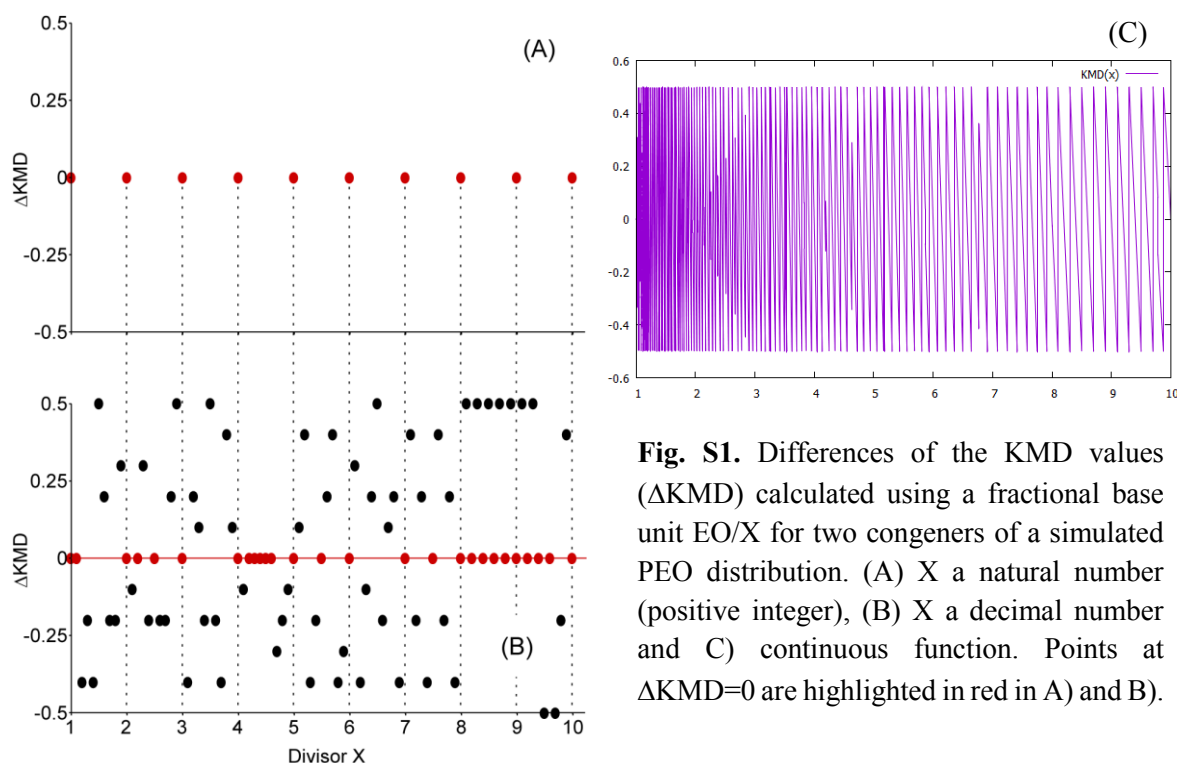


Fig. S1. Differences of the KMD values (Δ KMD) calculated using a fractional base unit EO/X for two congeners of a simulated PEO distribution. (A) X a natural number (positive integer), (B) X a decimal number and (C) continuous function. Points at Δ KMD=0 are highlighted in red in (A) and (B).

- 1) H. Sato, S. Nakamura, K. Teramoto, T. Sato. Structural Characterization of Polymers by MALDI Spiral-TOF Mass Spectrometry Combined with Kendrick Mass Defect Analysis. *J. Am. Soc. Mass Spectrom.* 25: 1346-1355, 2014.

