Analysis of High Performance and Engineering Finished Commercial Polymeric Products Using MALDI-TOF MS

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1. Overview

Three different finished commercial polymeric products: polyetherimide (PEI), polyethylene terephthalate (PET), and nylon 6, representative of the plastic pollutants commonly found in the environment as macro-, micro- and nano-plastics, were analyzed using MALDI-TOF MS. Resulting mass spectra were imported into Polymerix software to generate polymer statistics. End group analysis was performed based on residual mass calculations, software suggested structures and complemented through literature review.

2. Introduction

Polymers and plastics are a ubiquitous part of modern life and form the basis of many finished products used. Clothing, toys, and pipes are a small range of finished products made of polymers. Finished products produced to sustain modern lifestyles can ultimately lead to plastic waste, including macro-, micro-, and nano-plastics. Identifying polymer chemistry for both ends of a finished product's lifecycle is vital; for quality control of a finished product at its beginning and possible remediation strategies at its end. The manufacturing of new and greener alternatives to traditional polymeric materials also requires thorough characterization.
MALDI-TOF MS is a powerful tool to elucidate several key parameters of synthetic polymers including monomers, number of repeating units, and possibly end groups. It also represents an alternative and complementary tool for the characterization of plastic pollution in environmental samples.

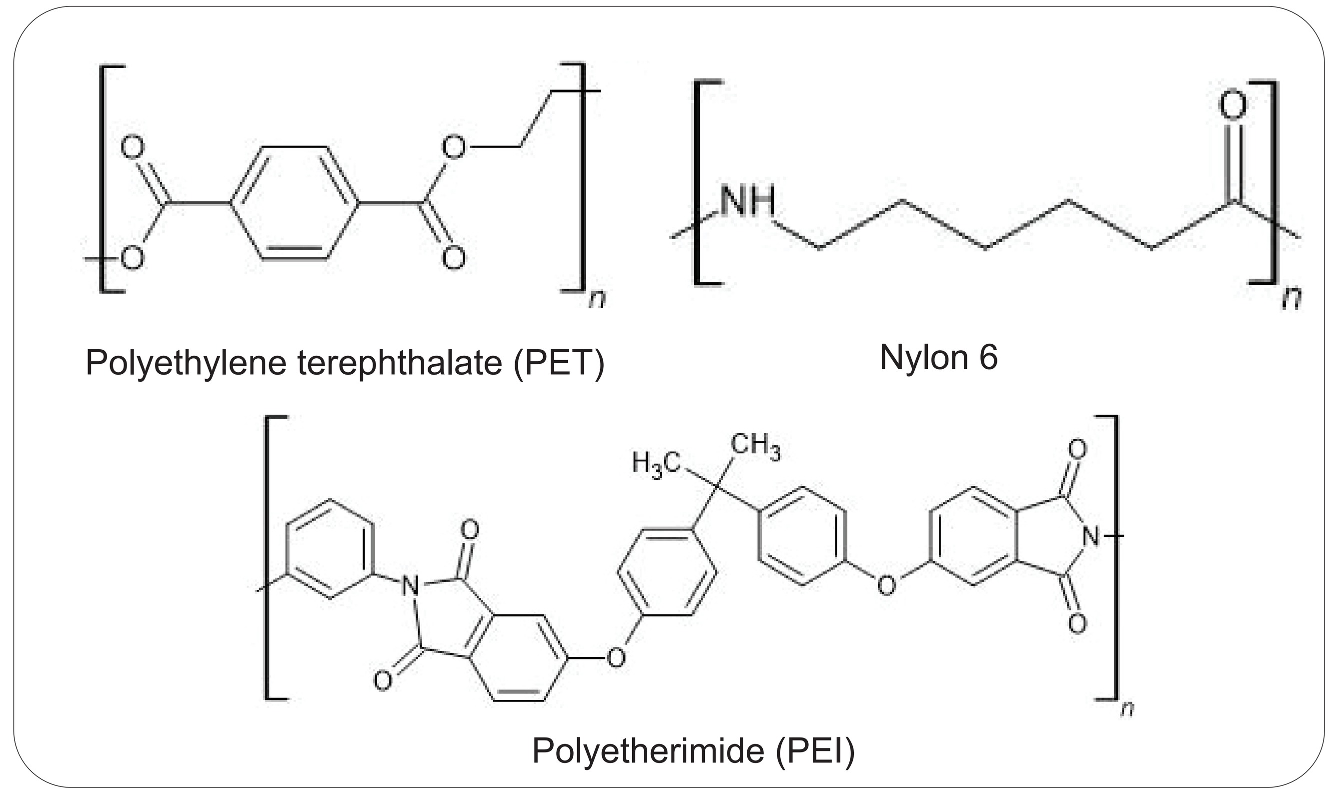


Figure 1. Structures for the repeating units of polyethylene terephthalate, nylon 6, and polyetherimide.

3. Methods

Three targets: PEI, PET and nylon 6 provided by an advanced plastics manufacturer and distributor were shaved from finished commercial plastic products and dissolved in 1 mL of solvent. A portion of each solution was mixed with an optimized combination of matrix and cationization agents (see 4.1. Method Development). Optimal chemicals included dithranol and CHCA as the matrices and NaTFA as the cationization agent. The MALDI target