Structural analysis of polyethylene terephthalate combining an on-plate alkaline degradation method and tandem time-of-flight mass spectrometry

Product：Mass spectrometry(MS)

Introduction

Matrix assisted laser desorption/ionization (MALDI) mass spectrometry is a powerful tool for the analysis of synthetic polymers. This technique, when combined with a high-resolution time-of-flight mass spectrometer, can be used to identify differences in monomer, polymer end groups, and their molecular weight distributions. However, there are limitations to doing accurate mass analysis of high molecular weight polymers. For example, as the polymer molecular weight increases, the ionization efficiency, detection sensitivity, and ratio of monoisotopic ions used for accurate mass analysis all decrease. One way to address this is to use an "on-plate alkaline degradation" method [1] that was previously published in which high molecular weight polyester or polycarbonate are partially hydrolyzed by an alkaline reagent to form smaller oligomers that can then be analyzed by high-resolution MALDI-TOFMS. This degradation into oligomers is not only advantageous for accurate mass analysis but also for structural analysis by using tandem time-of-flight mass spectrometry (TOF-TOF). In this report, we investigated the structural analysis of the polyethylene-terephthalate (PET) polymer exposed to the on-plate alkaline degradation method by using the JMS-S3000 "SpiralTOF™-plus" with TOF-TOF option. The SpiralTOF™-plus uses an ultra-high resolution TOF for MS1 which allows monoisotopic precursor selection and a reflectron TOF for MS2 to analyze the product ion spectra produced from high energy collisional induced dissociation (HE-CID).

Experiment

PET (film) was dissolved in hexafluoro-2-propanol (HFIP) solution at a concentration of 10 mg/ml. The matrix compound 2,4,6-trihydroxyacetophenone (THAP) was dissolved in HFIP/tetrahydrofuran (THF) at a concentration of 10 mg/ml. Sodium hydroxide (NaOH) 10 mg/ml methanol solution was used for on-plate alkaline degradation. The high resolution mass spectra were measured by using SpiralTOF positive ion mode, and HE-CID measurements were performed in TOF-TOF positive ion mode.

[Sample treatment for on-plate alkaline degradation]

1. Spot the sample solution on the target plate.
2. Spot and dry the NaOH solution on the sample spot.
3. After on-plate decomposition, the sample spot was desalted with purified water.
4. Spot the THAP HFIP/THF solution on the dried sample spot.

Results

Figure 1 shows the mass spectra before and after applying the on-plate alkaline degradation method. Before the on-plate alkaline degradation, there were two characteristic cyclic oligomer series observed in the mass spectrum. However, after the on-plate decomposition, there were 10 different series observed in the sample. The proposed structures for peaks 1-3 are shown in Figure 1C.
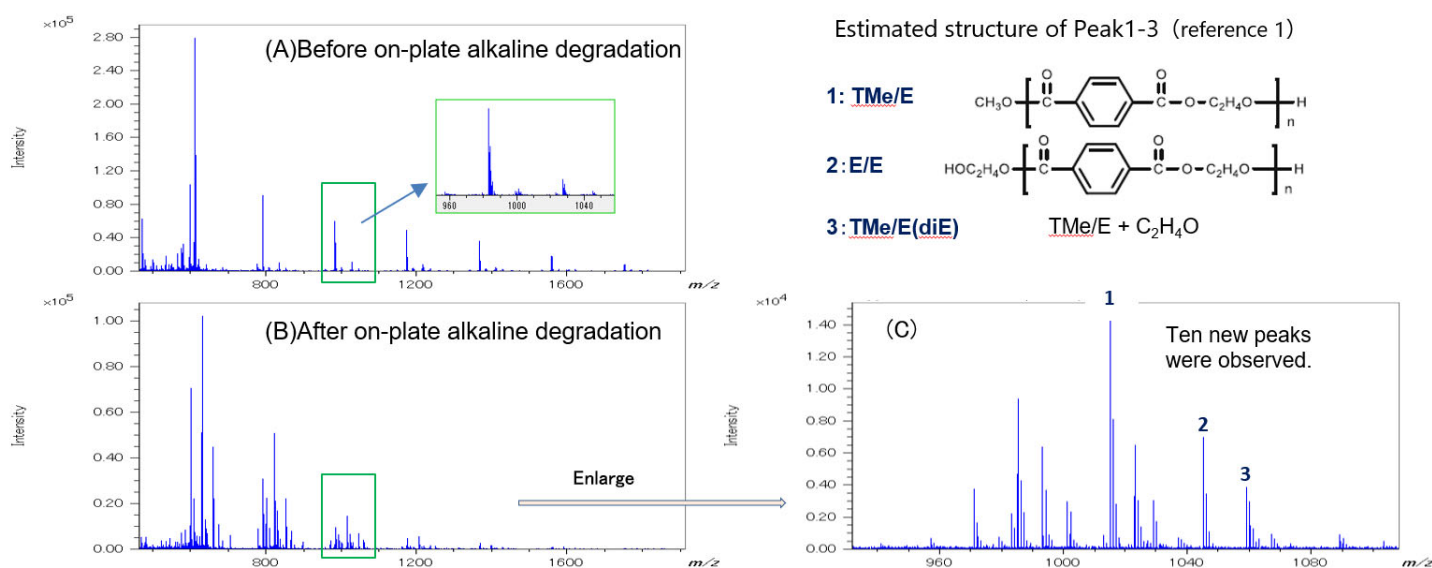

