Matrix-assisted Laser Desorption Ionization Time-of-flight (MALDI-TOF) Mass Spectrometry for Advanced Polymer Characterization

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Basis of Technique

MALDI-TOF is a mass spectrometry measurement commonly used for polymers, proteins, nucleic acids, and similar organic compounds. The technique involves the irradiation of co-crystallized sample and matrix material to induce “soft ionization”. The matrix absorbs UV light, sublimates the crystals, and transfers a proton (or adduct ion) to the sample. This technique is “soft” because sample fragmentation is usually avoided; as opposed to harsher ionization techniques employed in GC/MS or LC/MS. A magnetic field is then applied to the ionic cloud to accelerate the sample along the time-of-flight (TOF) tube. The TOF time is directly proportional to the ion’s mass divided by it’s charge.

$$TOF = Constant * \sqrt{m/z}$$

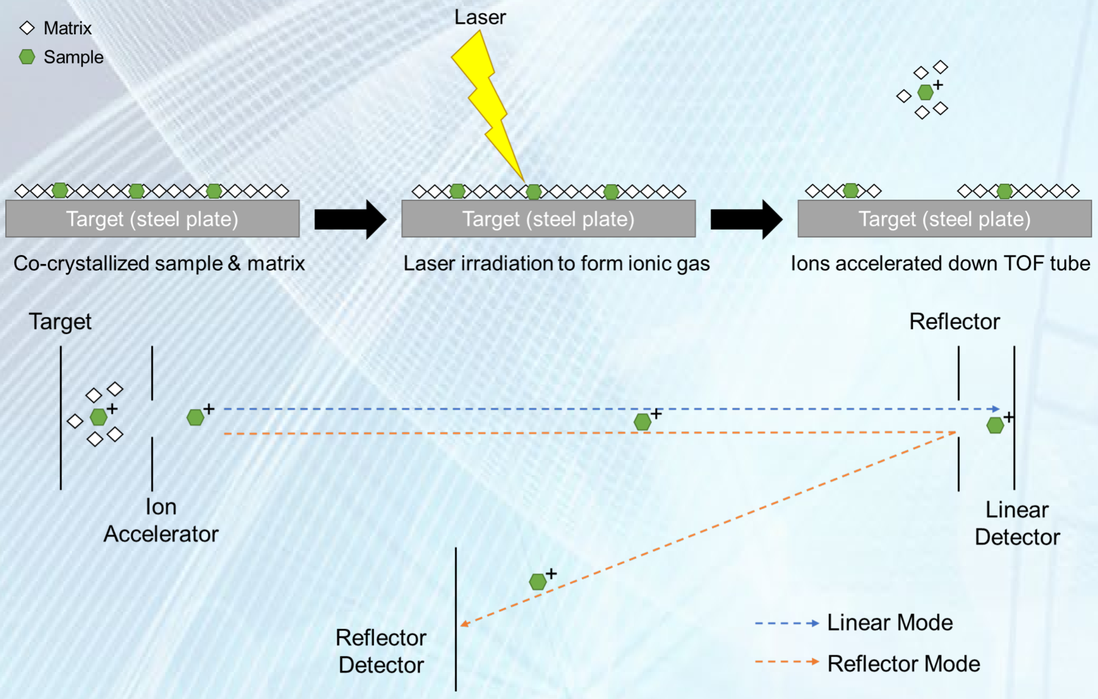
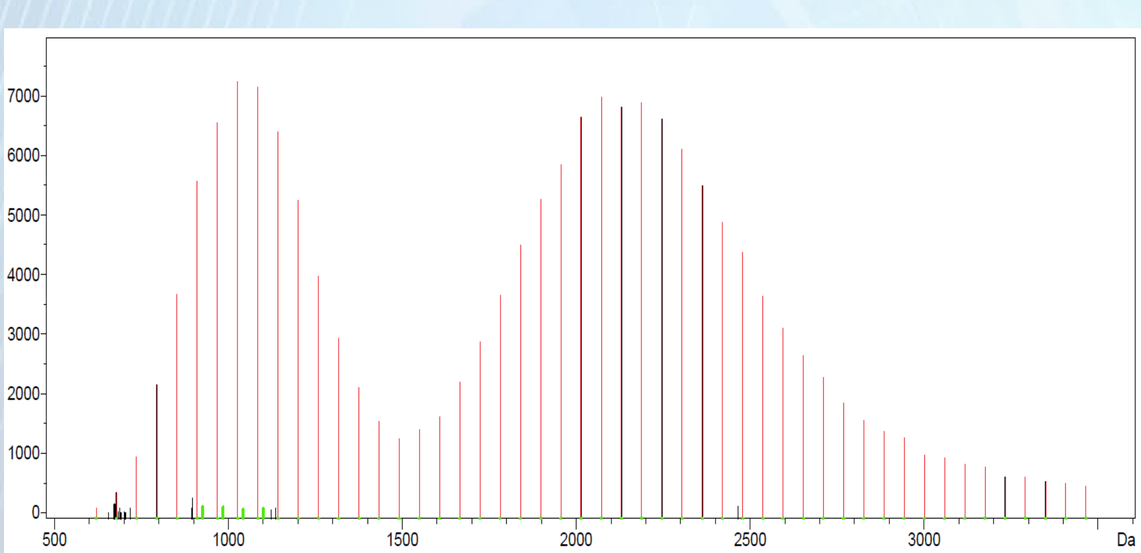


Figure 1- Diagram of MALDI-TOF ionization and detection process. Reproduced with permission from Bruker Daltonics.