2) Coefficients of expansion for different repeat units

The coefficient of expansion ε ($\Delta\text{KMD}^{(13\text{C}, 12\text{C})_{\text{EO}/X}} / \Delta\text{KMD}^{(13\text{C}, 12\text{C})_{\text{EO}}}$) is readily evaluated theoretically as a function of the divisor X by simulating the composition of two oligomers and calculating the associated KMD of ^{12}C and $^{13}\text{C}_1$ species. The so-calculated coefficients for a set of representative repeat units - namely ethylene (E, 28 Da), ethylene oxide (EO, 44 Da), propylene oxide (PO, 58 Da), dimethylsiloxane (DMS, 74 Da), vinyl acetate (VA, 86 Da), vinyl pyrrolidone (VP, 111 Da) and ethylene terephthalate (ET, 192 Da) - are depicted in **Fig. S2A**. No general trend is found in terms of X value (with an *apparent* random evolution of $\varepsilon(X)$) but it appears that the average coefficient of expansion ε tends to decrease if the mass of the repeat unit is increasing. Such evolution is highlighted in **Fig. S2B** with the plot of the amplitude of the expansion ($\varepsilon(\text{max}) - \varepsilon(\text{min})$) as a function of the mass of the repeat unit, exhibiting a clear exponential-like decay. In other words, it means an optimum value for the divisor X will be larger and larger as the repeat unit is becoming bigger and bigger.

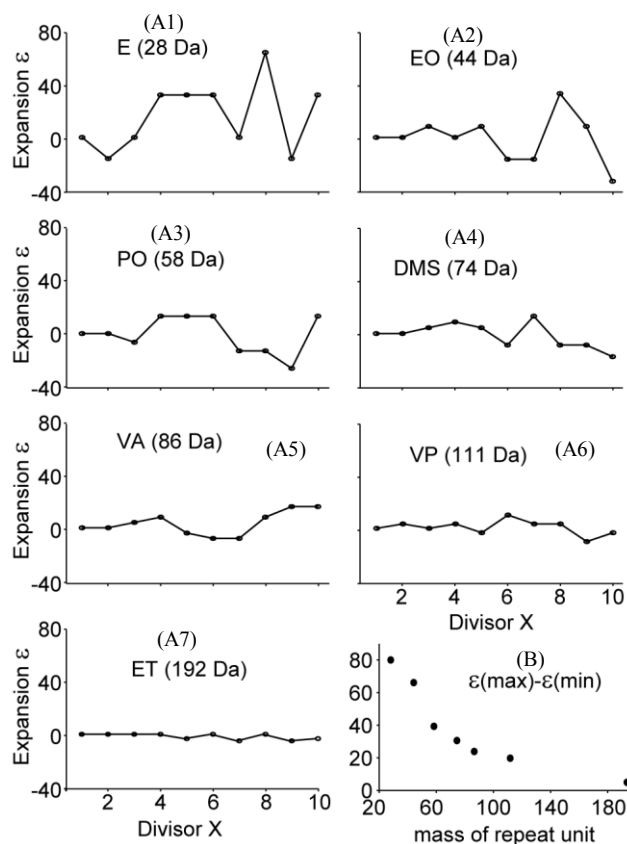


Fig. S2. (A) Coefficients of expansion ε of the KMD plot calculated for ethylene (E), ethylene oxide (EO), propylene oxide (PO), dimethylsiloxane (DMS), vinyl acetate (VA), vinyl pyrrolidone (VP) and ethylene terephthalate (ET) as a function of the divisor X . (B) $\varepsilon(\text{max}) - \varepsilon(\text{min})$ as a function of the mass of the repeat unit.

This situation is exemplified below for the case of a PET sample (MALDI MS spectrum depicted in **Fig. S3A** displaying three distributions from three sets of end-groups). Its KMD plot using ET as the base unit (**Fig. S3B**) do not discriminate the three series in a satisfactory extent. Using ET/5 offers a good separation of the three end-group sets but fails at resolving the isotope pattern (**Fig. S3C**). Contrary to the case of EO (44 Da) and DMS (74) for which EO/3 and DMS/6 are the best fractional base units, the value of the divisor X has to be increased up to 14 (isotope resolution, **Fig. S3D**) and 15 (end-groups discrimination + isotope resolution, **Fig. S3E**) for ET (192 Da) to obtain a satisfactory expansion of the KMD dimension and an indubitable improvement of the data visualization.

