

Visualizing fragmentation channels of polyethylene oxide with different end groups using the JMS-S3000 SpiralTOF™ with TOF–TOF option

Product used: Mass Spectrometry (MS)

Tandem mass spectrometry is a powerful tool for polymer characterization. It can obtain information about polymer end groups, repeating structures (linear, cyclic, or branched), and copolymerization. High-energy collision–induced dissociation (HE–CID) is a fragmentation method that is available only in tandem time-of-flight mass spectrometry (TOF–TOF). The informative fragmentation channels, which are difficult to observe with commonly used low-energy CID, are often observable in HE–CID spectra. In MSTips 270, we proposed a method to visualize this abundant structural information and enable intuitive analysis using the “Remainders of KM” (RKM) plot method. In this report, we applied the method to analyze polyethylene oxide (PEO) with different end groups.

Experiment

We dissolved polypropylene glycol HO (C₂H₄O)_nH, polyethylene glycol monolauryl ether HO (C₂H₄O)_nC₁₂H₂₅, and polyoxyethylene monocetyl ether HO (C₂H₄O)_nC₁₆H₃₃ in methanol (10 mg/mL). We used α-cyano-4-hydroxycinnamic acid (α-CHCA; 10 mg/mL in methanol) and sodium trifluoroacetate (NaTFA; 10 mg/mL in methanol) as matrix and cationizing agent, respectively. The sample, α-CHCA, and NaTFA were mixed at 1:10:1 (v/v/v), spotted on a target plate, and air dried. Product-ion spectra were acquired in positive-ion mode using JMS-S3000 SpiralTOF™ with the TOF–TOF option. We analyzed the data using msRepeatFinder version 3.0.

Product ion spectra

All product-ion spectra showed strong sodium-adduct ions [M+Na]⁺. The HE–CID spectra were acquired by selecting [HO(C₂H₄O)₂₈H+Na]⁺ (*m/z* 1273.7), [HO(C₂H₄O)_nC₁₂H₂₅+Na]⁺ (*m/z* 1265.8) and [HO(C₂H₄O)_nC₁₆H₃₃+Na]⁺ (*m/z* 1277.9) as precursor ions (Fig. 1). The red arrows in each product-ion spectrum in Figure 1 represent the mass difference corresponding to 44u (C₂H₄O). Several fragmentation channels with 44u interval were observed in each product ion spectrum; however, it is time consuming to assign each series one by one. Also note that the differences between the three polymers cannot be understood intuitively.

