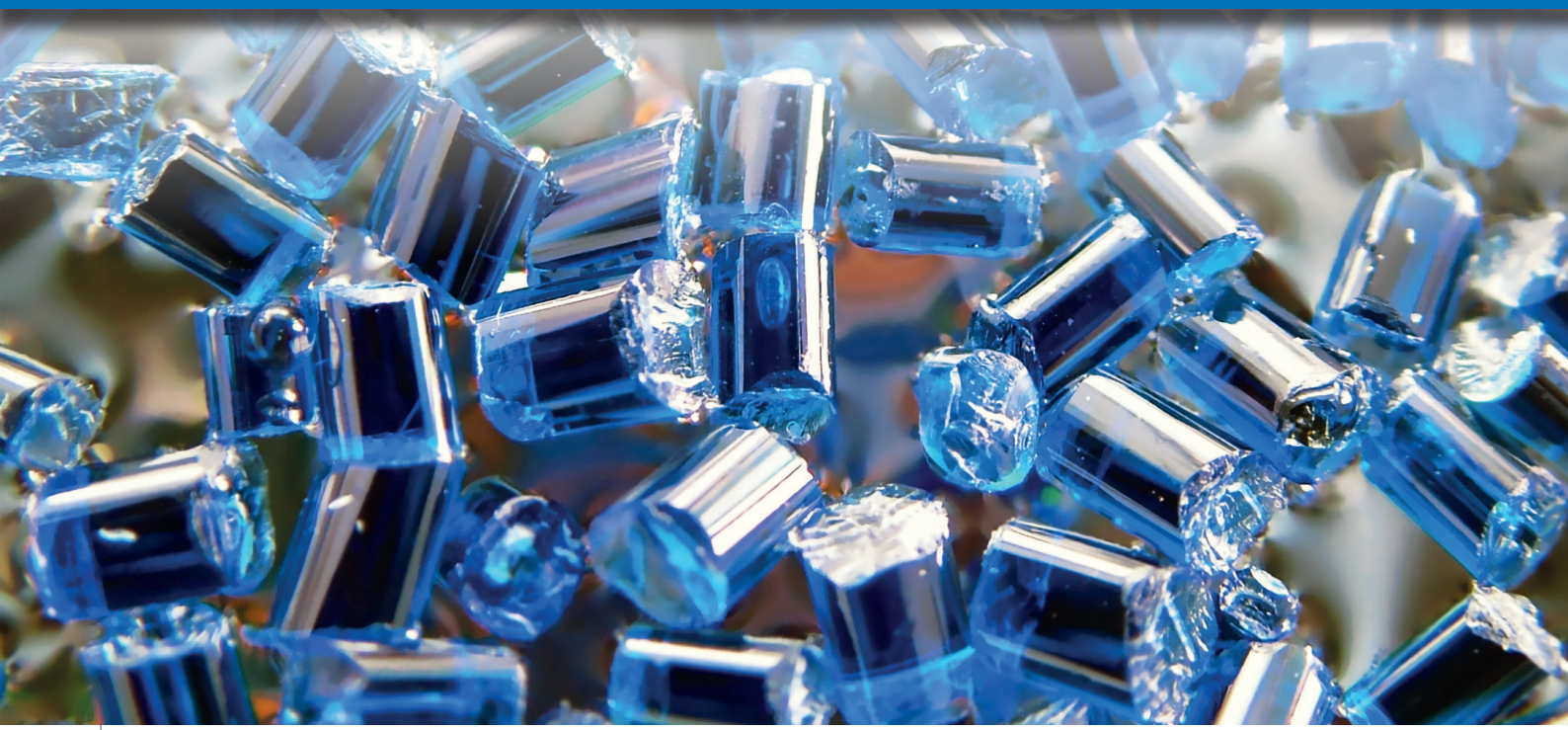

Polystyrene analysis using MALDI-TOF MS

Three polystyrene samples covering a mass range from 2 kDa to 200 kDa were analyzed using an autoflex maX MALDI-TOF MS.

