Application Note

Reliable End Group Determination for Polymers Using PMMA as a Model

Kirsten Craven

Waters Corporation

Abstract

This application note describes how Waters Xevo G2 QTof can be used to determine polymer end groups, using Poly Methyl Methacrylate (PMMA) as a model example. The Xevo G2 QTof is a hybrid Quadrupole Time-of-Flight mass spectrometer. The quadrupole allows precursor ions to be selected for fragmentation, which provides the analyst with additional structural information, a cleaner spectrum, and increases confidence in the origin of the ions detected.

Benefits

- MS/MS analysis for increased confidence
- Information about the end groups can help guide further chemical modifications
- Elemental Composition functionality to aid decision-making

Introduction

Polymers have incredibly diverse applications including paints, cosmetics, plastics, textiles, and food packaging. This range of applications requires a broad spectrum of properties that can be created by varying many aspects of the polymer, such as chain length, terminating and initiating end groups, polymer chemistry, cross linking, and the inclusion of additives during the manufacturing process.

In recent years, Electrospray (ESI) and Matrix Assisted Laser Desorption Ionization (MALDI) have become increasingly important for the analysis of polymers. These ionization techniques within mass spectrometry have allowed information to be collected on a range of polymer properties including end group analysis, backbone structure, and in some cases average molecular weight.[1,2]

The ability to accurately and reliably carry out end group analysis provides valuable information to both polymer manufacturers and polymer research scientists. Information about the end groups can be used to indicate the synthetic process followed and guide how further chemical modifications can be carried out.[3]

Some synthetic polymers, such as poly ethylene glycol, will ionize in ESI mode with the right settings by simply dissolving and infusing. Other polymers become much easier to analyze if they are mixed with a salt before analysis so that the polymer becomes cationized (gains a charge by bonding with the cation from an added salt). The fragmentation pattern of the polymer can be affected by the specific cation present,[2] and hence the structural information that can be gained from an MS/MS experiment.

This application note describes how Waters Xevo G2 QTof can be used to determine polymer end groups, using Poly Methyl Methacrylate (PMMA) as a model example. The Xevo G2 QTof is a hybrid Quadrupole Time-of-Flight mass spectrometer. The quadrupole allows precursor ions to be selected for fragmentation, which provides the analyst with additional structural information, a cleaner spectrum, and increases confidence in the origin of the ions detected.

Experimental

Samples

Three separate solutions were prepared of PMMA 4000, LiCl, and NaI, each at 1.0 mg/mL in methanol. These solutions were mixed and diluted to make the following:

100 ppm PMMA 4000 and 100 ppm LiCl in methanol

100 ppm PMMA 4000 and 100 ppm NaI in methanol

MS conditions

MS system:	Xevo G2 QTof
Ionization mode:	ESI+
Analyzer:	Resolution mode
Infusion rate:	10 μL/min
Acquisition rate:	1 spectrum/sec
Capillary voltage:	2.5 kV
Sample cone:	150 V
Extraction cone:	4.0 V
Source temp.:	150 °C

Desolvation temp.:	200 °C
Cone gas:	Nitrogen, 20 L/hr
Desolvation gas:	Nitrogen, 600 L/hr

LockSpray conditions

Compound:	Leucine enkephalin
Mass:	*m/z* 556.2771
Flow rate:	20 µL/min
Capillary voltage:	3.0 kV
Collision energy:	6.0 V

Results and Discussion

Figure 1 shows PMMA 4000 cationized with Li^+ and PMMA 4000 cationized with Na^+. Both singly and doubly charged ions are present in both spectra. The inserts show two ion clusters in more detail, the 0.5 *m/z* difference between the isotopes confirms this is a doubly charged species. We can see the majority of PMMA is present as $[M + 2Li]^{2}+$ and $[M + 2Na]^{2+}$.