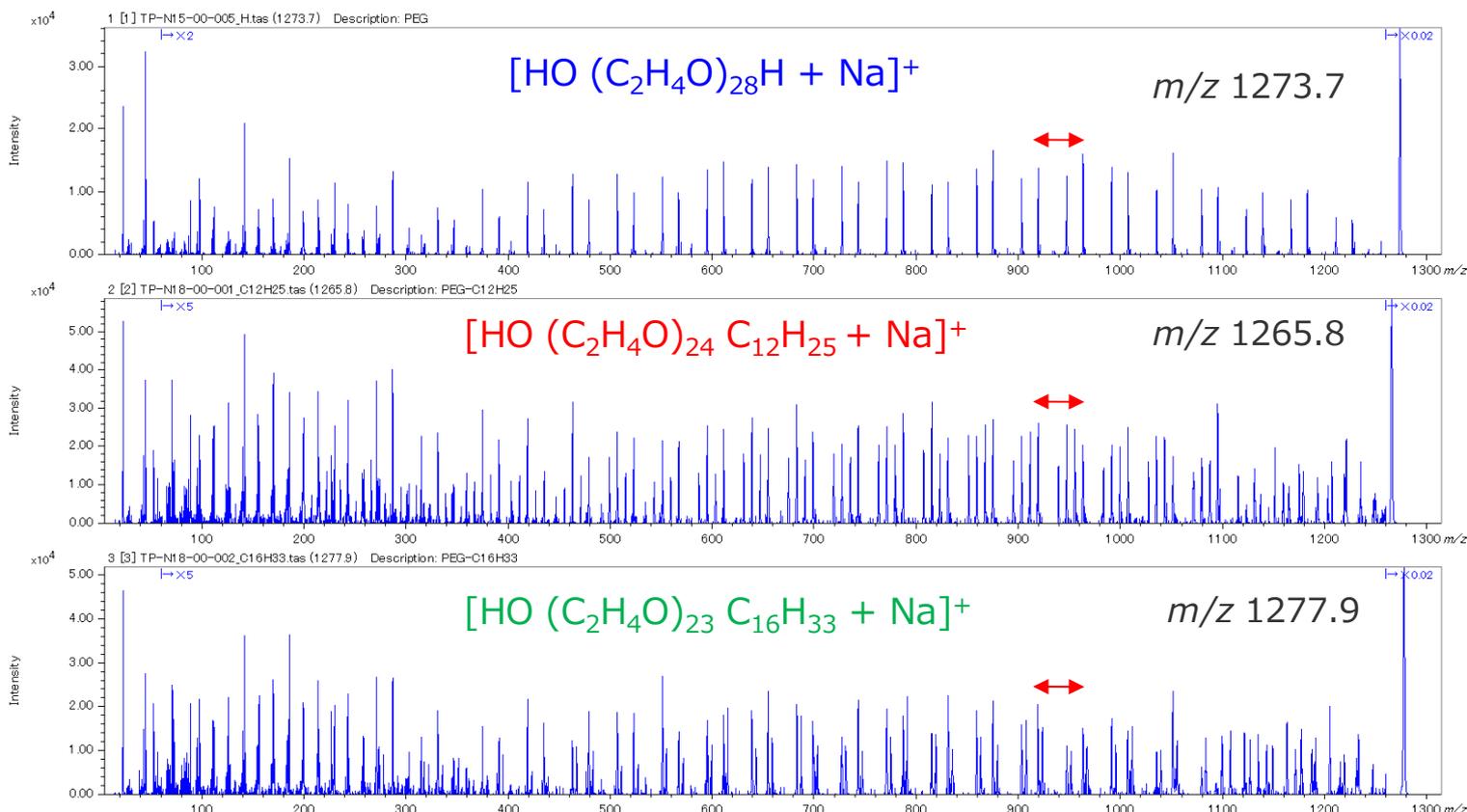


Figure 1. Product ion spectra of three types of polyethylene oxides.

Visualization of polymer series with Remainders of KM (RKM) plot

In Figure 2 below, product ion spectra of three types of PEO are overlaid in an RKM plot (base unit EO). We excluded the precursor and sodium ions from the display region in order to clarify the fragmentation channels of the repeating structures. In this figure, the peak colors of $[\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{H}+\text{Na}]^+$, $[\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{C}_{12}\text{H}_{25}+\text{Na}]^+$, and $[\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{C}_{16}\text{H}_{33}+\text{Na}]^+$ are overlaid as blue, red, and green, respectively. The peak series displayed in black denote fragment ions commonly observed in all three types of PEOs. The fragmentation peak series in the RKM plot of Figure 2 are divided into three characteristic parts, each of which is confirmed in Figures 3–5, respectively.

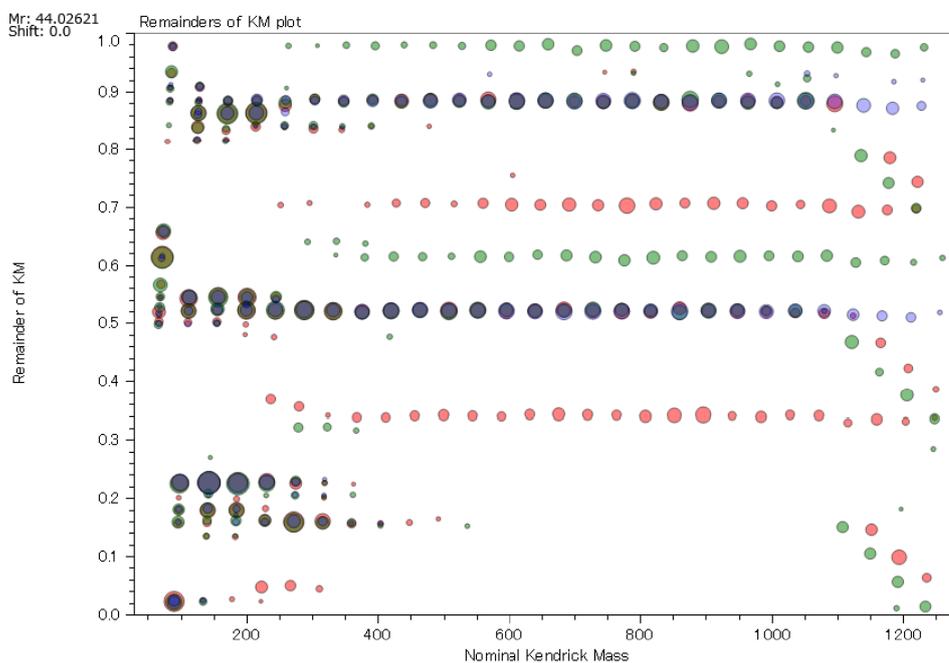


Figure 2. Overlaid RKM plot (base unit: propylene oxide $\text{C}_2\text{H}_4\text{O}$ from the repeat unit list) of three PEO types

First, we focused on the black series (Fig. 3), i.e., the series commonly observed in all product ion spectra. These two series were considered to be fragmentation channels that did not include different end-group structures. We confirmed them to be the fragmentation channels shown in Figure 3, which we observed as $[\text{M}+\text{Na}]^+$.

