SHIMADZU

Application News

MALDI-TOF Mass Spectrometry No.B44

Analysis of Recycled Polyesters by MALDI-TOFMS (3)

With the establishment of recycling-related laws in recent years, we are increasingly coming into contact with recycled plastic products. Along with this, there is a growing need for faster and more detailed analysis of recycled products. Typically, analysis of oligomers may provide sufficient information about the polyesters in these plastic products. Recently, MALDI-TOFMS has become one of the instruments of choice for analysis of oligomers as it allows acquisition of information on the terminal groups and monomer units very quickly.

However, even the use of MALDI-TOFMS can be problematic in the measurement and analysis of multi-component substances or when contaminants are present. The use of size exclusion chromatography in conjunction with MALDI (SEC-MALDI) is now gaining acknowledgment as an effective means of resolving this problem.
Here, we introduce an example of analysis of polyethylene terephthalate as a recycled polymer using precipitation for the rough separation of the oligomers together with SEC-MALDI.

For the polyethylene terephthalate (PET) samples, we used commercially-available PET chips, a wipe-sheet for cleaning (recycled product), and a PET beverage bottle. Analysis of the samples was conducted following precipitation processing (see Application News No. B42). Further, Shimadzu's analysis software "Polymer" was used for post-acquisition analysis. Fig. 1 shows the mass spectra of PET oligomers obtained following extraction by the precipitation method. The 192-dalton mass difference characteristic of PET oligomer distribution was detected, and Fig. 2 shows the structures of the cyclic and linear chain types that were primarily detected. A comparison of these mass spectra clearly underscores the difference in the 3 types of oligomers. On the other hand, when comparing these to the SEC chromatograph of Fig. 3, it is clear that there are some contradictions. In the SEC results, the oligomers of the recycled product show the widest molecular weight distribution, while that mass spectrum shows the narrowest distribution. In addition, signals that appear to originate from sources other than PET were detected. This suggested that sample preparation only by precipitation is insufficient. With that, we conducted SEC-MALDI analysis as the next step.

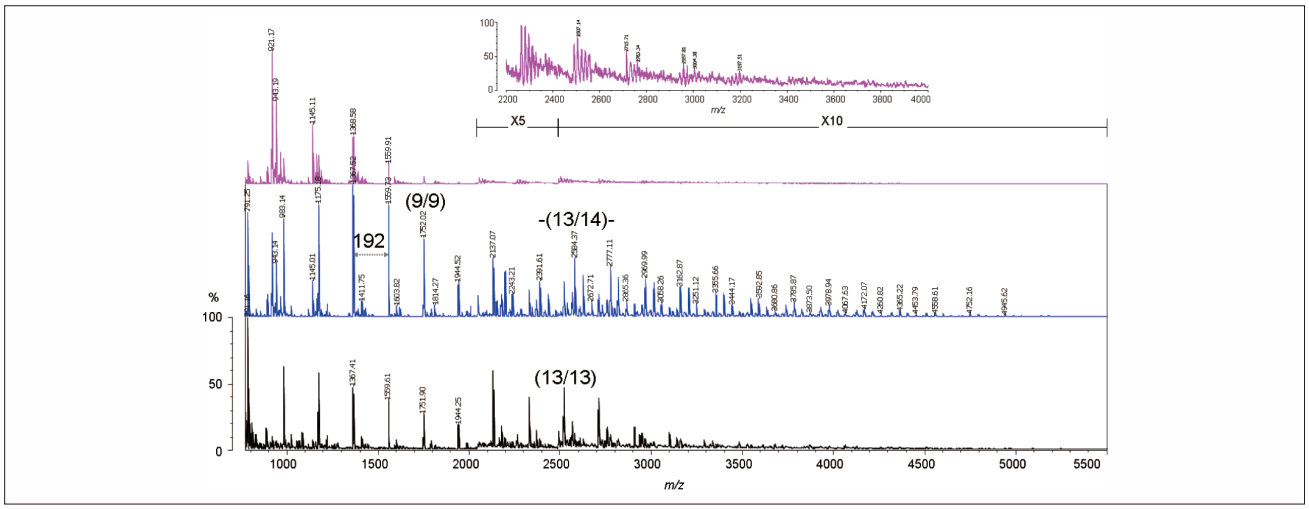

Fig. 1 Mass Spectra of PET Oligomers Extracted by the Precipitation Method – Upper; Wipe-Sheet (recycled), Middle; PET Bottle, Lower; Commercially-Available PET Chips

