

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
- ALDI-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 conjugate¹, in chemotherapy as a nanoparticle drug delivery system² and in the colourant industry as a controlled release capsule for dyes³. The ability to analyse this polymer using MALDI allows for rapid characterisation and confirmation of synthesis products for busy laboratories.

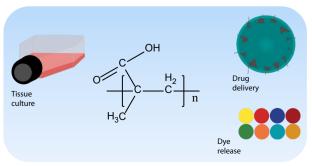


Fig. 2 PMAA structure and industrial applications.

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 H₂O. 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) H₂O/MeCN. Di-ammonium hydrogen citrate (DAC) solution was prepared at 50 mg/mL in H₂O. DAC was added to the matrix solution in a ratio of 9:1 matrix:DAC.

0.5 μ L of 10 mg/mL sodium acetate (NaOAc) was applied to the spot and allowed to dry prior to spotting 0.5 μ L sample and 0.5 μ L 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).

| 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) |

Table 1 Measurement Conditions.

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.

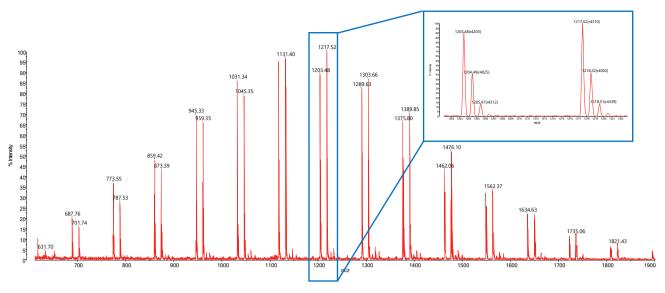


Fig. 3 PMAA spectrum acquired in negative ion mode on the MALDI-8030. Inset: Expanded view demonstrating the resolution achieved.

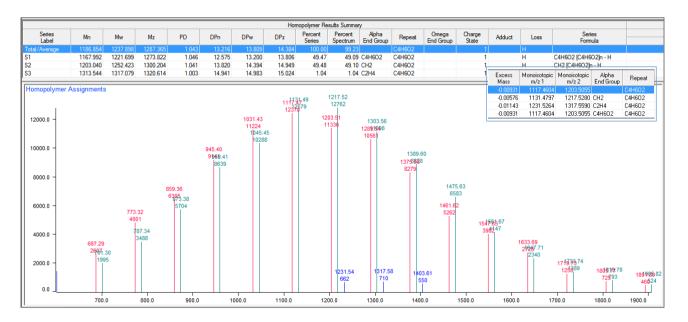


Fig. 4 PMAA data processing in Polymerix. Top: Polymer indices calculation; Bottom: Assignment of monomer units to polymer series. Inset: low excess mass adds confidence to assignments.

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

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



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