Abstract

For all samples, several characteristic values were determined, including the average molecular weights M_n and M_w, the monomer mass, the sum-mass of the present end-groups and, to a certain extent, even the chemical compositions.

Introduction

The production of polymer materials is currently under severe economic pressure. Therefore, quality control of raw materials or finished goods is of increasing importance in order to avoid product failure or even health risks. A standard procedure for the detection of the average molecular mass of polymer samples is size exclusion chromatography. This technique, however, cannot reveal the chemical structures behind the detected polymer masses. Other methods like FTIR or NMR spectroscopy can be used to generate chemical information.

Unlike the aforementioned technologies, **M**atrix **A**ssisted **L**aser **D**esorption/**I**onization-**T**ime **O**f **F**light **M**ass **S**pectrometry (MALDI-TOF MS) offers the unique possibility to detect the average molecular weights and concurrently delivers detailed information on the chemical composition of the sample.

A detailed workflow for the analysis of synthetic polymers by MALDI-TOF MS is also given in ISO 10927:2018-10 [1].

Keywords:
MALDI, autoflex maX, Polymer, Polystyrene

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Experimental

The polystyrene samples with M_p = 1920 Da (PS1) and M_p = 210 kDa (PS3) were purchased from Polymer Standards Services GmbH (Mainz, Germany). A polystyrene sample with molecular weight M_p = 19 kDa (PS2) was purchased from Polymer Laboratories LTD (Church Stretton, UK).

All samples were dissolved in THF at a concentration of 10 g/L. DCTB, prepared at 20 g/L in THF, was used as the matrix. Silver trifluoroacetate, was prepared as the doping salt at a concentration of 0.1 M in THF. The polymer, matrix, and salt solutions were mixed in a ratio 3:20:1 for PS1 and PS2 and 3:100:1 for PS3. A droplet of the mixture (0.5 μL) was hand-spotted onto three spots of a gound steel target plate.

An autoflex® maX (Bruker Daltonics) MS system, operating in reflector mode for sample PS1 and in linear mode for samples PS2 and PS3, was used for data acquisition. All spectra were measured in the positive ion mode and calibration was performed on polystyrenes prepared on neighboring sample positions.

Data acquisition and calibration were carried out with COMPASS for flex 1.4 (Bruker Daltonics), followed by polymer signal analysis using PolyTools 1.0 SR 1 (Bruker Daltonics).

Results

The oligomer distribution of the PS1 sample was found to be in the mass range of 1000 to 3300 Da as shown in Figure 1. The average monoisotopic mass difference between the individual mass signals is 104.0624 Da, which is in good agreement with the theoretical monoisotopic mass value of 104.0626 Da for C_8H_8. The isotopic distribution of a single oligomer is shown in Figure 1 (inset). The presence of silver in the molecular ion may be inferred from the strong intensity of the +2 isotope. The analysis of the spectrum using PolyTools is displayed in Figure 2. The program automatically identifies the monomer unit as styrene and performs the extrapolation of the ion series towards lower masses until the residue mass is below the monomer mass. As the residual mass is the combination of the masses of the two end-groups and the cation, PolyTools determines the optimal combination of predefined editable entries. Polystyrene was defined within the PolyTools template and the end groups were found to be hydrogen and butyl, both in agreement with the supplier's information. As silver was added during the sample preparation (and the isotopic pattern also suggests the presence of silver), the spectrum interpretation by PolyTools using the silver cation can be confirmed. In addition to the end-group analysis, PolyTools also calculates automatically