plate was spotted with 1 μL of the premixed solution of polymer, matrix and cationization agent and dried prior to analysis via AXIMA Performance (Shimadzu/Kratos, Manchester, UK). Mass spectra were imported into Polymerix (Sierra Analytics, Modesto, CA) for polymer statistical analysis. Instrument conditions are listed in Table 1.

4. Results

4-1. Method Development

For the finished commercial PEI product, dithranol was used as the matrix and NaTFA was used as the cationization agent. Different ratios of dithranol and NaTFA to the finished commercial PEI product were tested. It was found that mixing a volumetric ratio of nine parts of 20 mg/mL dithranol and 10 mg/mL NaTFA to one part of 20 mg/mL PEI yielded the highest signal.

For the finished commercial nylon 6 product, dithranol was used as the matrix and NaTFA was used as the cationization agent. Different ratios of dithranol and NaTFA to the finished commercial nylon 6 product were tested. It was found that mixing an equal volumetric ratio of 20 mg/mL dithranol and 10 mg/mL NaTFA to 20 mg/mL nylon 6 yielded the highest signal. It should be noted that dissolving 20 mg of commercial nylon 6 in formic acid took approximately 1 hour.

For the finished commercial PET product, CHCA was used as the matrix and NaTFA was used as the cationization agent. CHCA was used over dithranol as the matrix due to the higher signal intensities. Different ratios of CHCA and NaTFA to the finished commercial PET product were tested. It was found that mixing an equal volumetric ratio of 20 mg/mL CHCA and 10 mg/mL NaTFA to 20 mg/mL PET yielded the highest signal.

MS conditions (AXIMA Performance)

Laser Rep. Rate (Hz): 50
Polarity: Positive Mode
Laser Power: 100
Ion Gate (Blanking): 650
Profiles: 500
Linear

Finished Polymer Product	Pulsed Extraction	Mass Range
PEI	2000	700 - 10,000
Nylon 6	1500	700 -3000
PET	3000	700 - 4000

Figure 2. MALDI-MS analysis setting..

4-2. Polymer Statistics of Finished Polymeric Products

Mass spectra were exported as ASCII files and subsequently imported into Polymerix for analysis. Tables 1 – 3 contain the polymer statistics and proposed structure including end groups for figures 3 – 5, respectively. The symbols were retained.