Comparison to Gel Permeation Chromatography (GPC)

GPC has been the standard method for determining polymer molecular weights for decades but has some limitations. Inherently, GPC provides broad curves corresponding to the range of molecular weights present while MALDI-TOF can give resolution of exact masses corresponding to individual oligomers while in reflectron mode (Figure 3). GPC is limited to soluble polymers while MALDI is limited to ionizable polymers. GPC has a lower limit of molecular weights (~150 Da) while MALDI has an upper limit (~20 kDa for reflectron and ~500 kDa for linear mode). GPC can be slow at ~1 h per measurement while MALDI can be ~3 min per measurement. And GPC provides little information on the repeat units and end-groups where MALDI can give you precise identifications.

Alternatively, MALDI exhibits higher intensity peaks for lower molecular weight species which leads to difficulties in accurately measuring molecular weight distributions (MW, MN) for polydisperse (PD>~1.3) materials (Mass Discrimination). Finally, method development for new materials can take time (especially for non-polar polymers) to determine an appropriate recipe for a new polymer.



n	ser.	rep.unit	orig. resid.	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
1	1	~ PPG	40.8732	-0.12715	H	OH	Na	1826.06	2062.07	1.12924	31.4791	97.5	50
2	2	~ PPG	56.6576	-0.33766	OH	OH	Na	985.268	989.599	1.00440	16.9848	0.4	4

Figure 2- Polymer ladder data for poly(propylene glycol) reference standards with repeat unit and end-group identification.

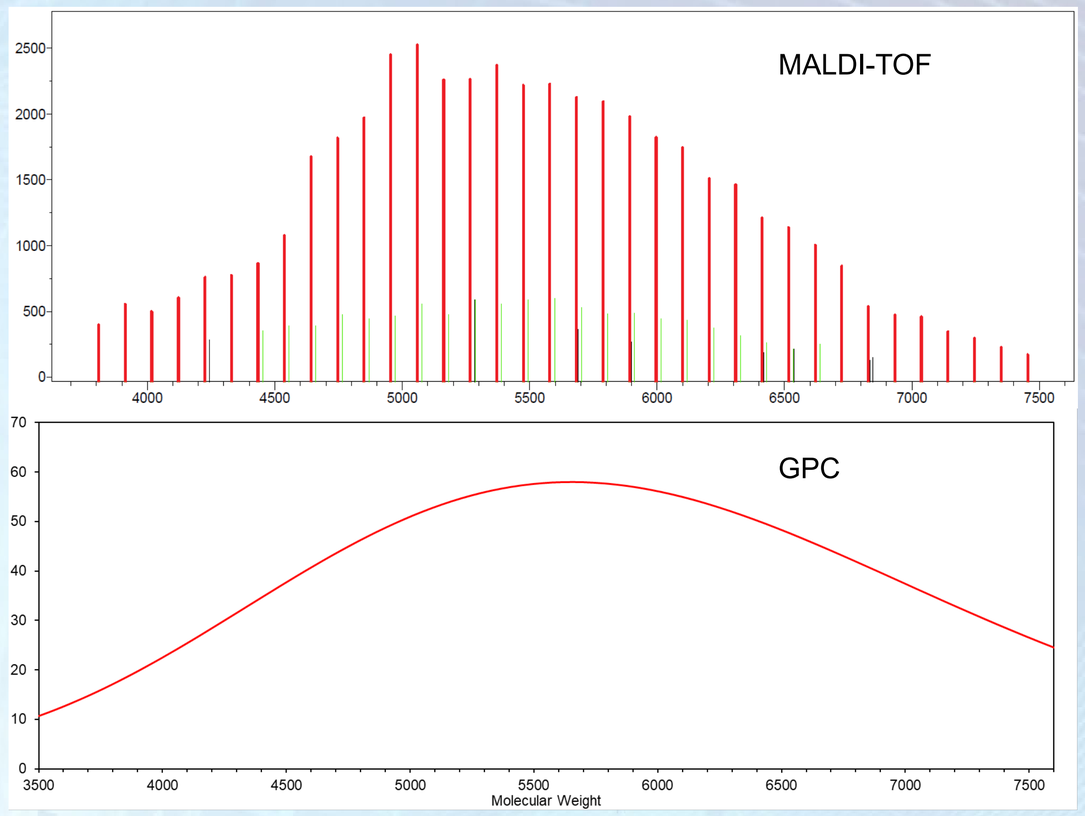


Figure 3- Comparison plots of MALDI-TOF & GPC data for a polystyrene reference standard with M_P = 5400. Y-axes are arbitrary units of intensity.

