

## Breaking Boundaries in High-Mass Polymer Analysis with neofleX™ Benchtop MALDI-TOF

neofleX benchtop MALDI-TOF provides research-grade performance in a lab-space-efficient form factor making it an ideal platform for enhanced characterization of synthetic polymers throughout an extended molecular mass range of up to several hundred kiloDaltons.

### Abstract

MALDI-TOF MS is a key analytical method for polymer analysis providing accurate molecular weight information and unbiased polymer distribution profiles.

The neofleX benchtop MALDI-TOF instrument incorporates latest innovative MALDI technologies, such as smartbeam 3D laser, optimized ion optics, and next-generation detectors. In combination with a compact benchtop design, these advances enable exceptional performance in the analysis of large synthetic polymers and other macromolecules of molecular weights far beyond 100 kDa.

We demonstrate here the superior high-mass capabilities of the neofleX MALDI-TOF instrument using high-molecular-weight polystyrenes as an example. The results highlight significantly improved resolution and sensitivity across an extended mass range up to 500 kDa and beyond. At the same time, the instrument provides 30,000 resolving power in the lower  $m/z$  range enabling structural insight for high-molecular-weight polymers by analysis of MALDI in-source decay fragments proving the neofleX as a highly versatile platform for advanced polymer research.

Keywords:  
Polymers, high molecular weight, high mass, MALDI-TOF, MALDI-MS, neofleX, PolyTools

## Introduction

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF MS) is a well established, indispensable tool for polymer characterization due to the accurate molecular weight information and unbiased polymer distribution profiles it provides. While MALDI-TOF offers unique access to a virtually unlimited mass range, analysis of high-molecular-weight (HMW) polymers in the mass range of several hundred kiloDaltons has remained a challenge with regard to resolution and sensitivity, thus becoming a limiting factor in advanced polymer research.

The new neoflex MALDI-TOF MS instrument overcomes previous limitations by utilizing Bruker's latest MALDI technologies, such as smartbeam 3D laser for highly efficient sample ablation and ionization, enhanced ion optics for lossless ion transmission and a new generation of detectors providing optimal sensitivity across an ultrawide  $m/z$  range. These innovations, accommodated in an attractive benchtop form factor, translate directly into a unique level of performance providing particular benefit to the analysis of large synthetic polymers and other macromolecules with molecular weights far beyond 100 kDa while maintaining up to  $R=30,000$  resolving power in the lower mass range.

We demonstrate the outstanding neoflex high-mass performance on the example of HMW polystyrene samples. Presented data clearly illustrate enhanced resolution and sensitivity neoflex delivers for polymer samples with molecular weights up to 500 kDa. In addition, we utilize the instrument's ultimate resolving power in the analysis of MALDI in-source decay fragments for instant verification of the repeat unit present in HMW polymers.