Mass spectra for commercial PEI product show the presence of at least three different distributions of PEI with different end groups. The peaks of each distribution are separated by a Δ m/z value of 592 ± 1 which is the monoisotopic mass of a PEI monomer. Spectra were analyzed using Polymerix polymer analysis software and further literature search was used to propose several end groups with one of the three different distributions of PEI being cyclic.

Mass spectra for commercial nylon 6 product was dominated by one distribution. The peaks of this distribution are separated by a Δ m/z value of 113.1±0.1 which is the monoisotopic mass of a monomer of nylon 6. After further literature search it was proposed that this distribution of nylon 6 were cyclic nylon 6 species.

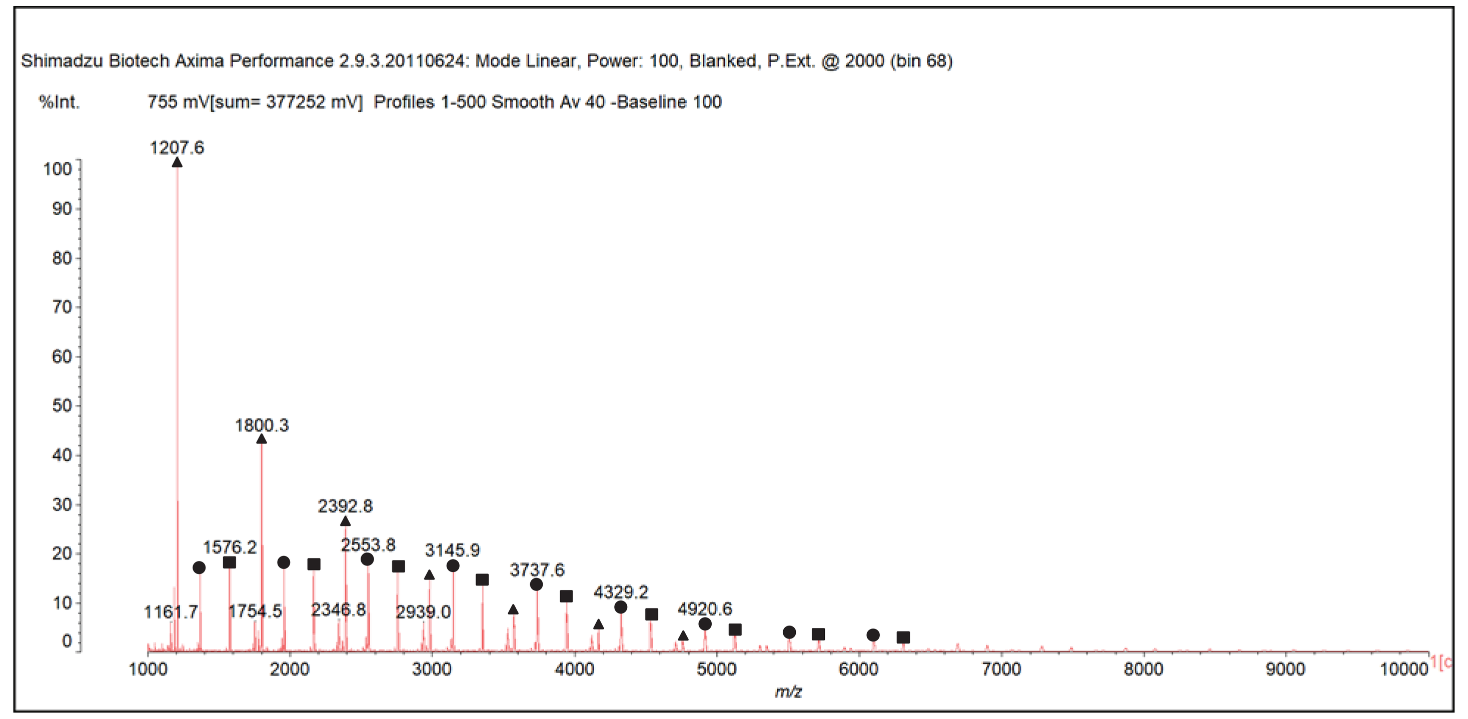


Figure 3. Mass spectrum of PEI. The triangle, circle, and square symbols represent distributions of PEI differentiated by their end groups. Information regarding end groups can be found in Table 2.