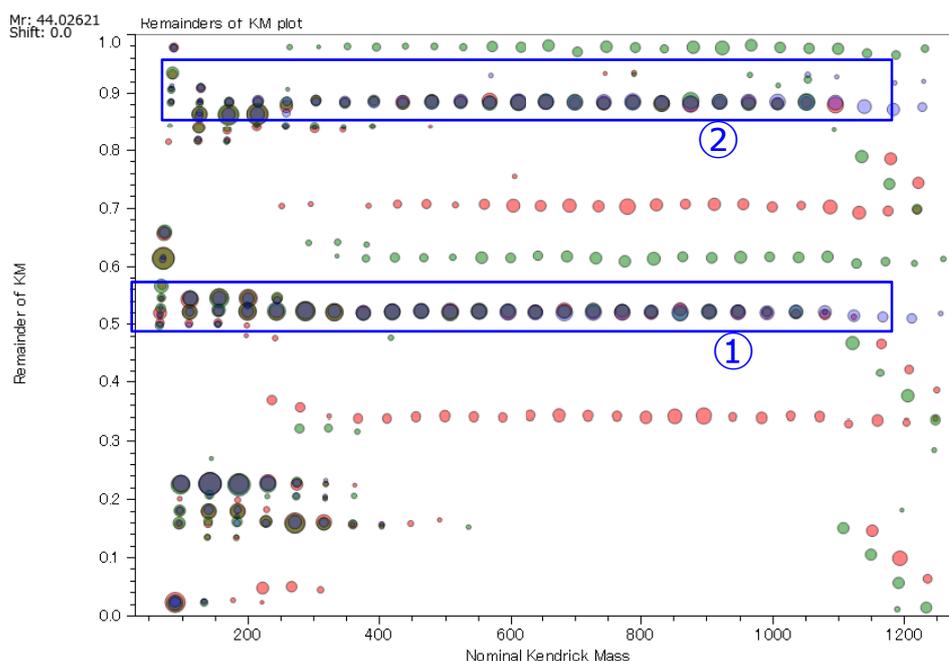
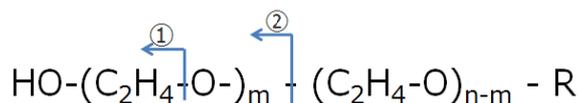


Figure 3. Common peaks in RKM plot of three types of polyethylene oxides.

Second, we focused on the series of red and green (Fig. 4). These four series were considered to be fragmentation channels, which included different end-group structures. We confirmed these as the fragment channels shown in Figure 4, which we observed as $[M+Na]^+$. Third, we focused on the series with slope (Fig. 5), which we observed in the part near the precursor ion (right side of RKM plot). "Series with slope" are series without 44u intervals. They have 14u (CH_2) intervals and are assigned to be the alkyl chain cleavage, which is a unique fragmentation channel in HE-CID.

Conclusion

It is easy to visualize the fragmentation channels of polymer series using an RKM plot. By overlapping product-ion spectra obtained from precursor ions with different end groups in an RKM plot, fragmentation channels common to all PEOs can be distinguished from fragmentation that is dependent on end-group composition. This is a proven method for helping to analyze different series of end groups observed in the mass spectra of polymers in real samples.

