Structural analysis of polyethylene terephthalates with different crystallinity using JMS-S3000 "SpiralTOF™-plus 2.0"

Product used: Mass Spectrometer (MS)

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester obtained by polycondensation of ethylene glycol and terephthalic acid, and has excellent properties such as transparency, toughness, rigidity, and heat resistance (Figure 1). PET can be roughly divided into two types depending on processability: crystalline PET (C-PET) and amorphous PET (A-PET). C-PET has a high density due to the regular arrangement of the molecules in the crystallized part, and is characterized by high strength and heat resistance. A-PET is characterized by high impact strength and easy bending. However, due to long-term use or exposure to heat, the amorphous portion of A-PET slowly crystallizes, causing internal stress due to changes in density and breaking the polymer chains, resulting in poor flexibility, impact resistance, and strength. Therefore, a polymer was devised in which about 30-40% of the ethylene glycol in PET was replaced with cyclohexanedimethanol; this polymer is called glycol-modified PET (G-PET, PETG) (Figure 2). G-PET is treated as an amorphous resin because the polymer does not crystallize during molding. In a previous report [1], we performed structural analysis of two types of commercially available PET resins (PET film and PET plate) using reactive pyrolysis GC-TOFMS and NMR, and confirmed that the PET film was PET and the PET plate was G-PET. In this report, we analyzed the oligomer region of the same samples using a high-resolution MALDI-TOFMS JMS-S3000 "SpiralTOF™-plus 2.0" in combination with Kendrick Mass Defect (KMD) analysis.

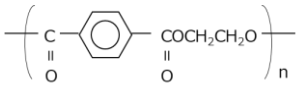


Figure 1 PET (A-PET & C-PET) structural formula

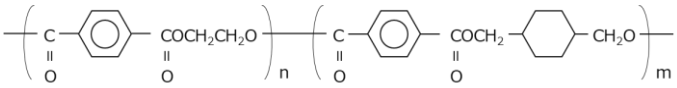


Figure 2 G-PET structural formula

Experiments

For the samples, commercially available PET film and PET plate were freeze-ground and dissolved in HFIP at a concentration of 10 mg/mL. 2',4',6'-trihydroxyacetophenone (THAP) was used as the matrix, and sodium trifluoroacetate was used as the cationization agent. Mass spectra were acquired using JMS-S3000 (JEOL Ltd.) in Spiral positive ion mode. KMD analysis was performed using msRepeatFinder V6 (JEOL Ltd.).

Results

The mass spectra of the PET film and the PET plate are shown in figure 3. From the PET film, mainly cyclic oligomers were observed as $[M+Na]^+$ (figure 3a). The PET plate gave more complex mass spectra than the PET film. Since the PET plate was previously reported [1] as G-PET, we proceeded with the analysis assuming that it was a copolymer of $C_{10}H_8O_4$ (192.042u) and $C_{16}H_{18}O_4$ (274.121u). As a result, the mass spectrum was found to contain multiple polymer series with 192u and 274u repeating units (figure 3b). In this way, information consistent with the structure obtained from reactive pyrolysis GC-TOFMS and NMR was obtained in the oligomer region as well. On the other hand, detailed analysis is difficult especially from the mass spectrum of the PET plate, so KMD analysis was performed.