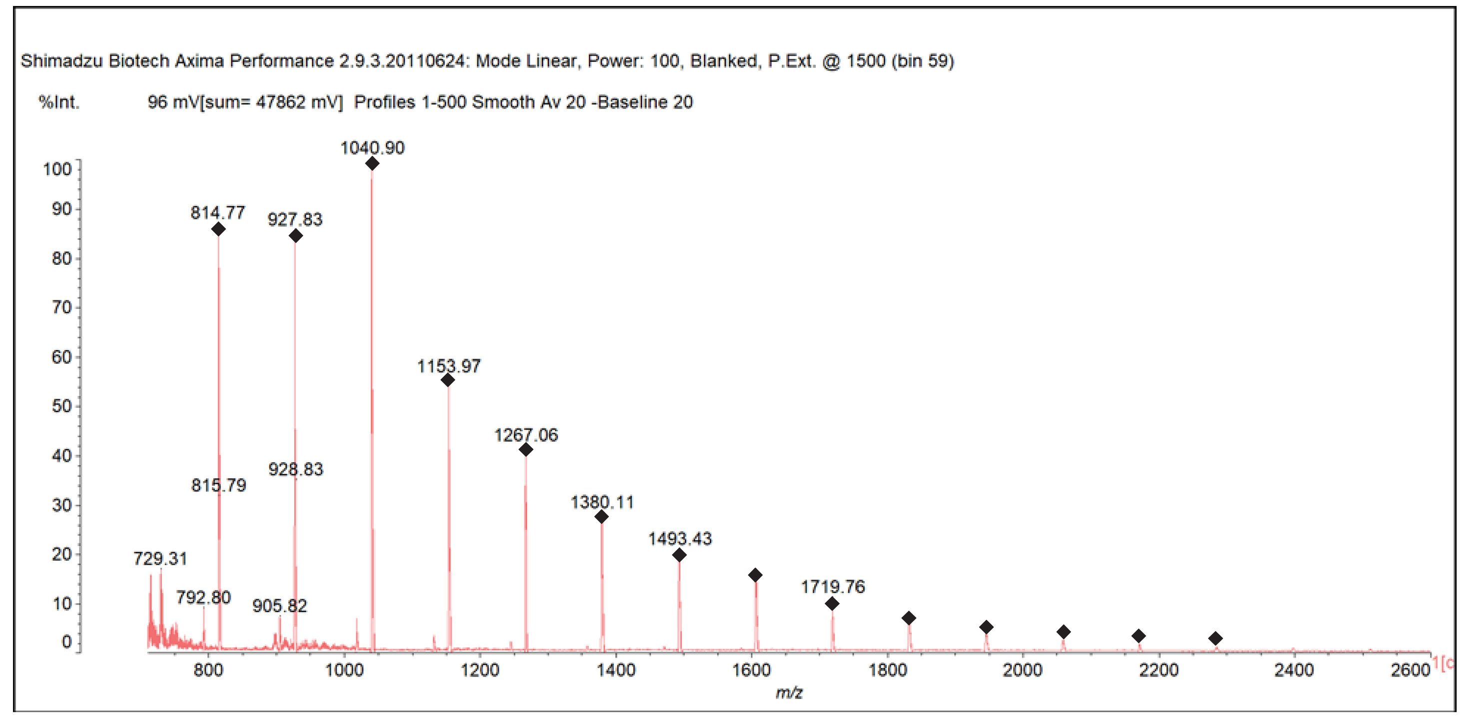


Figure 4. Mass spectrum of nylon 6. Only one major distribution of the polymer is present, labelled with a diamond symbol.