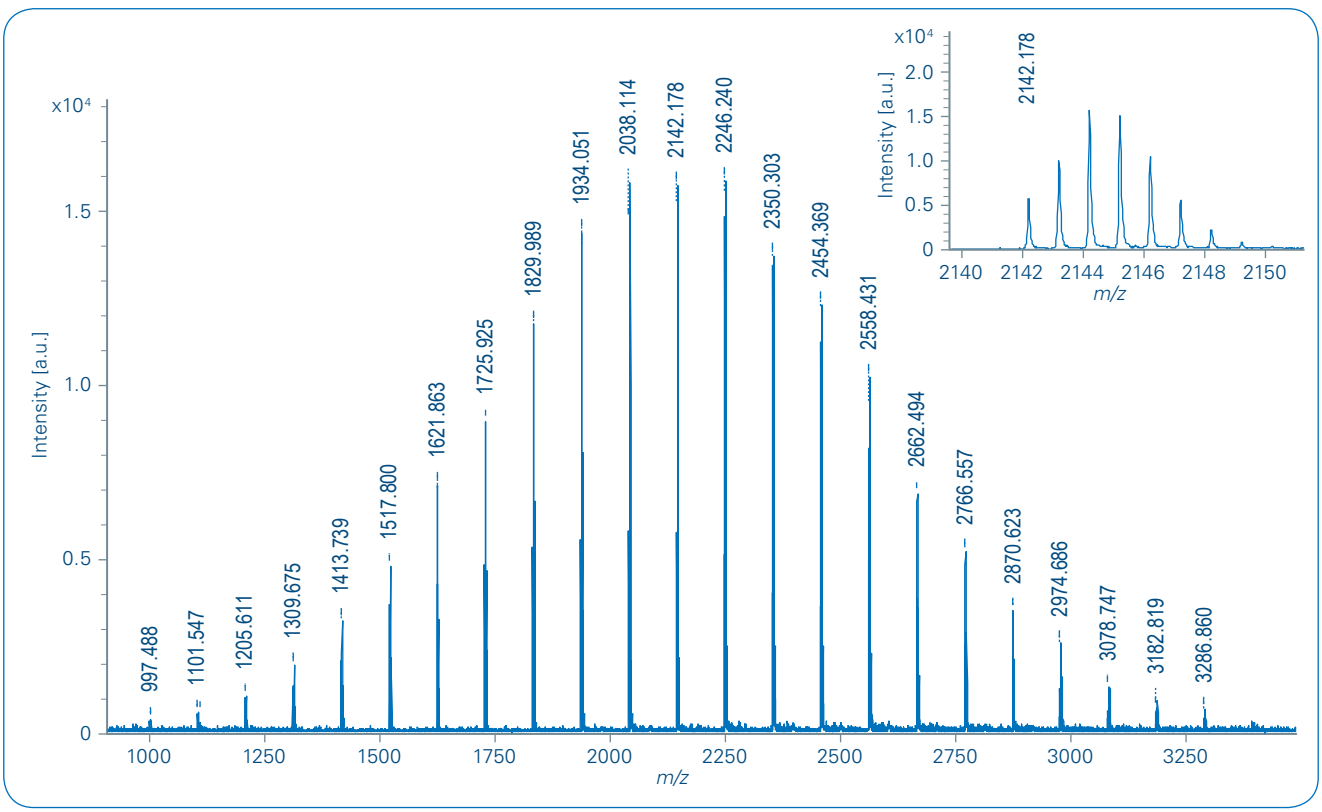

Figure 1: MALDI-TOF mass spectrum of polystyrene in the 2 kDa mass range obtained in reflector mode. Clearly one series of ion signals can be observed corresponding to one end-group combination present in the sample. The insert shows the isotopic distribution of the 19mer attached by Ag^+

the average molecular weights M_n (2137.67 Da) and M_w (2212.31 Da), the dispersity $Đ_M$=1.035, the degree of polymerization (DP, 20.54), and the percentage of the total ion signal covered by the individual ion series.

