

## MASS SPECTROMETRY FOR POLYMERS

### Benefits and analytical considerations for MS analysis of polymers

The benefit of mass spectrometry is the ability to make absolute mass measurements at a molecular level rather than an average across a whole sample, making mixtures easier to deal with. Dual-stage mass spectrometry (MS/MS) can provide detailed structural information about the repeat unit chemistry, end groups and backbone connectivity with both detail and confidence.



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## INTRODUCTION

Interest and research in the polymer industry have increased in recent years for several reasons, including the push towards green chemistry, increasing product complexity, and reduced availability of petroleum products as a feed stock.

Petroleum products are becoming more expensive as reducing global supplies have become increasingly inaccessible, and extraction methods have become more costly. These products are also difficult to dispose of due to their poor biodegradability. The consequence of this has caused the rebirth of polymer synthesis and the need to fully characterize new polymer systems from environmental sustainable sources of feed stocks.

In addition to these changes, polymers are being used for more sophisticated applications that require more detailed characterization. While traditional approaches such as gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) spectroscopy are incredibly powerful, alternatives are being considered. The introduction of atmospheric pressure ionization techniques have opened up the possibility of mass spectrometry to this industry. Typically Electrospray ionization (ESI) and Matrix Assisted Laser Desorption Ionization (MALDI) are used.

The benefit of mass spectrometry is the ability to make absolute mass measurements at a molecular level rather than an average across a whole sample, making mixtures easier to deal with. Dual stage mass spectrometry (MS/MS) can provide detailed structural information about the repeat unit chemistry, end groups, and backbone connectivity with both detail and confidence.

## Definitions

Monomer:	A molecule that can be bonded to other identical molecules to form a polymer
Dimer:	A molecule or molecular complex consisting of two identical molecules linked together
Trimer:	A polymer comprised of three monomer units
Oligomer:	A polymer whose molecules consist of relatively few repeating units
Polymers:	A chemical compound or mixture of compounds formed by polymerization and consisting essentially of repeating structural units (monomers)

## INSTRUMENT MODES OF OPERATION

Mass spectrometers measure the mass-to-charge ratio ( $m/z$ ) and intensity of an ion. If a synthetic polymer is being analyzed there will be a distribution of masses, typically with a Gaussian distribution. If ESI is used, multiple charge states are highly probable.

Waters® Xevo® and SYNAPT® QToF instruments can be operated in either MS or MS/MS mode, depending on the type of information that is required. MS mode records all the ions that are present within the selected mass range. MS/MS mode involves the selection of a precursor ion in the quadrupole, fragmenting the precursor ion by applying energy in the collision cell before the fragment ions are detected (illustrated in Figure 1). It is the information obtained from the fragment ions that allow for structural elucidation to take place.

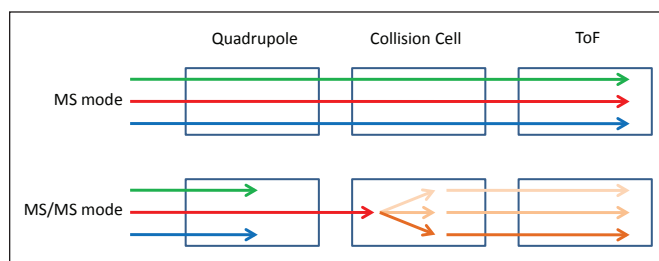


Figure 1. Illustration of MS and MS/MS operating modes.

## MS analysis

Single stage MS analysis can be used to provide basic average molecular weight measurements. It is important to be aware there are many different MS technologies. Axial extraction of the ions into a ToF analyzer introduces the least bias into the average molecular weight measurement. The detail of the technology will affect analytical implications/limitations such as the mass range that is accessible, mass resolution, and the ability to do MS or MS/MS analysis. It can also be used to confirm the target compound has been made if the reaction pathway is well understood. A typical mass spectrum run by ESI is shown in Figure 2, and demonstrates the ability to identify the ions and interpret the data.