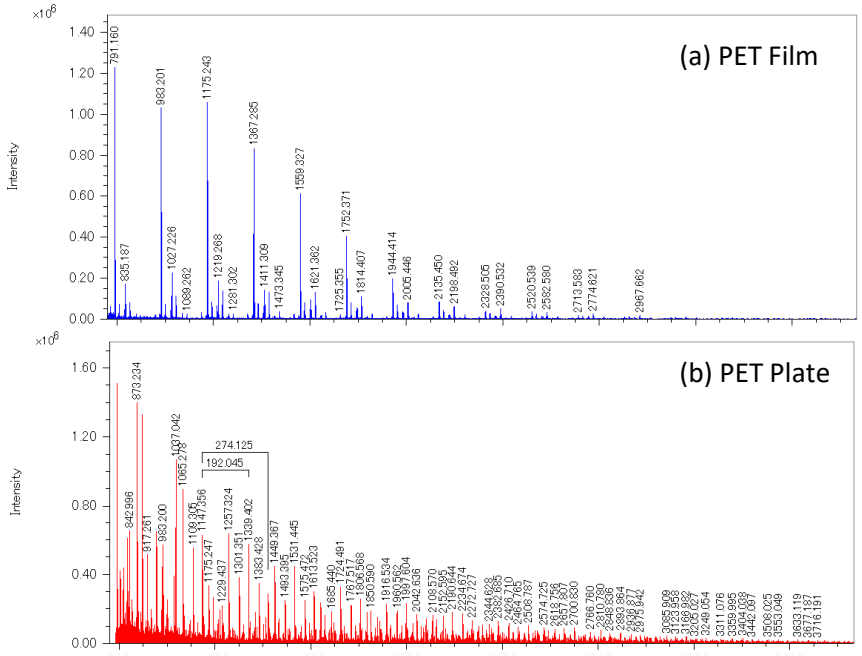


Figure 3
The mass spectra from the PET film and the PET plate

Figure 4 shows the mass spectra of the PET film and the PET plate as KMD plots (Base unit: $C_{10}H_8O_4$, Divisor: 199). Figure 4a shows the KMD plot of the PET film. A horizontal series parallel to the horizontal axis is observed, which indicates that the PET film is a homopolymer of PET with a repeating unit of $C_{10}H_8O_4$. As a result of end group analysis, two series, cyclic structure and cyclic structure + (C_2H_4O), were observed as $[M+Na]^+$. Figure 4b shows the KMD plot of the PET plate, in which two lattice-like series were observed. These were series of copolymers of $C_{10}H_8O_4$ (192.042 u) and $C_{16}H_{18}O_4$ (274.121 u). In addition, the positions of the two lattice series on the KMD plot revealed that they have a cyclic structure and a cyclic structure + (C_2H_4O), just like those from the PET film. The degree of polymerization plots for these two structures are shown in Figure 5. The degree of polymerization plots for both were found to be similar. The molar ratio of $C_{10}H_8O_4$ to $C_{16}H_{18}O_4$ was also calculated from the degree of polymerization plots (the values in parentheses are calculated excluding the homopolymer of $C_{10}H_8O_4$). As a result, the ratio of ethylene glycol to cyclohexanedimethanol was calculated to be approximately 7:3.