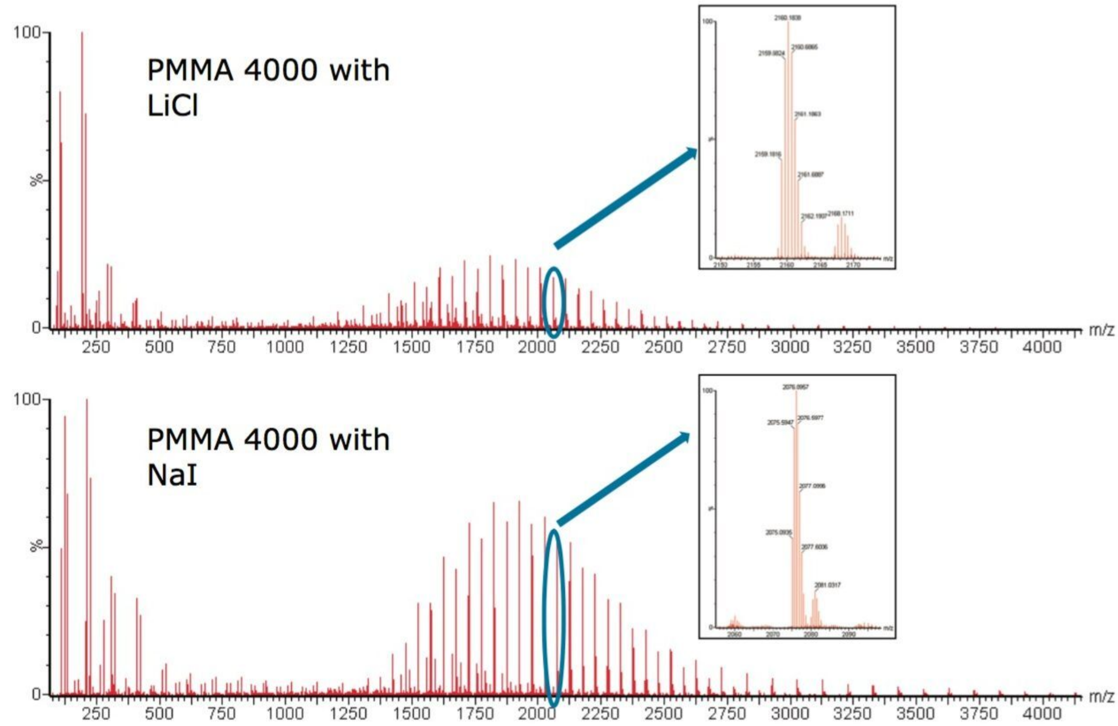


Figure 1. PMMA 4000 cationized with Li$^+$ (upper spectrum) and PMMA 4000 cationized with Na$^+$ (lower spectrum).

MS/MS experiments were carried out on the abundant oligomeric ions of the 38-mer for both the lithiated and sodiated PMMA, with *m/z* 1910 and 1926 respectively. The spectra from the MS/MS experiments are shown in Figure 2.

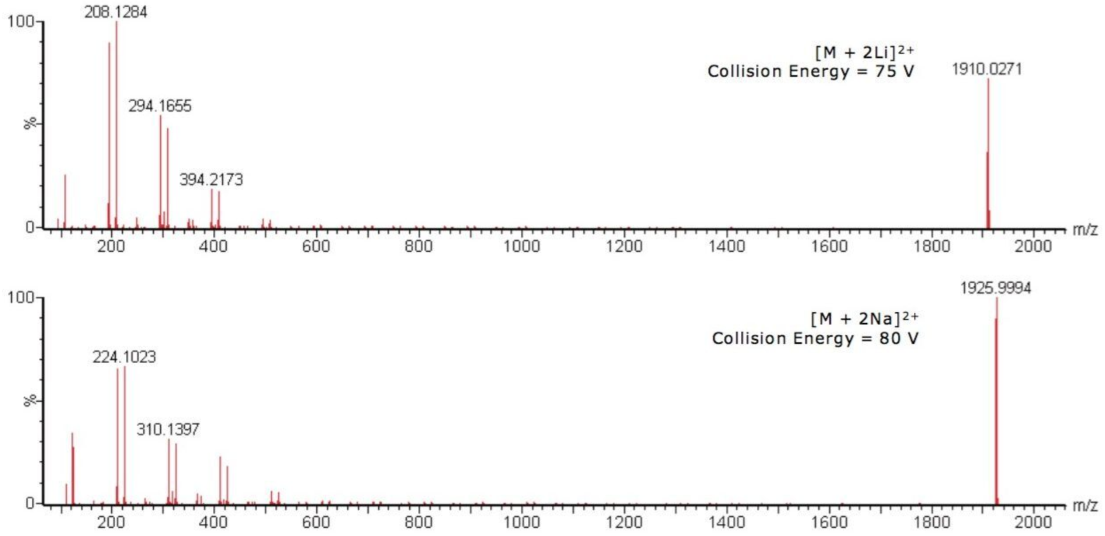


Figure 2. MS/MS spectra for PMMA 4000. The precursor ions chosen were m/z = 1910 and 1926, for lithiated and sodiated ions respectively.

MS/MS results for the lithiated and sodiated PMMA show the same trend, each having two series of ions 100 *m/z* units apart. Figure 3 shows the PMMA monomer repeat unit, which has a mass of 100 Da. The sodiated results are 16 *m/z* units higher than the lithiated, which is consistent with the mass difference between the two cations.

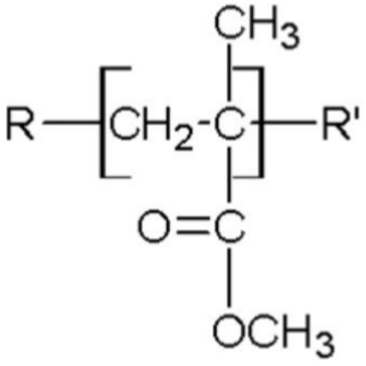
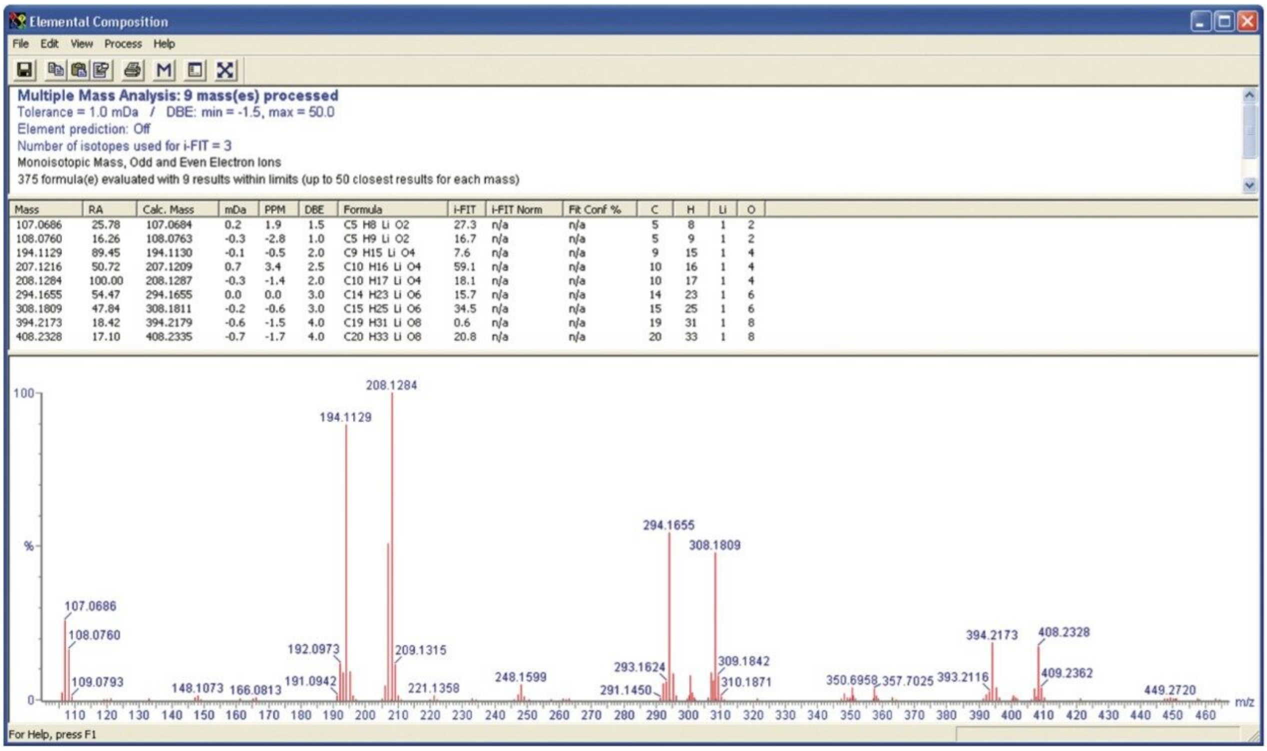


Figure 3. PMMA monomer repeat unit.

The results for lithiated PMMA have been considered in more detail using an option within MassLynx Software called Elemental Composition (EleComp). EleComp can be found in the Tools dropdown list in the Spectrum window. Figure 4 shows the EleComp results for masses above 15% relative abundance within the selected portion of the spectrum. EleComp has calculated possible formulae that could create ions of these masses. The results show that the ions of interest are within 1 mDa of the theoretical exact mass.



Multiple Mass Analysis: 9 mass(es) processed
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotopes used for i-FIT = 3
Monoisotopic Mass, Odd and Even Electron Ions
375 formula(e) evaluated with 9 results within limits (up to 50 closest results for each mass)

Mass	RA	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	Li	O
107.0686	25.78	107.0684	0.2	1.9	1.5	C5 H8 Li O2	27.3	n/a	n/a	5	8	1	2
108.0760	16.26	108.0763	-0.3	-2.8	1.0	C5 H9 Li O2	16.7	n/a	n/a	5	9	1	2
194.1129	89.45	194.1130	-0.1	-0.5	2.0	C9 H15 Li O4	7.6	n/a	n/a	9	15	1	4
207.1216	50.72	207.1209	0.7	3.4	2.5	C10 H16 Li O4	59.1	n/a	n/a	10	16	1	4
208.1284	100.00	208.1287	-0.3	-1.4	2.0	C10 H17 Li O4	18.1	n/a	n/a	10	17	1	4
294.1655	54.47	294.1655	0.0	0.0	3.0	C14 H23 Li O6	15.7	n/a	n/a	14	23	1	6
308.1809	47.84	308.1811	-0.2	-0.6	3.0	C15 H25 Li O6	34.5	n/a	n/a	15	25	1	6
394.2173	18.42	394.2179	-0.6	-1.5	4.0	C19 H31 Li O8	0.6	n/a	n/a	19	31	1	8
408.2328	17.10	408.2335	-0.7	-1.7	4.0	C20 H33 Li O8	20.8	n/a	n/a	20	33	1	8

Figure 4. Elemental Composition results for lithiated PMMA (38-mer) analyzed in MS/MS mode. Results for masses above 15% relative abundance within the selected portion of the spectrum are displayed.

With this information it is possible to propose the structure, shown in Figure 5. Nomenclature for the fragments has been taken from the Proceedings of the 54th ASMS Conference.[4]

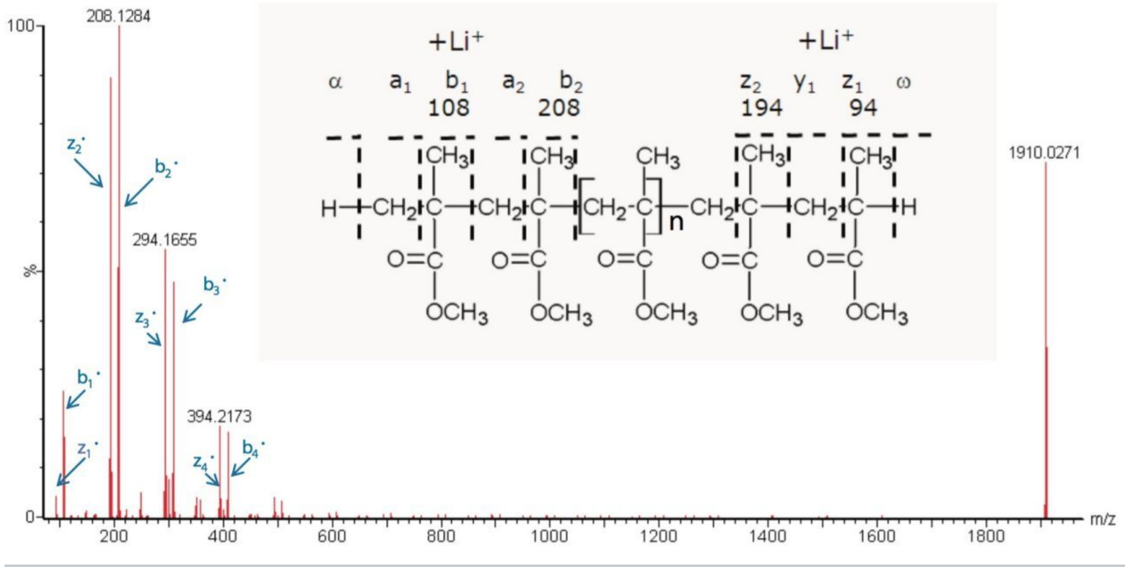


Figure 5. Proposed structure for PMMA end groups with corresponding spectrum.

Conclusion

- Data from the Xevo G2 QTof were successfully used to propose the end group structure for PMMA 4000, using an approach that is appropriate for many polymer systems. This is a very valuable measurement for the industry as it can indicate the synthetic process followed and guide how further chemical modifications can be carried out.
- Operating the QTof in MS/MS mode provides the analyst with additional structural information, a cleaner spectrum, and increases confidence in results.
- The Elemental Composition tool within MassLynx Software quickly provides the analyst with automated formulae information.

References

1. A T Jackson, K Thalassinos, R O John, N McGuire, D Freeman, J H Scrivens. Polymer. 51 (2010) 1418-1424.

2. A T Jackson, S E Slade, J H Scrivens. International Journal of Mass Spectrometry. 238 (2004) 265-277.
3. G Montaudo and R Lattimer. Mass Spectrometry of Polymers. Boca Raton: CRC Press LLC; 2002. 68 p.
4. A T Jackson, R P Lattimer, P C Price, W E Wallace, M J Polce, C Wesdemiotis. Proposal for a common nomenclature of fragment ions in the mass spectra of synthetic polymers. Proceedings of the 54th ASMS Conference on Mass Spectrometry and Allied Topics, Seattle, WA, May 28-June 1, 2006.

Featured Products

MassLynx MS Software <https://www.waters.com/513662>

720004252, March 2012