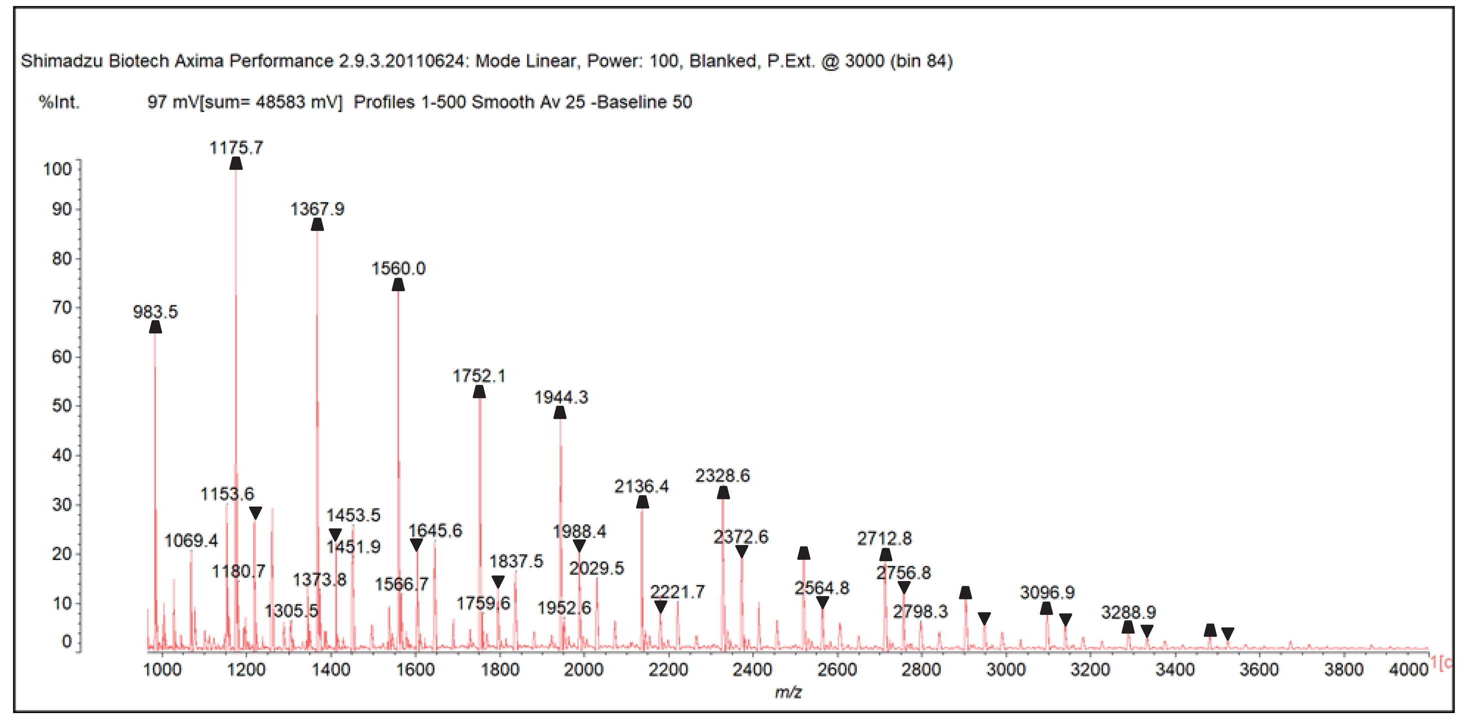


Figure 5. Mass spectrum of PET product. Out of four major distributions, two have proposed structures for the end group and are labelled with a trapezoid and inverted triangle.

Table 1. Polymer statistics of the commercial finished PEI product; proposed structures and end groups.