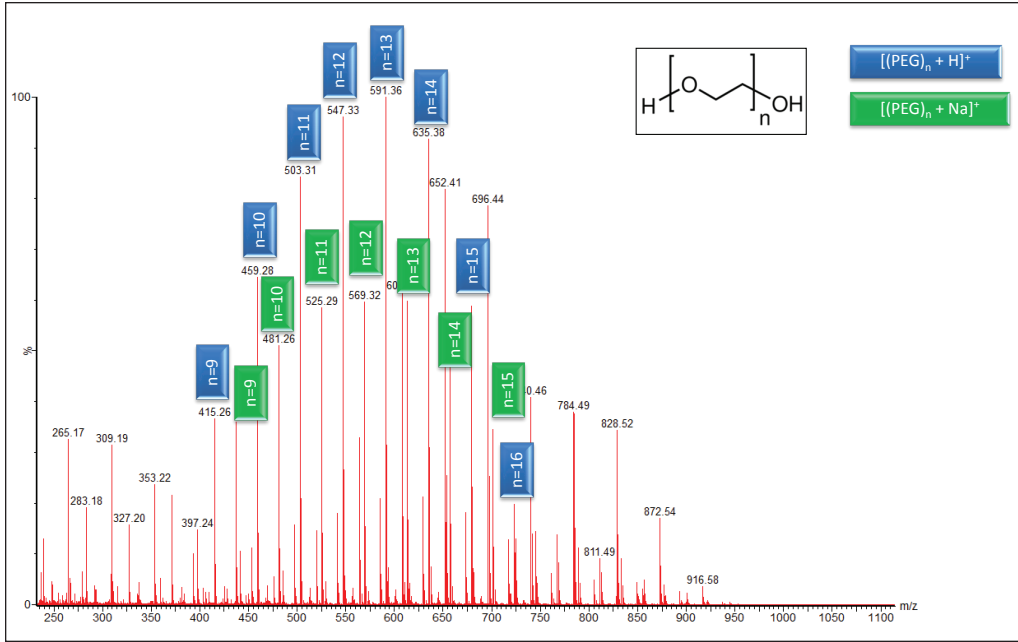


Figure 2. A typical mass spectrum that has been annotated to show the identification of several ions.

### Standard calculations

A synthetic polymer sample will typically contain a distribution of chain lengths. The range of chain lengths within a polymer is called molecular weight (MW) distribution. These measurements/calculations are done because the MW affects the performance of the product, as can be seen in Table 1.

Property/process parameter	Effect of high MW	Effect of low MW
Impact strength	↑	↓
Melt velocity	↑	↓
Processing temp.	↑	↓
Flex life	↓	↑
Brittleness	↑	↓
Drawability	↓	↑
Softening temp.	↑	↓
Stress-crack resistance	↓	↑
Melt flow	↓	↑

Table 1. Effects of molecular weight on the physical properties of a polymer.

There are a number of molecular weight average calculations which are shown in Figure 3. Several averages/values are required to fully characterize a distribution. This is because it may not be possible to differentiate between different distributions by Mn alone.

A polymer is comprised of species (chains) of varying lengths. Each chain is characterized by its molecular weight, Mi, and its abundance ni. I is the polydispersity index.

$$\begin{aligned}
 M_n &= \frac{\sum niMi}{\sum ni} & M_w &= \frac{\sum niMi^2}{\sum niMi} & M_z &= \frac{\sum niMi^3}{\sum niMi^2} \\
 M_{z+1} &= \frac{\sum niMi^4}{\sum niMi^3} & I &= \frac{M_w}{M_n}
 \end{aligned}$$

Figure 3. Molecular weight average calculations.

Table 2 and the calculations associated with it demonstrate the need for more than one average weight value.

Polymer 1		Polymer 2	
Mass	Ion intensity	Mass	Ion intensity
5	1	8	1
10	2	10	2
15	1	12	1

Table 2 . Illustrative information for Mn and Mw calculations.

**Polymer 1**  $M_n = (5 + 20 + 15) / 4 = 10$

**Polymer 2**  $M_n = (8 + 20 + 12) / 4 = 10$

One value (Mn here) cannot differentiate two different distributions.

**Polymer 1**  $M_w = (25 + 200 + 225) / (5 + 20 + 15) = 11.3$

**Polymer 2**  $M_w = (64 + 200 + 144) / (8 + 20 + 12) = 10.2$

Small variations in the low Mw area will affect Mn but not Mw, Mz.

Small variations in the high Mw area will affect Mz+1, Mz, Mw but not Mn.