## Experimental

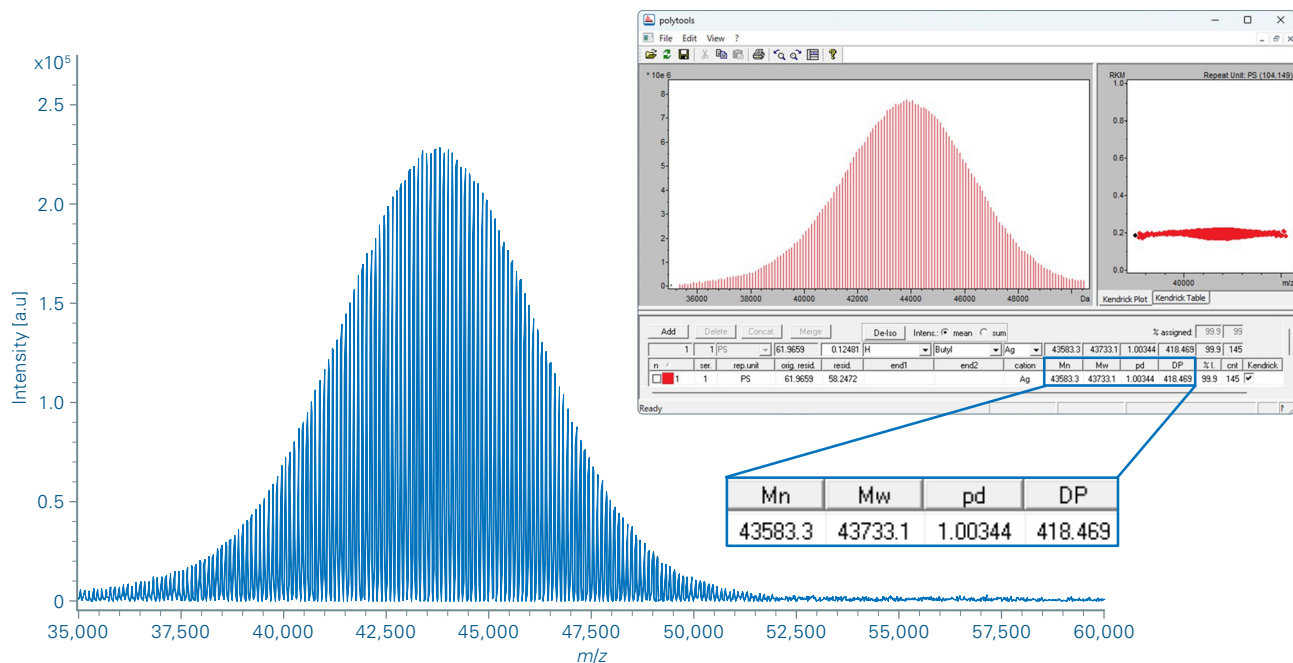
Polystyrenes with average molecular weights 44, 97, 150, 190 and 400 kDa were purchased from Sigma-Aldrich. All samples were dissolved in THF at a concentration of 10 g/L. DCTB, prepared at 20 g/L in THF, was used as a MALDI matrix. Silver trifluoroacetate solution (2 g/L in THF) was used as a cationizing additive to promote the formation of  $[M+Ag]^+$  molecular ions. Sample, matrix and salt solutions were premixed in a volume ratio, depending on polymer molecular weight, between 3:20:1 and 3:100:1, and sub-microliter aliquots of the mixture were applied as a thin layer onto an MTP 384 Ground Steel MALDI target plate.

Data acquisition was performed on a neoflex benchtop MALDI-TOF/TOF instrument in either linear or reflector MS operation mode. All spectra were acquired in positive ion polarity.

Data processing, i.e. smoothing, baseline correction and peak picking, was performed in flexAnalysis 5.0.

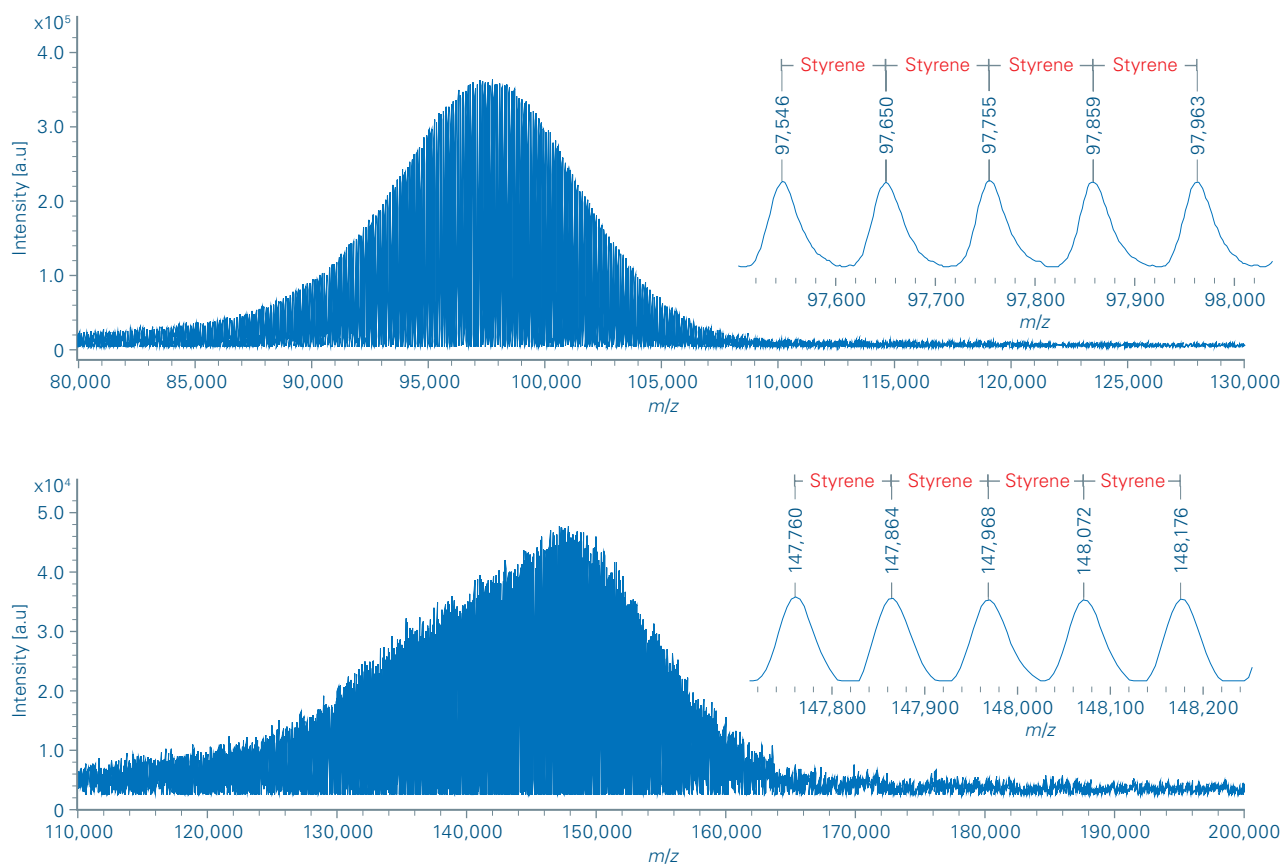
Data analysis was performed using Bruker PolyTools 2.0 software.