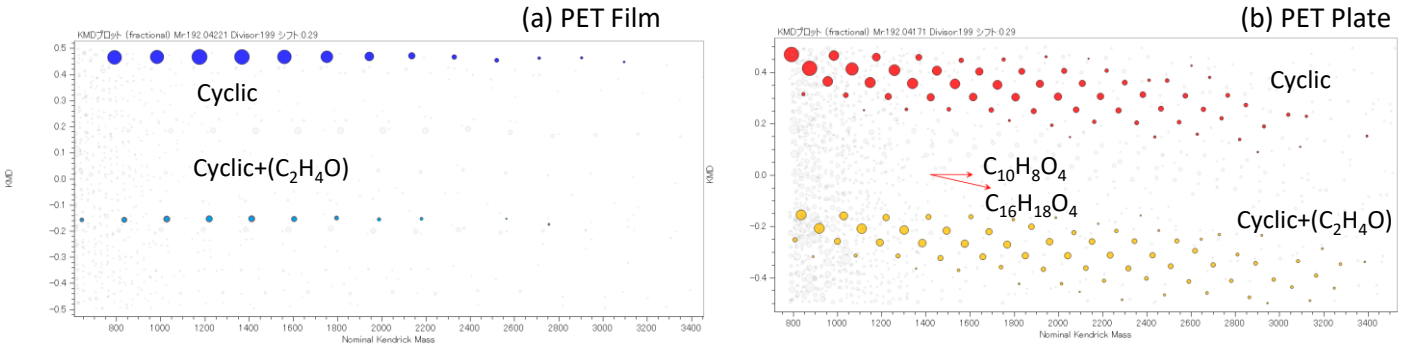
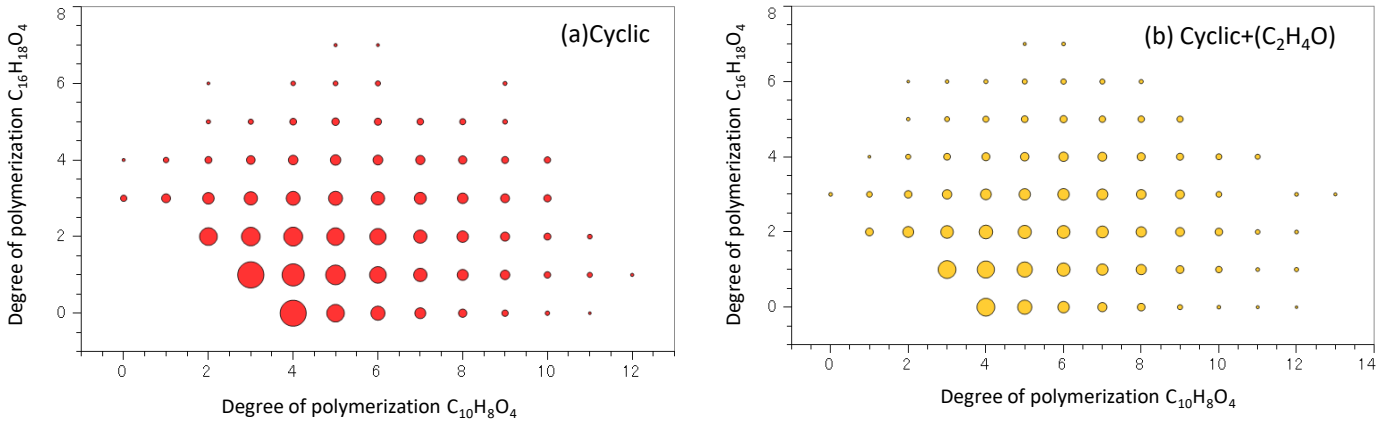


Figure 4 The mass spectra from the PET film (a) and the PET plate (b)



Molar ratio
$C_{10}H_8O_4$: 72.9% (68.8%), $C_{16}H_{18}O_4$: 27.1% (31.2%)

Molar ratio
$C_{10}H_8O_4$: 72.7% (69.1%), $C_{16}H_{18}O_4$: 27.3% (30.9%)

Figure 5 DP plot of Cyclic(a) and Cyclic+(C_2H_4O) (b) polymeric series of the PET plate

Conclusion

In this application note, we analyzed the oligomer components contained in commercially available PET film and PET plate using a MALDI-TOFMS. The results of the analysis using MALDI-TOFMS were easily interpreted by using the structural elucidation results obtained by reactive pyrolysis GC-TOFMS and NMR in a previous report [1]. While reactive pyrolysis GC-TOFMS and NMR analyze the bulk of the sample, MALDI-TOFMS allows selective structural analysis of oligomer regions. By creating a degree of polymerization plot, it is also possible to calculate the ratio of ethylene glycol and cyclohexanedimethanol in G-PET. Combining information obtained from various analytical techniques is effective for comprehensive structural analysis of polymers.

Reference

[1] MSTips No.400 Structural Analysis of Polyethylene Terephthalates with Different Crystallinity using Reactive Pyrolysis GC TOFMS and NMR

JEOL Ltd.
3-1-2 Musashino Akishima Tokyo 196-8558 Japan Sales Division Tel. +81-3-6262-3560 Fax. +81-3-6262-3577
www.jeol.com ISO 9001 • ISO 14001 Certified