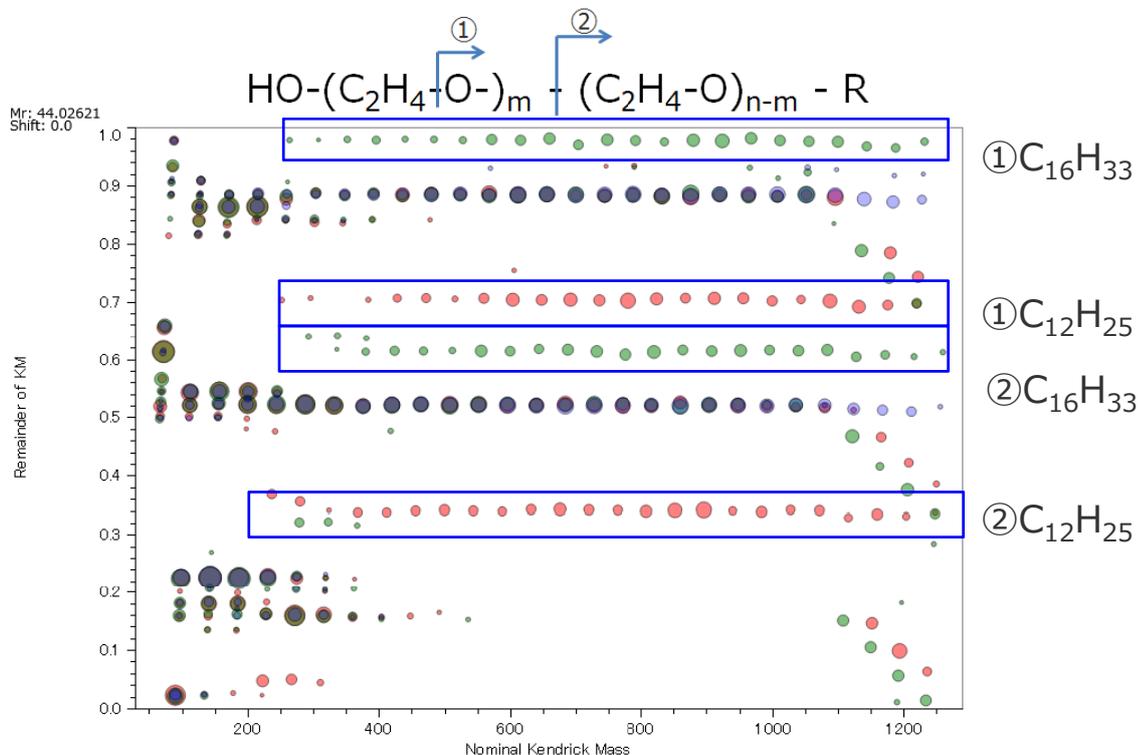


Figure 4. Peaks that are dependent on end group composition.

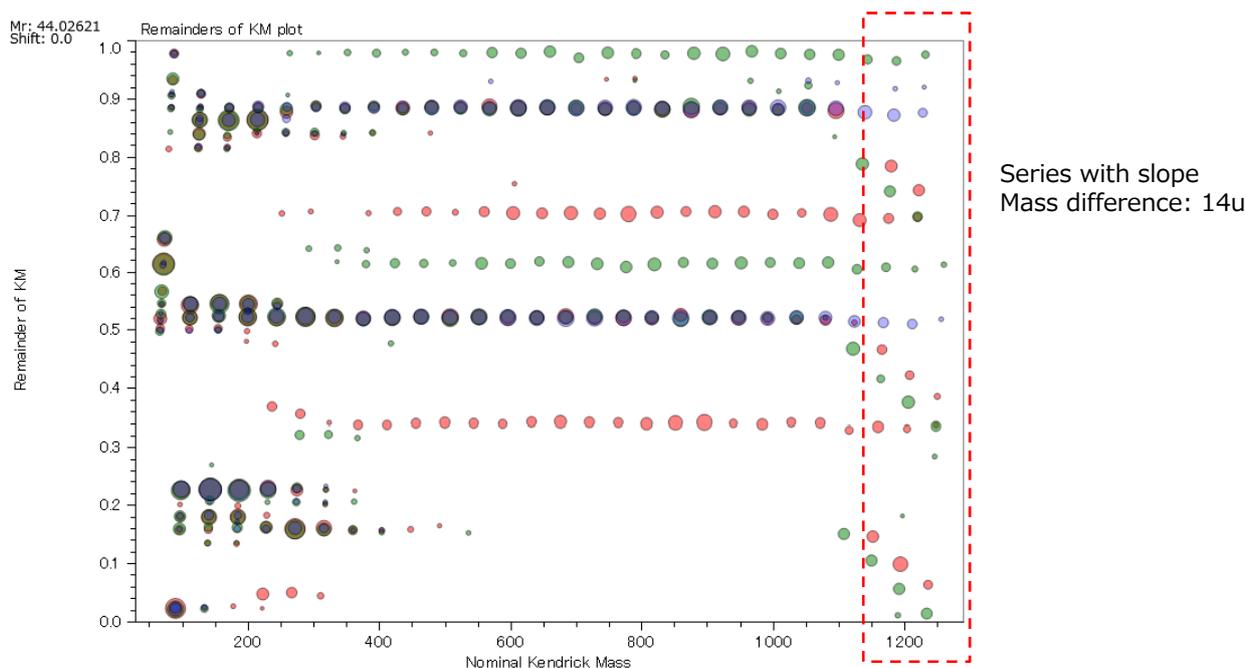


Figure 5. Peaks originating from charge-remote fragmentation of the alkyl chain in the end group.

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