The spectrum shown in Figure 3 was obtained from sample PS2 using linear mode of the autoflex maX. The average distance of 104.19 Da (average masses) between the signals in the spectrum is in good agreement with the theoretical average mass value of 104.15 Da for C_8H_8. The interpretation by PolyTools (Figure 4) confirms the expected combination of end-groups. Due to the lower mass accuracy of linear mode collection, the spectrum interpretation shows a residual mass of 0.23 Da, which is typical for a polymer in this mass range.

Even at much higher masses, e.g. between 100 - 300 kDa, still the average molecular weights can be calculated by PolyTools (Figure 5). As shown in Figure 6, at this high mass range the individual oligomers cannot be resolved. It is noteworthy that higher charged species appear in the spectrum such as one polystyrene molecule carrying two silver ions or a cluster of two polystyrene molecules sharing three silver ions (as the doubly charged dimer appears at the same mass as the singly charged monomer).

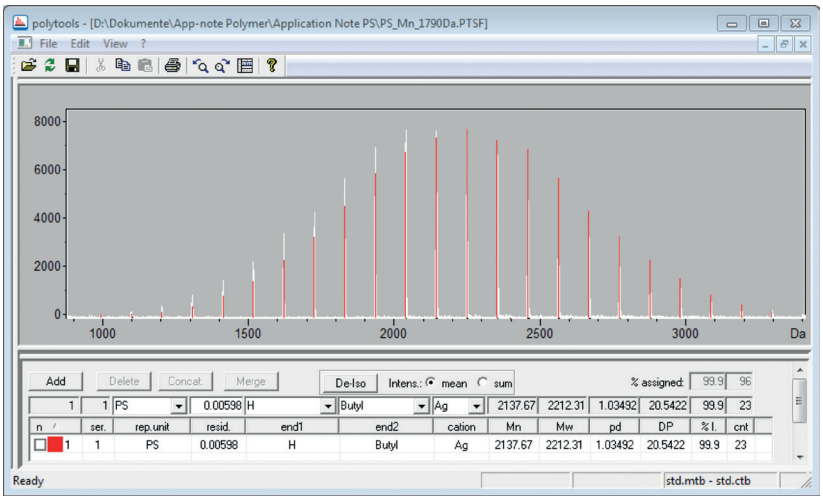

Figure 2: PolyTools interpretation of the spectrum of polystyrene in the 2 kDa mass range. Monomer detection, average mass calculations and end group analysis are done automatically