Figure 1. The mass spectra of PET oligomer (A) before and (B) after on-plate alkaline degradation treatment.
(C) Enlarged mass spectrum of PET after on-plate alkaline degradation.

Next, the $C_{10}H_8O_4$ KMD plots for the before and after on-plate alkaline degradation mass spectra are shown in Figure 2A and 2B, respectively. The before degradation sample showed two distinct series (blue: Cyclic, red: Cyclic + C_2H_4O). However, the after degradation sample showed a lower intensity for the original series as well as the emergence of several new series in the sample. The three series discussed in Figure 1C are colored as green: TMe/E, yellow: E/E, and orange: TMe/E(diE),.
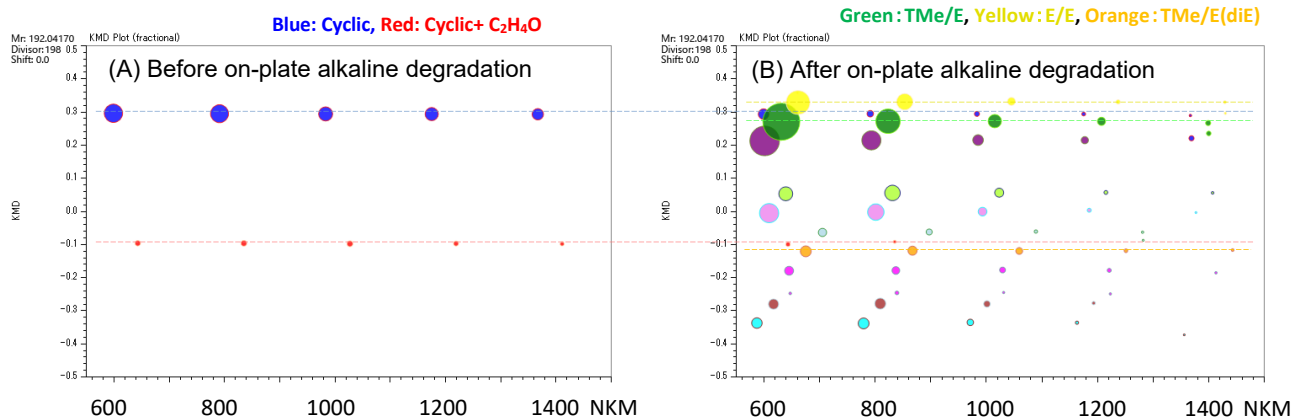

Figure 2. The KMD plots of PET before(A) and after(B) on-plate alkaline degradation（base unit $C_{10}H_8O_4$:192.04, x=198）

