SpiralTOF™

Analysis of EO-PO Random Copolymer by Using a Conventional HPLC and MALDI SpiralTOF MS

Introduction

Ethylene oxide (EO) – propylene oxide (PO) copolymers have been used as components of various functional materials. Detailed analyses of them, however, still remain challenging. As it turns out, it is difficult to detect all of the components by using mass spectrometry alone without chromatographic separation due to ion suppression effects. In this work we analyzed an EO-PO random copolymer by using an LC – MALDI-SpiralTOF MS system, with the expectation of detecting more components as a result of reduced ion suppression effects.

Experimental

A commercially available EO-PO random copolymer (Mn ~ 2,500) as shown in Fig. 1 was dissolved in water and used for the analyses. The mass spectrum shown in Fig. 2 was obtained by analyzing the sample solution with MALDI – SpiralTOF MS without HPLC separation.
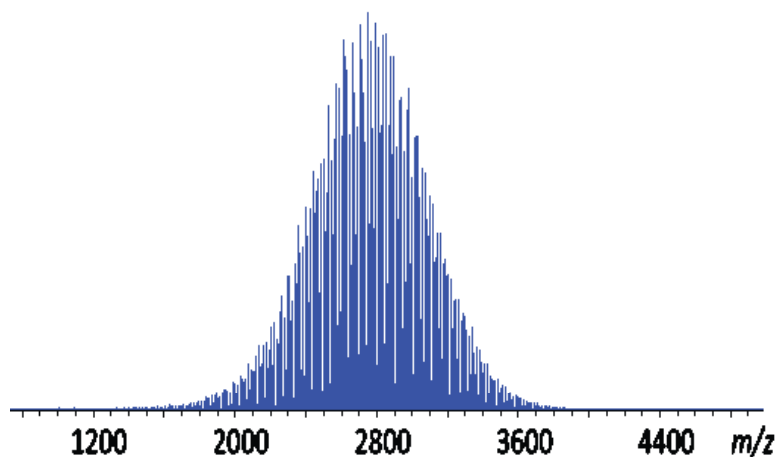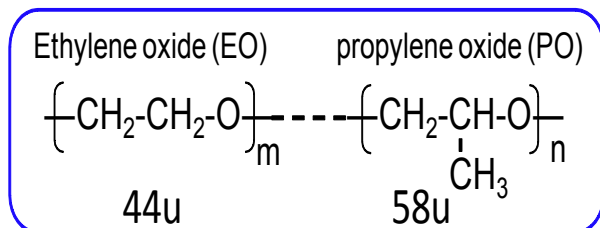

Fig.2 MALDI mass spectrum of EO-PO copolymer

Figure 1. EO-PO copolymer

Analytical conditions:
- HPLC system: Agilent 1200SL
- Mobile phase: A: water, B: Methanol
- Flow rate: 0.2 mL/min
- Injection volume (to the HPLC): 20 μL
- HPLC column: Imtakt Cadenza CD-C18 (150 x 2.0 mm)
- Fractionation: every 15 seconds (50 μL/fraction)
- Mass spectrometer: JMS-S3000 SpiralTOF (automated analysis with Spiral, Positive Ion mode)
- Amount of sample used for MS analysis: 1 μL from each fraction (no further concentration performed)
- Matrix / cationization agent: CHCA/NaI (in methanol)
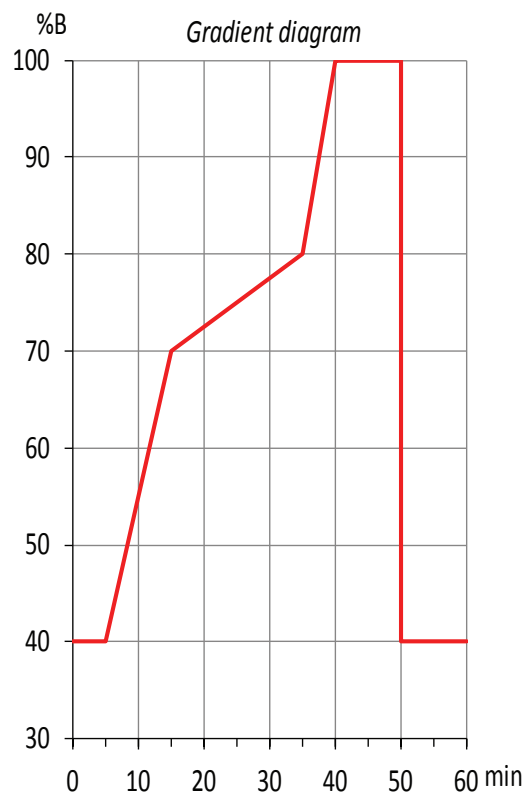- Target plate: HST μFocus 900 μm

Fig.3 Solvent gradient condition

Results and Discussion

Mass spectra acquired through automated measurements are shown in the "Survey View" of the msTornado Analysis software (Fig. 4). By assigning the signals in the data, it was found that the components were separated by HPLC according to the number of PO units in the components; the more PO units, (which are hydrophobic), present in a component, the later the observed retention time. Components with different numbers of PO units were separated by retention time; whereas components with different numbers of EO units were detected as peaks that are separated by m/z 44 in each mass spectrum.

At retention times before 22 min, hydrophilic components with more EO units and less PO units were detected below m/z 1,600. These hydrophilic components were not observed on Fig. 2 and were detected only after HPLC separation. Since detection of these components had not been expected, the gradient profile (Fig. 3) was not optimum for separating them according to the number of PO units present in them.

A comparison between with and without HPLC separation is shown on Fig. 5. Based on the peak pattern in the mass spectrum before separation (top), it is easy to surmise that the most abundant component EO47-PO11 (red) and another component EO39-PO17, which is 2 Da lower, are overlapping. However, peaks derived from a minor component EO39-PO17 (green) are barely discernible from the baseline noise. With HPLC separation, all overlapping minor components, including EO51-PO8 (purple) and EO55-PO5 (blue) are clearly observed with good S/N.
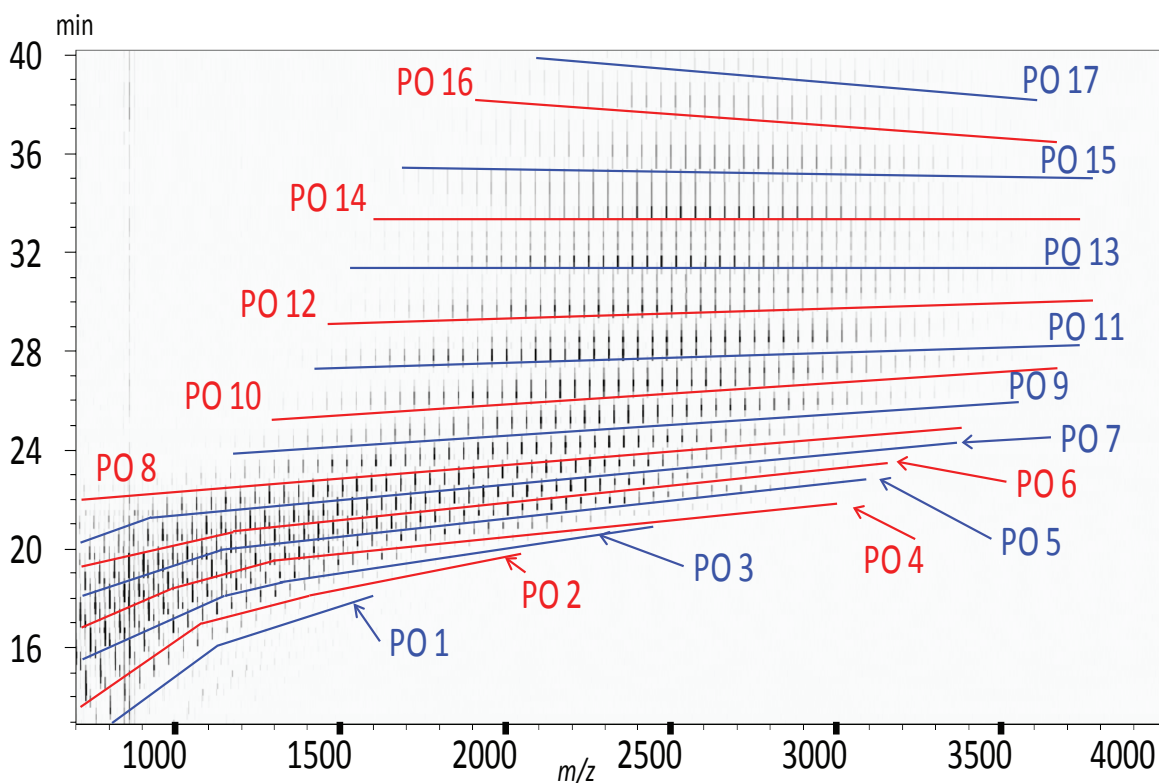

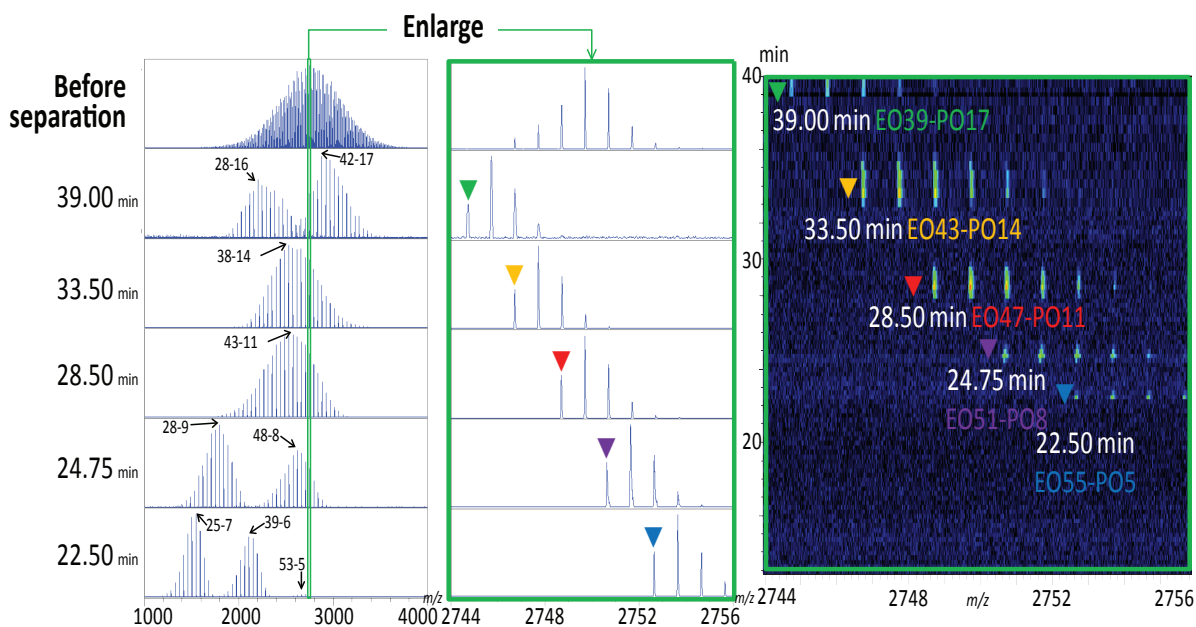Fig 4. Signal assignments on the "Survey View" of the msTornado Analysis software.

Fig.5 HPLC separation effect to reduced ion suppression (m/z 2744-2756)

Conclusion

Using a combination of conventional HPLC and MALDI-SpiralTOFMS is more effective in detecting the components of a complex EO-PO random copolymer than MALDI-TOF alone. Additionally, since MALDI predominantly produces single-charge ions, the distribution for the large number of components present in the sample was observed intuitively through the "Survey View" of the msTornado Analysis software.