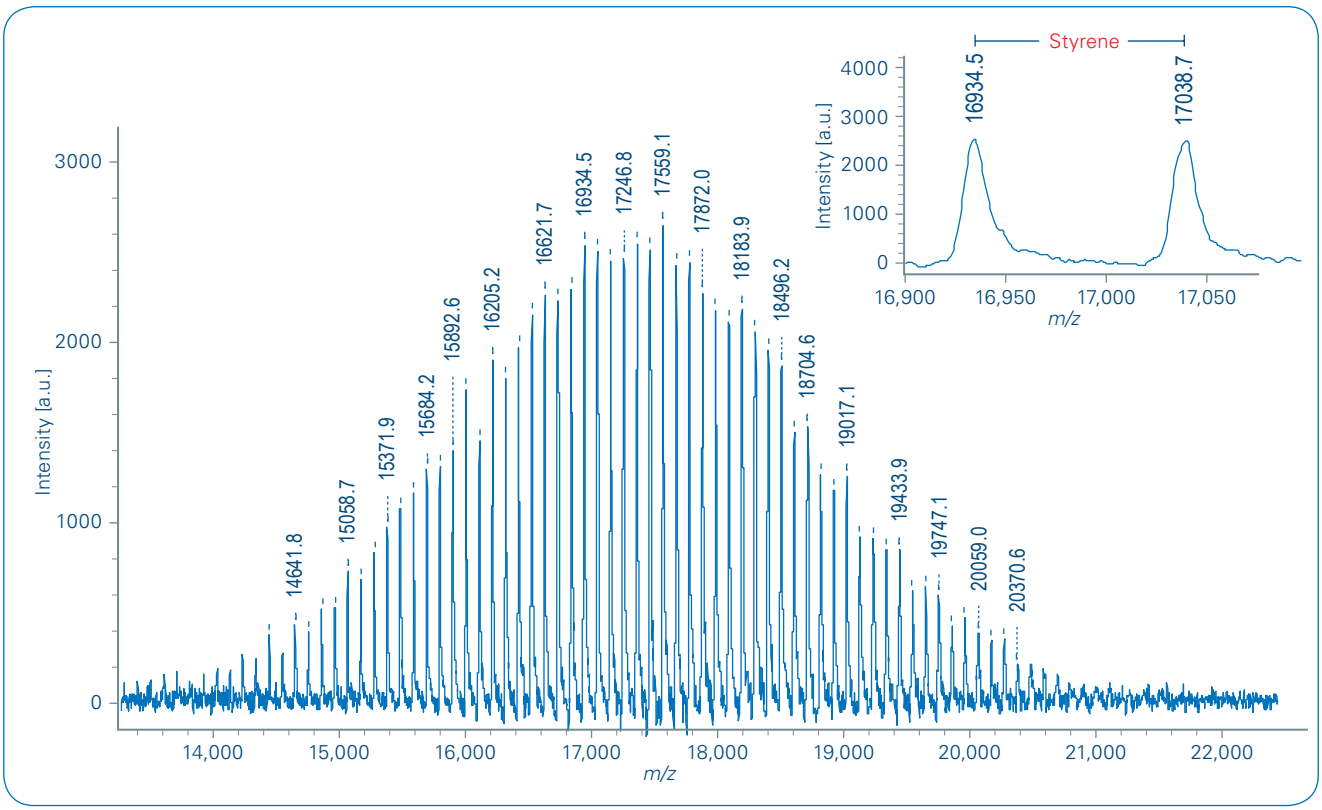

Figure 3: Spectrum of PS2 in the mass range 14 to 22 kDa acquired using the linear mode of the autoflex maX. In this mass range the isotopic resolution is lost, but the oligomers can be separated as shown in the insert

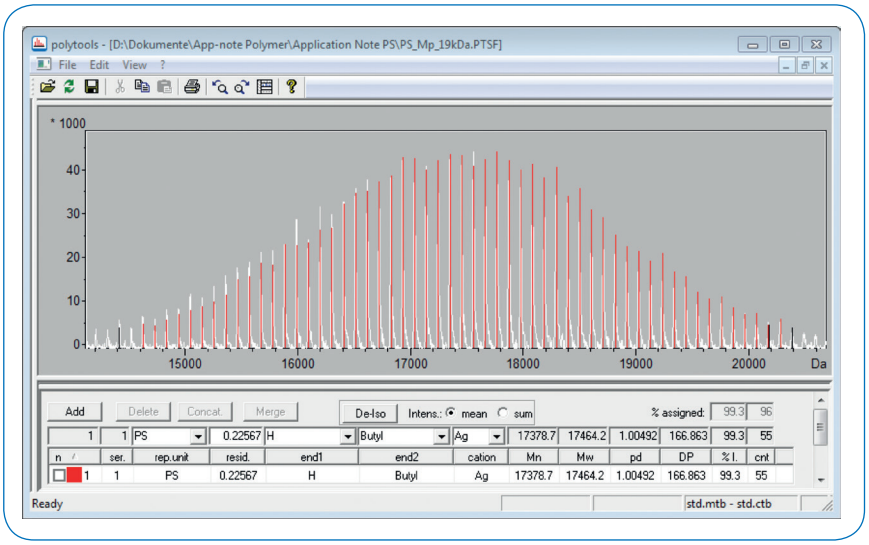

Figure 4: PolyTools interpretation of the spectrum of PS2. Using a slightly higher mass tolerance the monomer mass and the end-groups/cation are detected correctly