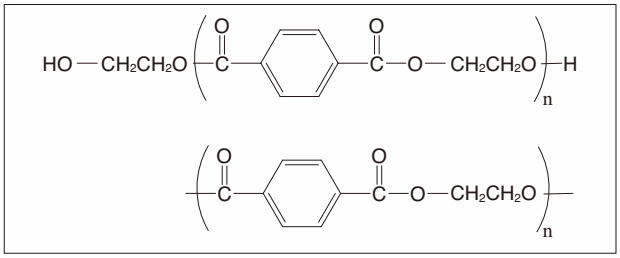

Fig. 2 Structures of Main PET Oligomer Detected

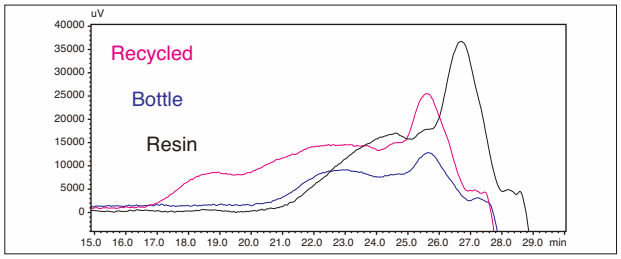

Fig. 3 SEC Chromatograms of PET Oligomers

Fig. 4 shows the SEC-MALDI measurement results. The oligomers from the recycled product showed the widest molecular weight distribution, and, linear chain oligomers were detected in the high mass region. In contrast, the molecular weight distribution of the oligomers from the beverage bottle was relatively narrow, and consisted almost entirely of cyclic oligomers. It is thought that in a beverage-related application, use of a high-quality polymer having few low-molecular weight oligomers is necessary to limit the possibility of leaching into the beverage. Thus, in this case, the result is quite appropriate. As for the commercially-available PET chips, it was found to be mid-way between those of the other 2 samples with respect to the molecular weight distribution and oligomer type. The molecular weights and types (linear or cyclic) of oligomers detected in the 3 samples are summarized in Table 1.

Thus, using the simple precipitation pretreatment procedure in conjunction with SEC-MALDI, it was shown that comparative assessment of recycled polyesters is possible even when they include contaminants.

* For details on the SEC-MALDI system, please refer to Application News No. B02.

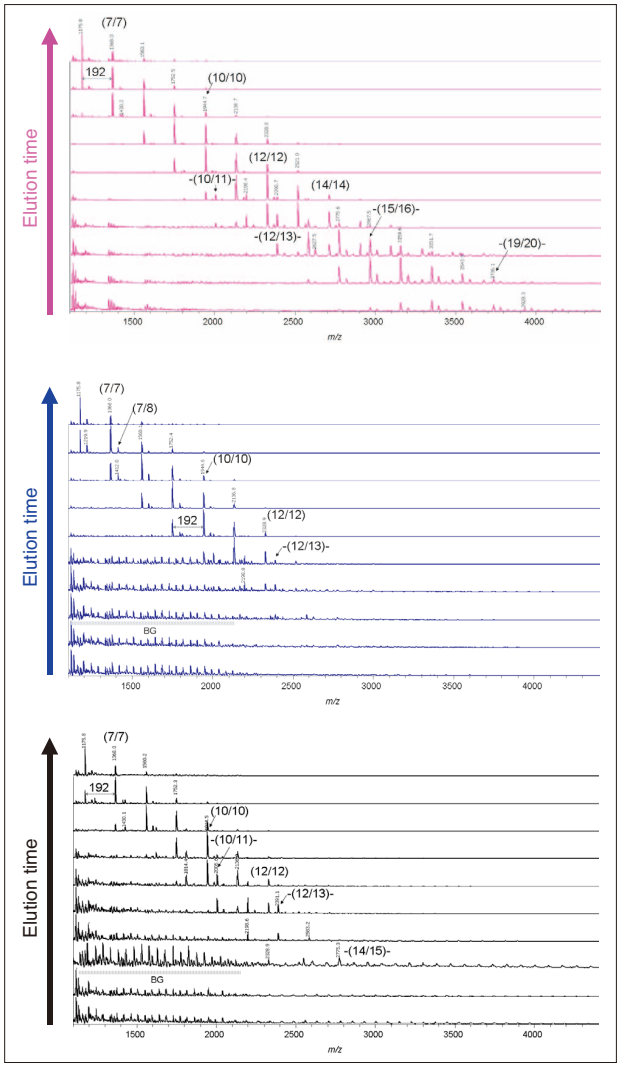

Fig. 4 Comparison of Various PC Oligomers by SEC-MALDI
Upper; Wipe-Sheet (recycled), Middle; PET Bottle, Lower; Commercially-Available PET Chips

Legend:
-(m/n)-: Linear oligomer
(m/n): Cyclic oligomer
m: Number of terephthalates
n: Number of butylene glycols