Important analytical considerations for MS analysis of polymers:

- Average molecular weight determined by MS will not give the same results as Size Exclusion Chromatography. Direct comparison of results from different techniques could be misleading. However, MS analysis will be able to give Mw values for samples relative to each other. As stated previously axial MALDI ToF introduces the least bias into the results.
- As the mass of the ions being measured increase, the isotope patterns caused by <sup>13</sup>C begin to get more complex and eventually overlap. This is demonstrated in Figure 4, which illustrates a theoretical isotope model for PEG with n=10,000, n=10,001, and n=10,002 – these three isotope modes represent three different chain lengths. Clearly the three isotope models overlap so the mass spectrum at this mass range is very complex, especially if we bear in mind that in a real sample, there will also be fragment ions and background interference. To be able to resolve two isotopes from different molecules, a resolving power of over four million would be required.

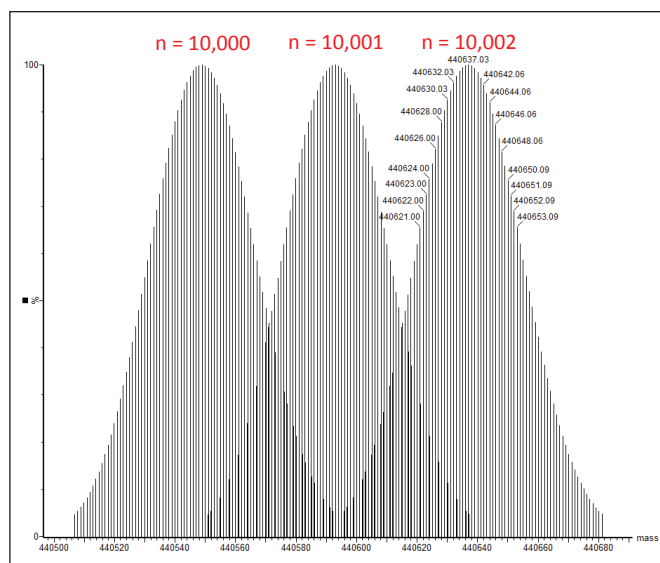


Figure 4 . Theoretical isotope model for PEG n = 10,000, 10,001, and 10,002.

### MS/MS analysis

MS/MS analysis allows for detailed structural characterization including the confirmation of repeat unit chemistry, end group determination, and backbone connectivity.

Polymers can form a range of structures and possibly contain more than one type of repeat unit. The order and connectivity of a polymer backbone affect the fragmentation pattern that is observed. Figure 5 shows some possible polymer structures.

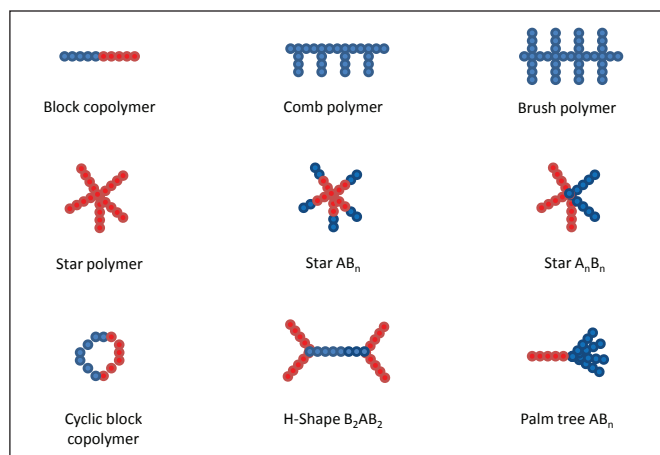


Figure 5 . Examples of polymer structures.

Structural analysis requires MS/MS analysis, which involves selecting a precursor ion in the quadrupole and fragmenting the ion in the collision cell, resulting in data such as that in Figure 6. This analysis was done to determine the end groups. Two dominant series of ions were observed, each caused by the presence of either the initiating end group ( $\alpha$ ) or the terminating end group ( $\omega$ ). Figure 6 shows the MS/MS spectrum which has been annotated to identify the ions.