Potential Applications

Analysis of mixtures with different end-groups and additives as shown in Figure 2. Co-polymer analysis for block and random polymers including through a combination of soft ionization and induced fragmentation (LIFT MS/MS) as shown in Figure 4. Failure analysis through quick identification of contaminant species and for determining if the desired plasticizer additives are present. Kendrick defect plots are produced by software and are convenient, visual guides for determining what homologous materials are present and what differences are occurring between lots. Polymer architecture analysis (including branch sizes) is possible in some cases. Surface analysis by depositing matrix crystals over areas of interest (limited to ~1mm samples).

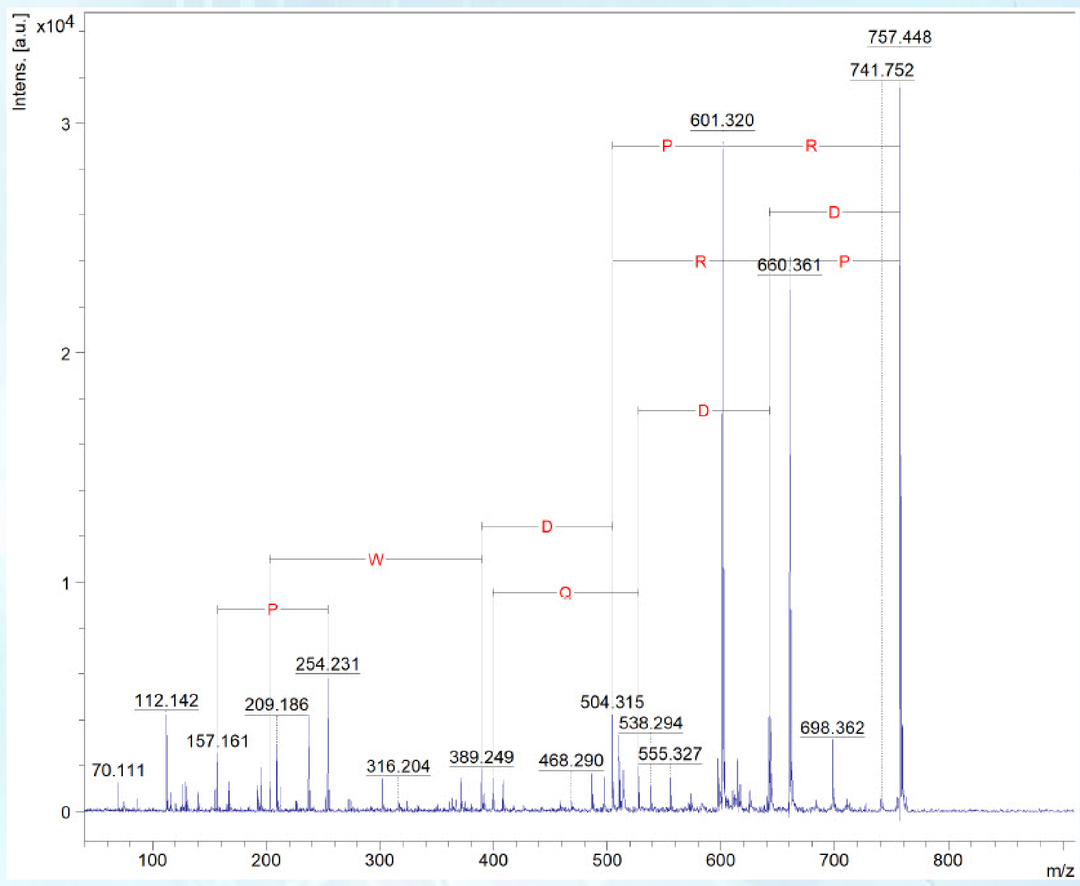


Figure 4- LIFT MS/MS example data from Bradykinen peptide standard (Parent Mass 757.44 Da) showing amino acid fragments. Can also be utilized for polymer analysis especially for random vs. block co-polymer determination.

Summary

MALDI-TOF mass spectrometry is a new capability at KCNSC presenting opportunities for in-depth analysis of polymers and similar organic compounds. This method is unique compared to other MS measurements by avoiding compound fragmentation to measure full molecular weights. The results can be a valuable addition to the data collected through GPC-MALS while being significantly faster to perform. Measurements include repeat unit and end-group identification, co-polymer analysis, identification of plasticizers and contaminants, polymer architecture studies, and surface analysis.

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