Table 1 Summary of Results by SEC-MALDI

ID Formula	Chemical Formula	Theoretical Mass (ma)	Origomer PET	Origomer Bottle	Origomer regenerated
TA6 EG6 Na	C60 H48 O24 Na	1175.24	●	●	●
TA6 EG6 Na H2O	C60 H50 O25 Na	1193.25			
TA6 EG7 Na	C62 H52 O25 Na	1219.27		●	
TA6 EG7 Na H2O	C62 H54 O26 Na	1237.28			
TA7 EG7 Na	C70 H56 O28 Na	1367.28	●	●	●
TA7 EG7 Na H2O	C70 H58 O29 Na	1385.30			
TA7 EG8 Na	C72 H60 O29 Na	1411.31		●	
TA7 EG8 Na H2O	C72 H62 O30 Na	1429.32	●		
TA8 EG8 Na	C80 H64 O32 Na	1559.33	●	●	●
TA8 EG8 Na H2O	C80 H66 O33 Na	1577.34			
TA8 EG9 Na	C82 H68 O33 Na	1603.35		●	
TA8 EG9 Na H2O	C82 H70 O34 Na	1621.36	●		
TA9 EG9 Na	C90 H72 O36 Na	1752.38	●	●	●
TA9 EG9 Na H2O	C90 H74 O37 Na	1770.38			
TA9 EG10 Na	C92 H76 O37 Na	1796.40		●	
TA9 EG10 Na H2O	C92 H78 O38 Na	1814.41	●		
TA10 EG10 Na	C100 H80 O40 Na	1944.42	●	●	●
TA10 EG10 Na H2O	C100 H82 O41 Na	1962.43			
TA10 EG11 Na	C102 H84 O41 Na	1988.44			
TA10 EG11 Na H2O	C102 H86 O42 Na	2006.45	●		●
TA11 EG11 Na	C110 H88 O44 Na	2136.46	●	●	●
TA11 EG11 Na H2O	C110 H90 O45 Na	2154.47			
TA11 EG12 Na	C112 H92 O45 Na	2180.48			
TA11 EG12 Na H2O	C112 H94 O46 Na	2198.50	●		
TA12 EG12 Na	C120 H96 O48 Na	2328.50	●	●	●
TA12 EG12 Na H2O	C120 H98 O49 Na	2346.51			
TA12 EG13 Na	C122 H100 O49 Na	2372.53			
TA12 EG13 Na H2O	C122 H102 O50 Na	2390.54	●		●
TA13 EG13 Na	C130 H104 O52 Na	2520.54			●
TA13 EG13 Na H2O	C130 H106 O53 Na	2538.55			
TA13 EG14 Na	C132 H108 O53 Na	2564.57			
TA13 EG14 Na H2O	C132 H110 O54 Na	2582.58	●		●
TA14 EG14 Na	C140 H112 O56 Na	2712.58			●
TA14 EG14 Na H2O	C140 H114 O57 Na	2730.59			
TA14 EG15 Na	C142 H116 O57 Na	2756.61			
TA14 EG15 Na H2O	C142 H118 O58 Na	2774.62	●		●
TA15 EG15 Na	C150 H120 O60 Na	2904.62			●
TA15 EG15 Na H2O	C150 H122 O61 Na	2922.64			
TA15 EG16 Na	C152 H124 O61 Na	2948.65			
TA15 EG16 Na H2O	C152 H126 O62 Na	2966.67			●
TA16 EG16 Na	C160 H128 O64 Na	3096.67			
TA16 EG16 Na H2O	C160 H130 O65 Na	3114.68			
TA16 EG17 Na	C162 H132 O65 Na	3140.69			
TA16 EG17 Na H2O	C162 H134 O66 Na	3158.70			●
TA17 EG17 Na	C170 H136 O68 Na	3289.71			
TA17 EG17 Na H2O	C170 H138 O69 Na	3307.73			
TA17 EG18 Na	C172 H140 O69 Na	3333.74			
TA17 EG18 Na H2O	C172 H142 O70 Na	3351.75			●
TA18 EG18 Na	C180 H144 O72 Na	3481.76			
TA18 EG18 Na H2O	C180 H146 O73 Na	3499.77			
TA18 EG19 Na	C182 H148 O73 Na	3525.78			
TA18 EG19 Na H2O	C182 H150 O74 Na	3543.79			●
TA19 EG19 Na	C190 H152 O76 Na	3673.80			
TA19 EG19 Na H2O	C190 H154 O77 Na	3691.81			
TA19 EG20 Na	C192 H156 O77 Na	3717.82			
TA19 EG20 Na H2O	C192 H158 O78 Na	3735.83			●
TA20 EG20 Na	C200 H160 O80 Na	3865.84			
TA20 EG20 Na H2O	C200 H162 O81 Na	3883.85			
TA20 EG21 Na	C202 H164 O81 Na	3909.87			
TA20 EG21 Na H2O	C202 H166 O82 Na	3927.88			

● ; (red circle) High intensity
● ; (blue circle) Low intensity
White row: Cyclic oligomer
Pale yellow row: Linear oligomer

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