## Results



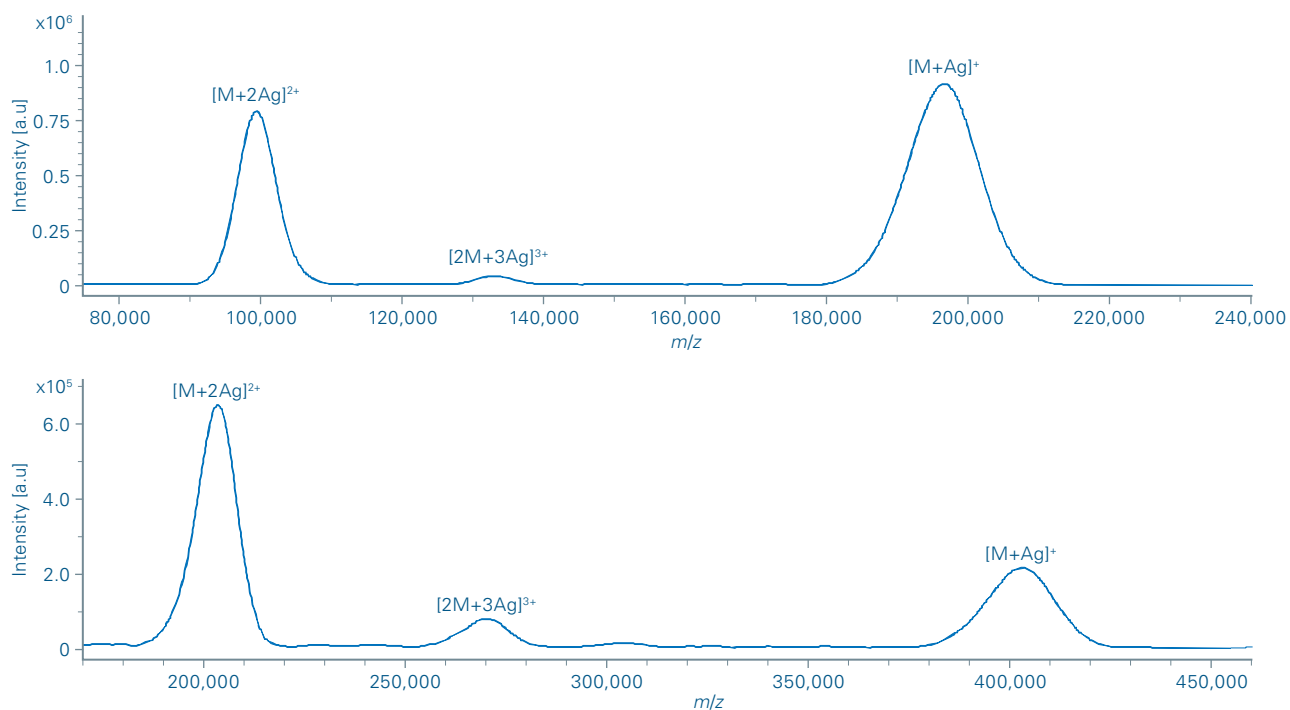
**Figure 1.** MALDI-TOF spectrum of polystyrene 44 kDa acquired in reflector mode.