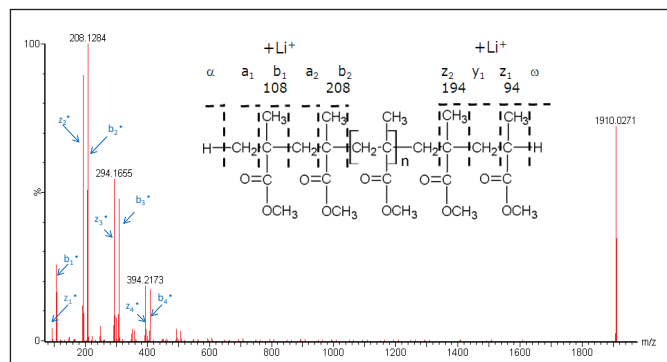


Figure 6. MS/MS spectrum of polymer methyl methacrylate and the bond cleavages responsible for the most intense ions.

The process for identifying backbone connectivity is similar. Again MS/MS analysis is performed. Figure 7 shows an example using polylactide, the MS/MS analysis produces two series of ions that have been labelled with a diamond or circle. This is due to the loss of different end groups, either the initiator or terminator. Figure 8 shows the proposed fragmentation mechanism responsible for one of the series (labelled with a circle) and provides an example of how the process works. Understanding the fragmentation pattern confirms the backbone connectivity and/or the end groups.

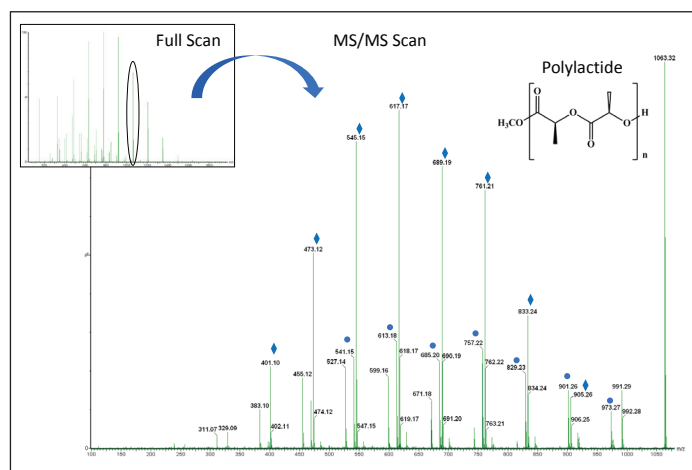


Figure 7. MS/MS spectrum of sodiated polylactide.

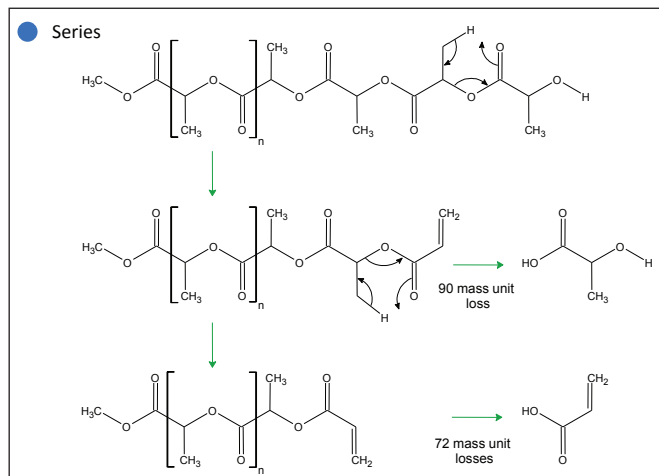


Figure 8. Proposed fragmentation pathway associated to the MS/MS results in Figure 7.

The backbone connectivity and end groups also affect the physical properties of the polymer which is why these types of analysis are performed. If a polymer manufacturer wishes to perform modifications to a polymer knowing the chemistry of the end groups will aid the decisions about how to carry out the chemical reactions required.

Polymeric ions with an  $m/z$  value greater than 4000 tend to be more challenging to get useful MS/MS spectra from. While it is difficult to put an absolute value on the upper mass limit for polymer MS/MS analysis it is a good guide and important to be aware of.

## Ion mobility

Ion mobility can also be used to help with the challenge of polymer analysis. Ion mobility separates ions according to their size and shape providing the analyst with additional information and the potential to simplify data. Within the SYNAPT instrument (Figure 9), the ion mobility cell sits between the quadrupole and the time-of-flight regions. The mobility cell itself is a series of ring electrodes, to which a pulsed DC current is applied across the cell. This essentially creates a wave that carries the ions through the cell. Moving in the opposite direction from the ions is a stream of nitrogen gas, creating friction against the traveling ions. There is less friction among the smaller ions than the larger ones and as a consequence, the smaller ions elute from the mobility cell faster.