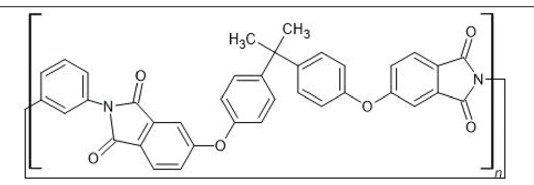
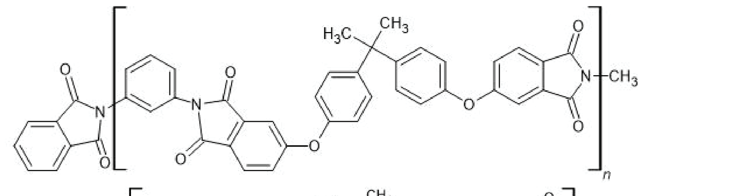
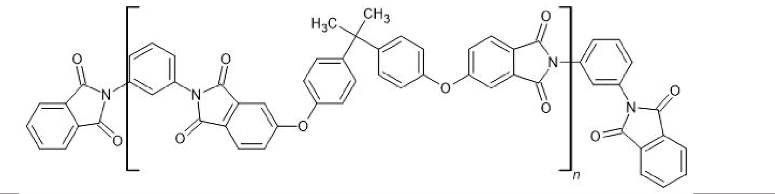
Label	M_n	M_w	M_z	Polydispersity	Proposed Structure
▲	2401.3	3565.1	5202.0	1.485	
●	3221.6	4584.3	5816.9	1.423	
■	3237.8	4478.7	5684.5	1.383	

Table 2. Polymer statistics of the commercial finished nylon 6 product; proposed structures and end groups.

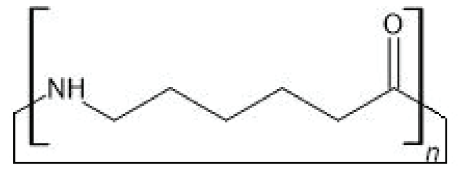
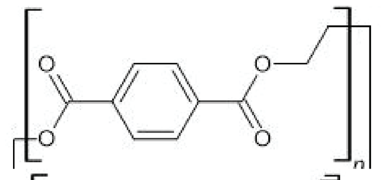
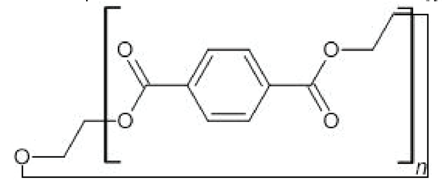
Label	M_n	M_w	M_z	Polydispersity	Proposed Structure
◆	1279.7	1480.3	1777.0	1.157	

Table 3. Polymer statistics of the commercial finished PET product; proposed structures and end groups.

Label	M_n	M_w	M_z	Polydispersity	Proposed Structure
⏢	1755.2	2112.1	2473.5	1.202	
▼	2003.6	2401.6	2751.3	1.203	

The mass spectra of the PET product show the presence of at least four different distributions of PET with different end groups. The peaks of each distribution are separated by a Δ m/z value of 192.1±0.2 which is the monoisotopic mass of a PET monomer. Polymerix polymer software and further literature search was used to propose end groups for two of the different distributions of PET. The distribution of m/z peaks contained cyclic PET species, among others. Another distribution of PET species are cyclic PET species with an additional ethylene glycol group.

5. Conclusions

PEI, nylon 6, and PET from finished commercial products were analyzed by MALDI-TOF-MS.
The mass spectra allowed for identification of polymers from a finished commercial product using the difference in mass caused by an increase in the number of repeating units. In addition, polymers with similar repeating units, but different end groups can be differentiated. Mass spectra can be used to obtain polymer statistics including M_n, M_w, M_z, polydispesity. The investigative approach used herein (mass spectra, software analysis, literature search) to confirm the presence and structure of various polymer species in the commercial product increased confidence in the analytical results without the need to use analytical standards. This work describes the initial development of a standard free methodology to identify polymers in consumer goods and environmental samples.