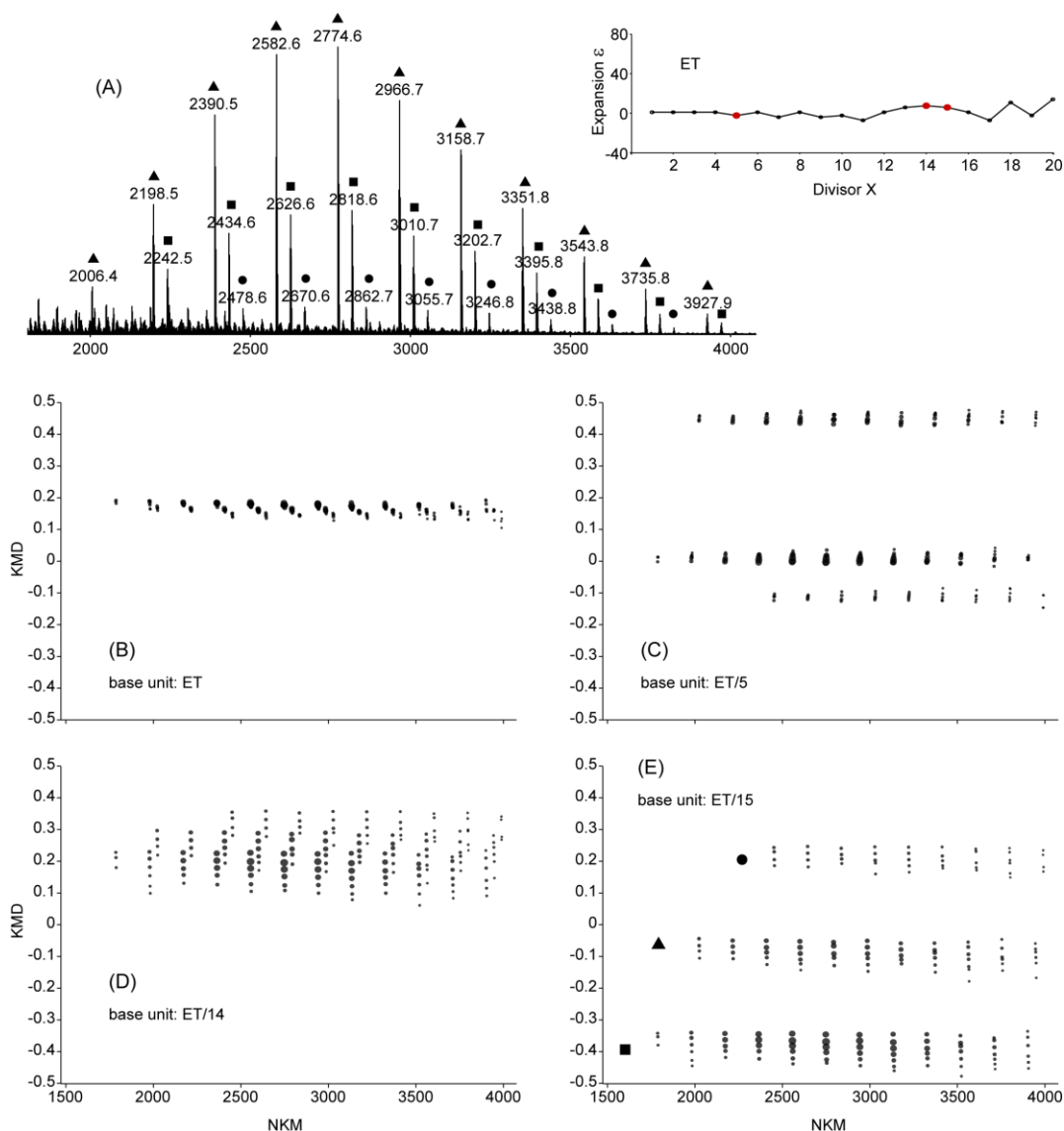


Fig. S3. (A) MALDI-MS spectrum of a PET sample (three distributions marked with black triangles, squares and circles). The variation of the coefficient of expansion with the divisor X is depicted in inset. (B-E) KMD plots using ET, ET/5, ET/14 and ET/15 as the base units.