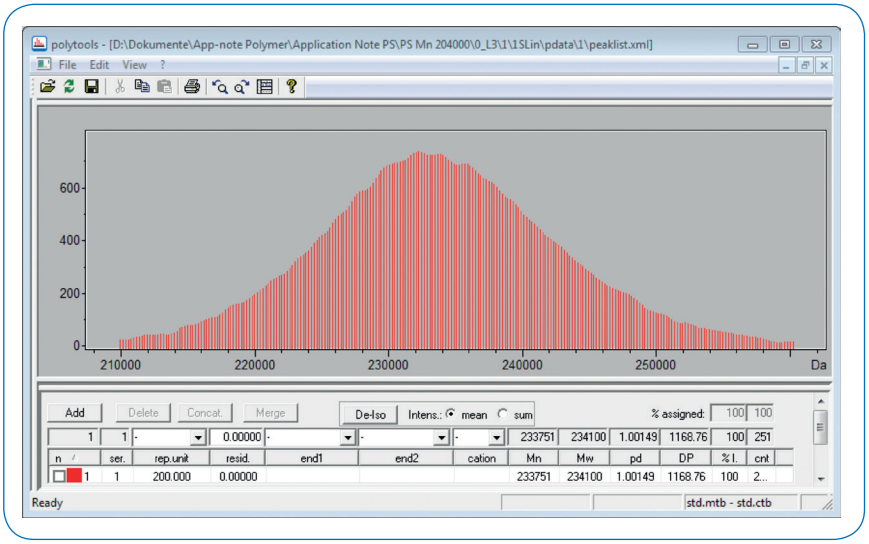

Figure 5: Using an artificially created peaklist, PolyTools is able to calculate average mass values for the spectrum of PS3

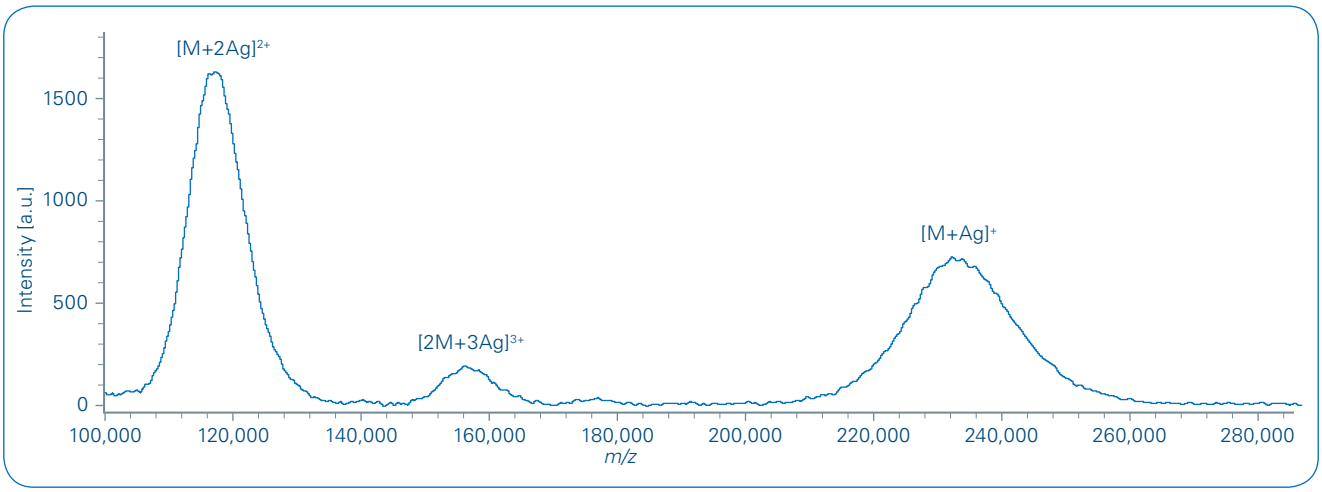

Figure 6: Linear mode MALDI-TOF spectrum of the PS3 sample in the mass range of 100 to 280 kDa. