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Application News

MALDI-TOF Mass Spectrometry Analysis MALDI-8030

Analysis of Negatively Charged Polymers using the MALDI-8030 Dual Polarity Benchtop MALDI-TOF Mass Spectrometer

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User Benefits

- Easy polymer data analysis on affordable benchtop MALDI-8030 with good isotopic resolution
- Data compatibility with Polymerix software produces confident results for polymer confirmation, indices and end-groups
- MALDI-8030 with Polymerix is appropriate solution for polymer chemists and synthesis laboratories using negative mode

■ Introduction

The MALDI-8030 (Fig 1) is the latest benchtop MALDI-TOF mass spectrometer from Shimadzu, building on the performance of the compact and powerful MALDI-8020. The MALDI-8030 offers the versatility to analyse samples in both positive and negative ion modes. In this article, we demonstrate the capability of the MALDI-8030 for the analysis of polymers that can not be easily analysed in positive ion mode.

Fig. 1 MALDI-8030 dual polarity benchtop MALDI-TOF mass spectrometer.

Polymethacrylic acid (PMAA, Fig 2) is a polymer with applications in tissue culture as a polymer conjugate[1], in chemotherapy as a nanoparticle drug delivery system[2] and in the colourant industry as a controlled release capsule for dyes[3]. The ability to analyse this polymer using MALDI allows for rapid characterisation and confirmation of synthesis products for busy laboratories.

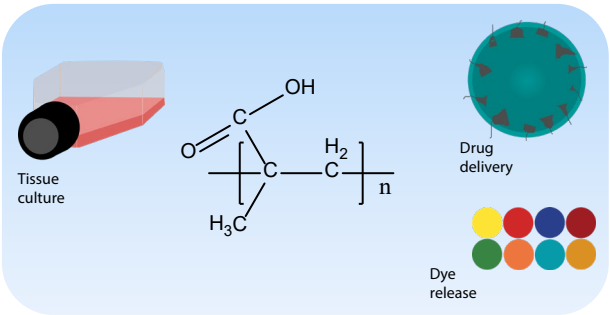

Fig. 2 PMAA structure and industrial applications.

■ Measurement Conditions and Samples

PMAA was purchased from Merck (Poly(methacrylic acid sodium salt) analytical standard, for GPC, 1,270) and was prepared at 10 mg/mL in deionised H_2O. Ion exchange was performed on the PMAA solution using activated Dowex 50W-X8 ion-exchange beads (IXB).

2,4,6-Trihydroxyacetophenone (THAP) matrix solution was prepared at a concentration of 10 mg/mL in 1:1 (vol/vol) H_2O/MeCN. Di-ammonium hydrogen citrate (DAC) solution was prepared at 50 mg/mL in H_2O. DAC was added to the matrix solution in a ratio of 9:1 matrix:DAC.

0.5 µL of 10 mg/mL sodium acetate (NaOAc) was applied to the spot and allowed to dry prior to spotting 0.5 µL sample and 0.5 µL matrix. Samples were left to dry completely before analysis in the MALDI-8030. Table 1 shows the measurement conditions.

The data was then exported as an ASCII file for processing in the third-party software Polymerix™ (Sierra Analytics).

Table 1 Measurement Conditions.

PMAA acquisition on MALDI-8030	
Polarity	Negative
Laser power	77
Mass range	700 - 4000
Pulsed extraction	1200
Low mass beam blanking	700
Profiles	270
Peak smoothing	None (raw data used)

■ Results of PMAA Analysis

The mass spectrum shown in Fig. 3 overleaf, demonstrates the good quality isotopically resolved data attainable using the MALDI-8030 in negative ion mode.

Using the accurate masses, it was easy for Polymerix to assign the peaks within the distribution to the polymer formula, confirm the polymer end-groups and calculate the polymer indices (Fig. 4). This was performed across three polymer series in the spectrum with a confident fit (excess mass close to zero, inset in Fig. 4). The determined relative abundance between the series is also shown.

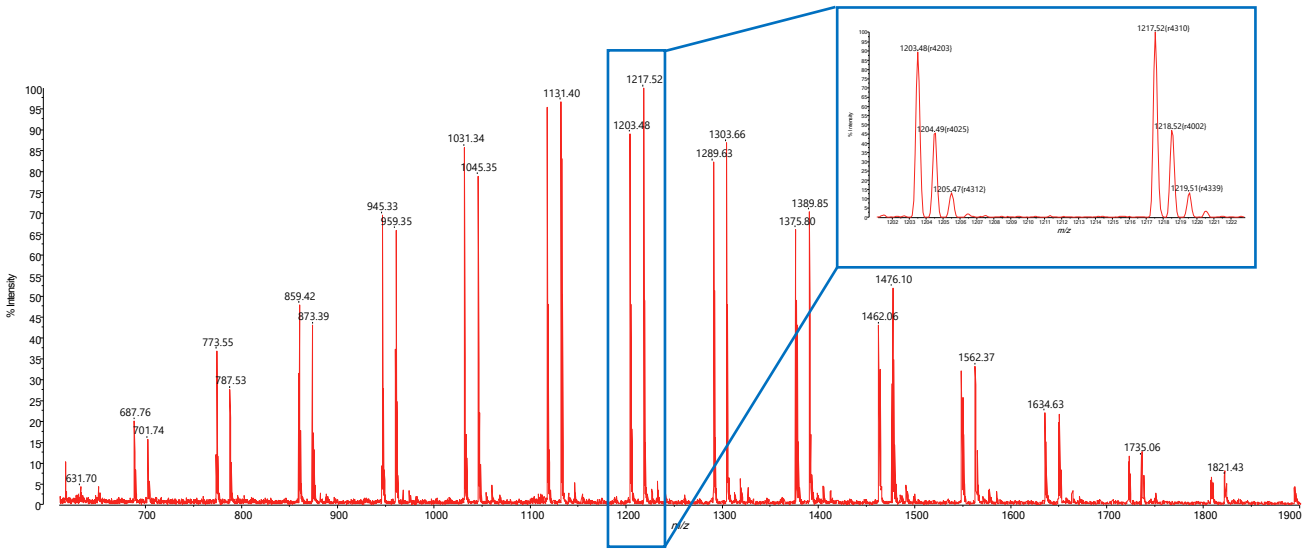

Fig. 3 PMAA spectrum acquired in negative ion mode on the MALDI-8030. Inset: Expanded view demonstrating the resolution achieved.

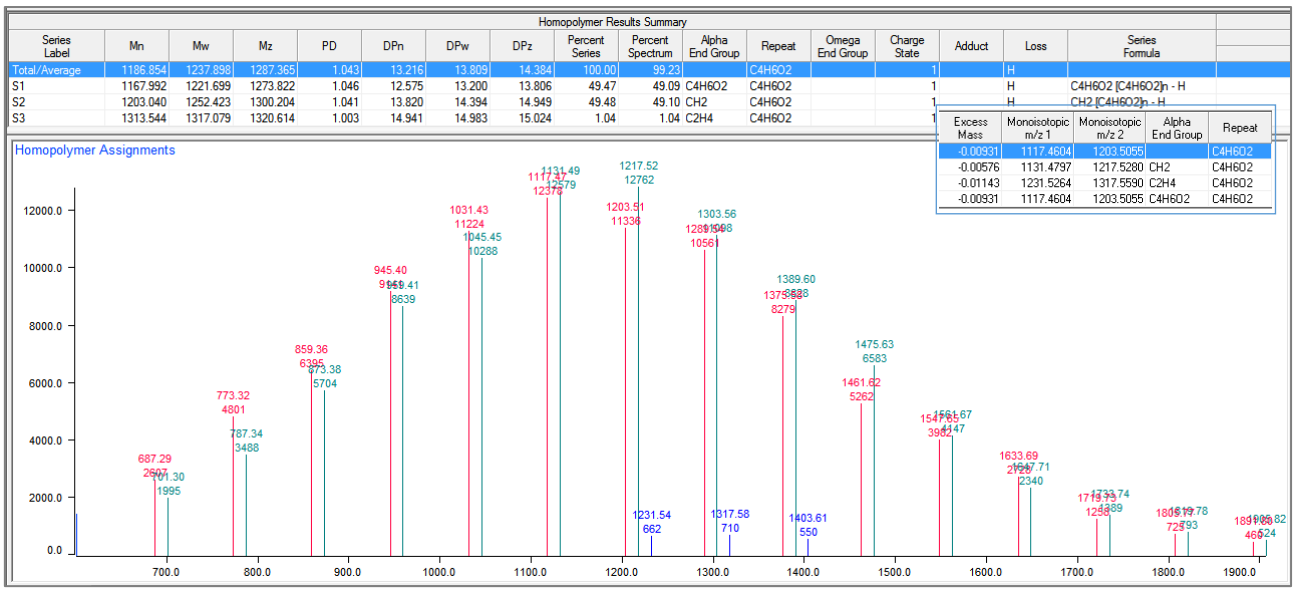

Fig. 4 PMAA data processing in Polymerix. Top: Polymer indices calculation; Bottom: Assignment of monomer units to polymer series. Inset: low excess mass adds confidence to assignments.

■ Conclusion

The MALDI-8030 produces high quality data in negative ion mode which, when combined with Polymerix software, leads to quick confirmation of monomer unit, the indices and end-group assignments with a high level of confidence.

This simple workflow is a suitable solution for polymer chemists and polymer manufacturing laboratories.

Polymerix is a trademark of SIERRA ANALYTICS, INC.

■ References

[1] Y. Shaojun et al. Journal of Materials Chemistry, 2012, 22(26), 13039-13049.

[2] A. Shalviri et al. Eur J Pharm Biopharm. 2012, 82(3), 587-597.

[3] T. Kida et al. Langmuir. 2012, 28(43), 15378-15384.

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