Three oligomers generated by on-plate alkaline degradation were selected for TOF-TOF analysis: TMe/E (*m/z* 1015), E/E (*m/z* 1045) and TMe/E(diE) (*m/z* 1059). Figures 3 and 4 show the product ion spectra for these ions. The product ion spectra showed common ions as well as several mass spectral peaks with separation intervals of 192u, which all suggest that these ions have similar structures. The estimated structure (n=5) and the fragmentation position are shown in each product ion spectrum. First, the E/E product ion spectrum (Figure 3A), which has the same end-group structure at both ends, was analyzed, and the product ions highlighted with blue arrows were used to support the estimated structure. Next, the product ion spectrum of TMe/E (Figure 3B), which has one end-group that is different from E/E, showed unique ions that were labeled with red arrows. The red and blue arrows highlight all of the product ions that supported this structure.
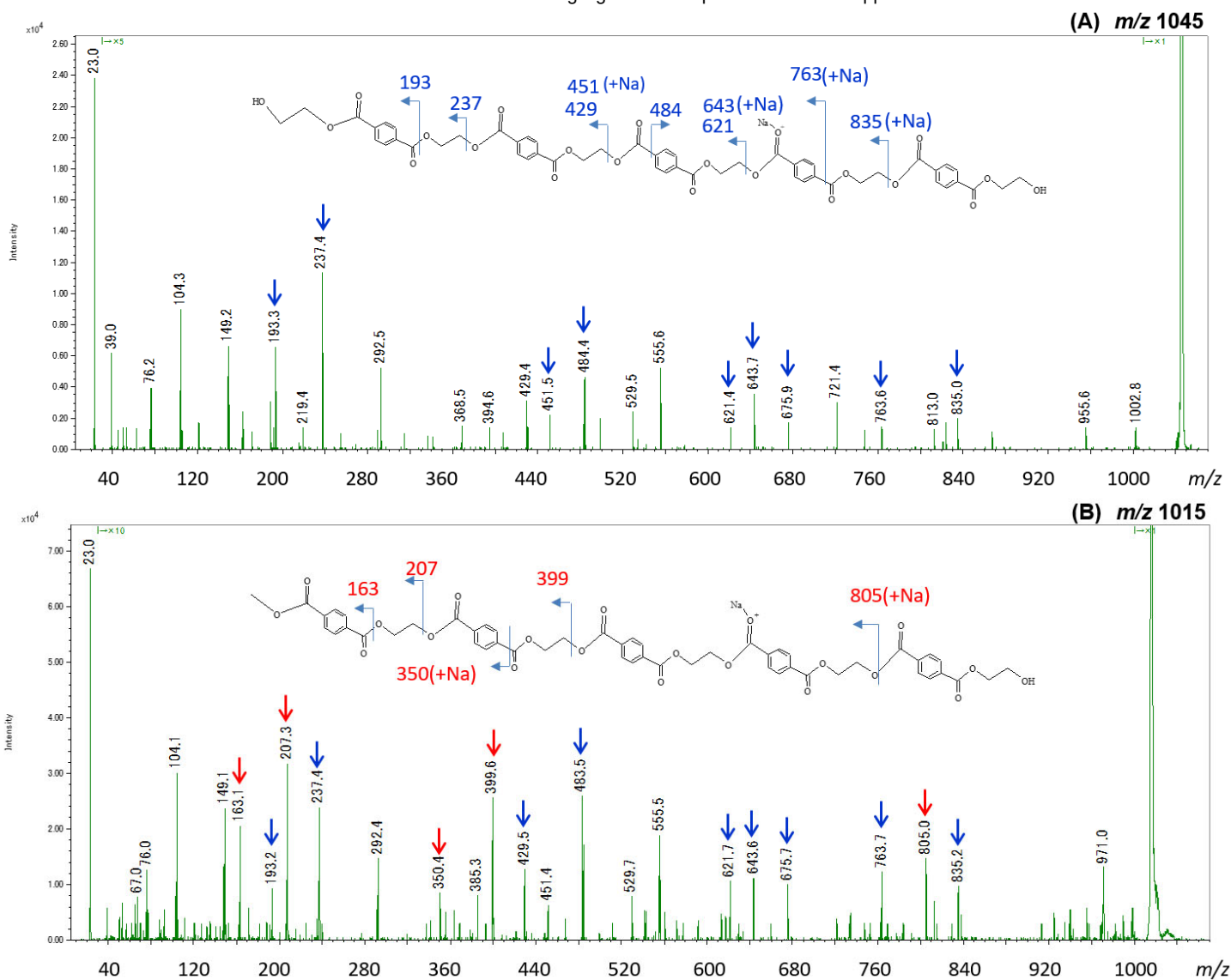

Figure 3. The PET product ion spectra for (A) *m/z* 1045 and (B) *m/z* 1015 after on-plate alkaline degradation.