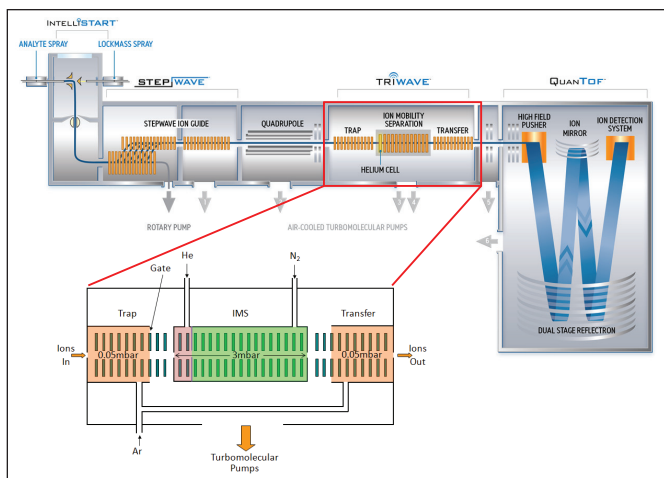


Figure 9. Ion mobility cell within the Waters SYNAPT instrument.

Figure 10 shows some example ion mobility data of a mixture of polymers. The  $m/z$  value is on the x-axis, drift time on the y-axis and ion intensity is represented by the colors. Within the mobility plot several series of ions can be seen. This is caused by the increasing mass and increasing size of an ion as the polymer grows by a repeat unit for each chemistry and charge state. The reason for the charge states being separated is that as the number of adducts increases on an ion the force felt by the pulsed DC current increases. So, an ion of higher charge elutes from the mobility cell faster for a given CCS compared to an ion of the same CCS but lower charge state.

The benefit of ion mobility for complex samples is the potential to separate and simplify data to allow interpretation with increased confidence. DriftScope™ Software allows analysts to interact and interpret ion mobility data. Figure 10 shows a mobility plot of a polymer mixture containing polymethyl methacrylate (PMMA) and poly ethylene glycol (PEG). Under the mobility plot are two mass spectra that have been extracted and displayed in isolation from the whole data set.

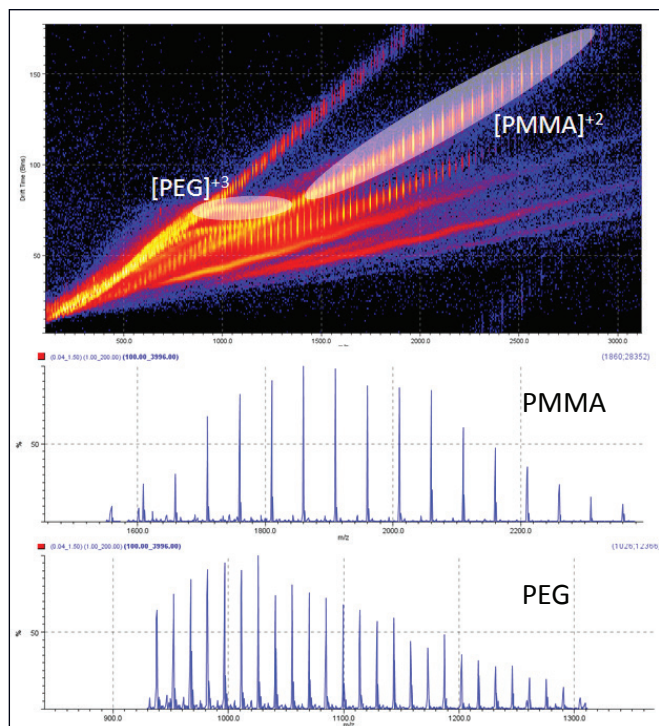


Figure 10. Mobility plot of a mixture of polymethyl methacrylate and poly ethylene glycol and extracted mass spectra of extracted ion series for each polymer.

## SUMMARY

As polymer applications become increasingly sophisticated mass spectrometry is highly likely to be more widely adopted for characterization. Its strengths are in the ability to make measurements on a molecular level and structural elucidation using MS/MS analysis.

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Waters Corporation  
34 Maple Street  
Milford, MA 01757 U.S.A.  
T: 1 508 478 2000  
F: 1 508 872 1990  
www.waters.com