The spectrum shows well resolved signals of oligomers in a distance of 104  $m/z$  representing the styrene monomer unit ( $C_8H_8$ ). Data analysis in PolyTools 2.0 software allowed for instant automated calculation of key polymer parameters, such as weight average molecular weight  $M_w$ , number average molecular weight  $M_n$ , dispersity (previously known as polydispersity  $pd$ ) and degree of polymerization  $DP$ .



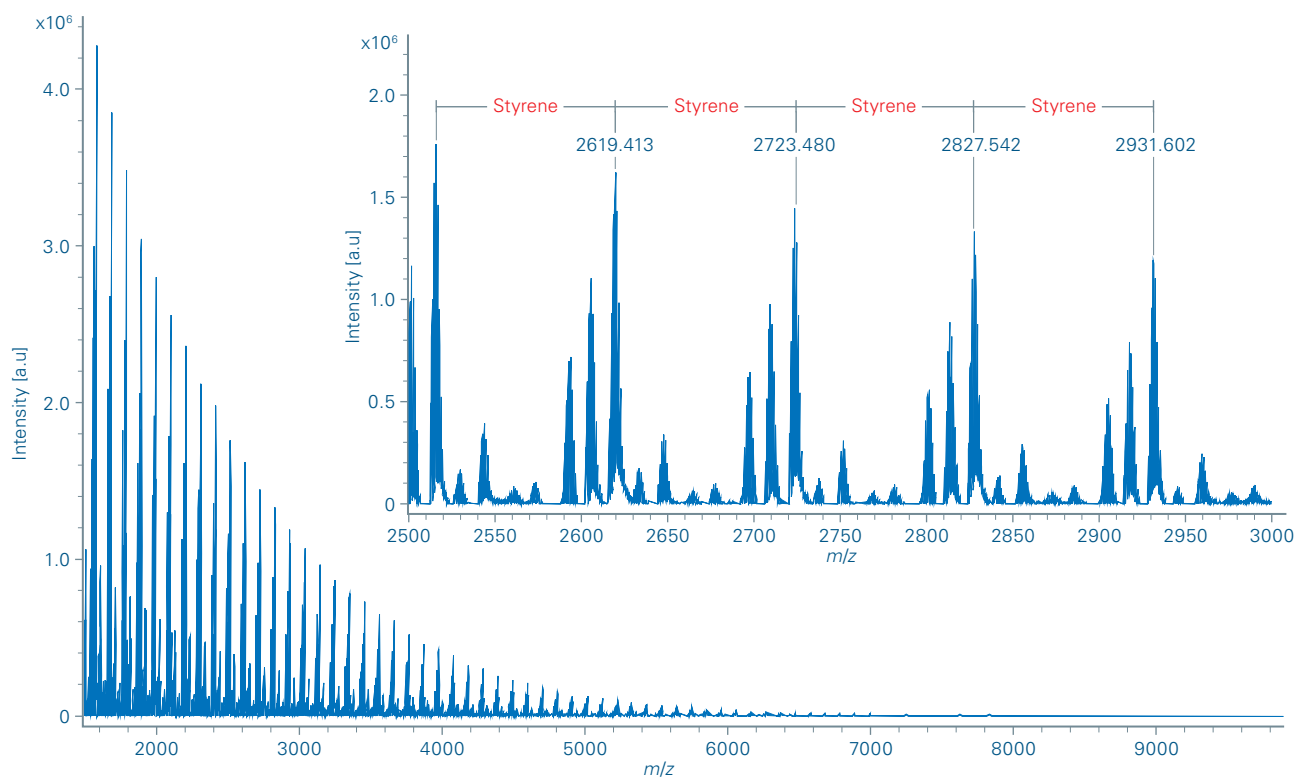
**Figure 2.** MALDI-TOF spectra of polystyrene 97 kDa and 150 kDa acquired in reflector mode.

As a benefit from the resolving power achieved in reflector mode, oligomeric resolution was maintained in the spectra of these high-mass polymer samples.