Next, the product ion spectrum of TMe/E(diE), which is estimated to have the [C_2H_4O] unit inside the repeat unit, was analyzed by using TOF-TOF mode. In addition to the peaks observed in Figure 3A and B (blue and red arrows), the characteristic peaks highlighted with green arrows in Figure 4 support the estimated structure shown. Since the peaks common to Figure 3A and B (m/z 163, 193, 207 and 237) correspond to the fragmentation channel near the end-group, it can be inferred that the [C_2H_4O] unit exists in the main chain.
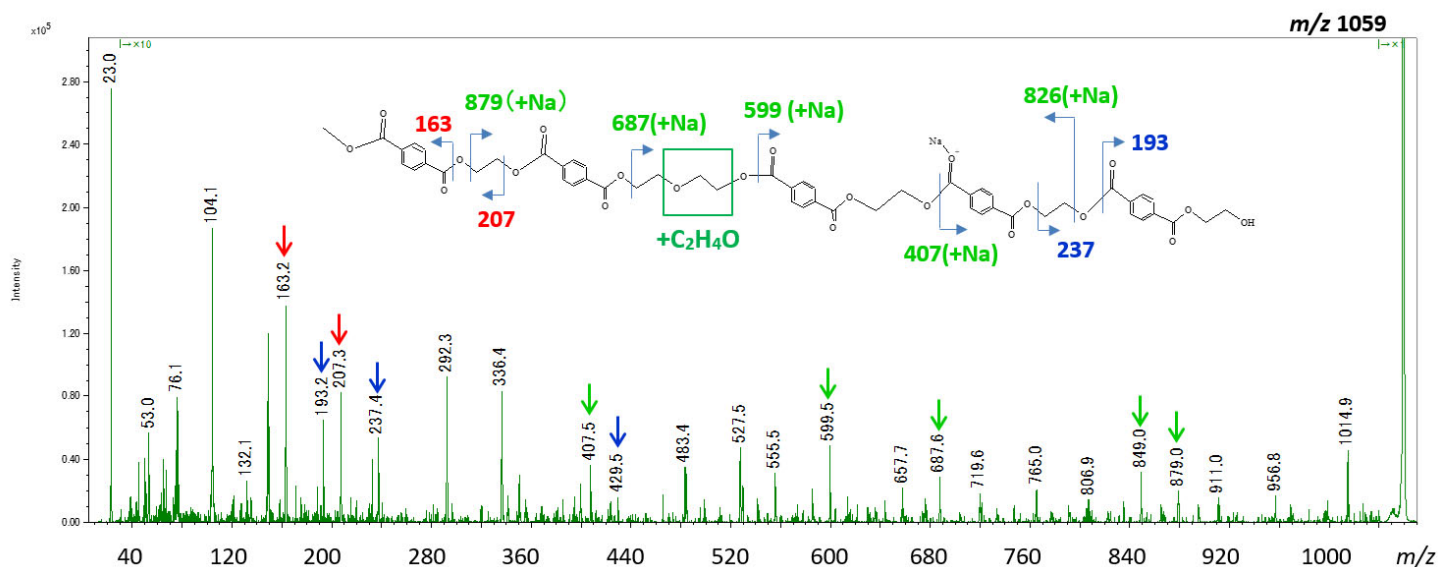

Figure 4. The PET product ion spectrum for *m/z* 1059 after on-plate alkaline degradation.

Conclusion

Structural analysis by TOF-TOF using HE-CID were performed on PET oligomers generated by on-plate alkaline degradation method. The results supported the estimated structures shown in Reference 1 and show that using a combination of on-plate polymer degradation with MS/MS structural analysis provides complementary information to accurate mass analysis.

Reference

1) S. Nakamura, T. Fouquet, H. Sato: *J. Am. Soc. Mass Spectrom.,* 30, 355 (2018).