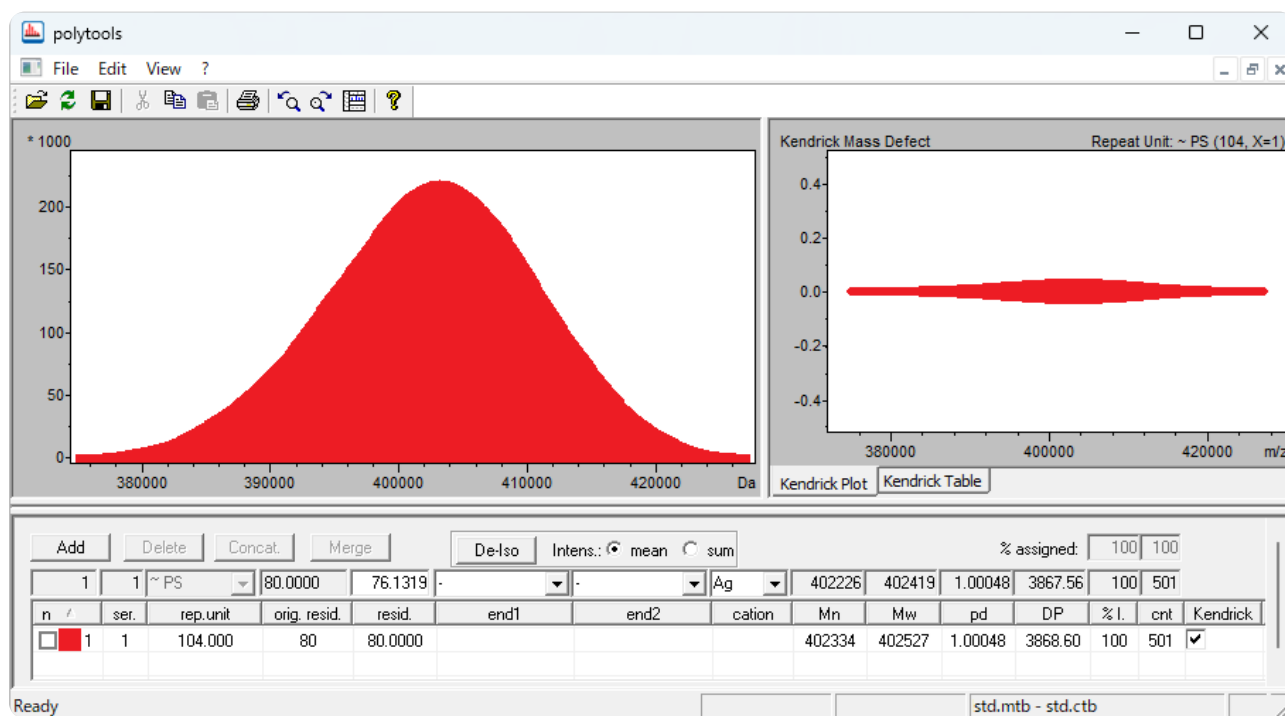
**Figure 3. MALDI-TOF spectra of polystyrene 190 kDa and 400kDa acquired in linear mode.**

Enhanced neoflex high-mass sensitivity allowed for reliable detection of polymer species with molecular weights of up to several hundred kiloDaltons. The repeat unit is no longer resolved in the intact-mass spectra of these large-size polystyrenes. However, verification of the repeat unit is easily possible by means of MALDI-HSD analysis (see Figure 4).



**Figure 4. MALDI in-source decay (MALDI-ISD) spectrum of polystyrene 400 kDa acquired in reflector mode at elevated laser fluence.**

The distance between fragment ions of 104 Da clearly confirms the styrene repeat unit, which was not directly visible from the intact-mass MALDI-MS spectrum of this high-molecular-weight polymer.



**Figure 5.** In combination with tailored spectra pre-processing in flexAnalysis software, PolyTools software is able to automatically calculate polymer parameters  $M_w$ ,  $M_n$ , pd and DP from continuous spectra (i.e. spectra lacking repeat-unit resolution) of high-molecular-weight polymer samples, such as the 400 kDa polystyrene shown here.

## Conclusion

- neofleX benchtop MALDI-TOF delivers exceptional performance in the analysis of synthetic polymers as a direct benefit from implementation of latest innovative Bruker MALDI technologies, i.e. smartbeam 3D laser, advanced ion optics and a new generation of detectors.
- neofleX allows for seamless detection of high-molecular-weight polymers ranging up to 400 kDa and beyond at improved resolution and sensitivity enabling reliable determination of key polymer parameters, i.e. molecular weight and unbiased polymer distribution profile.
- At the same time, the instrument provides up to  $R=30,000$  resolving power in the lower mass range enabling instant verification of repeat units in HMW polymers by MALDI-ISD analysis.
- neofleX's unique performance throughout an ultrawide analyte mass range makes it an indispensable, highly versatile analytical tool advancing macromolecular research and accelerating the development of new functional materials.

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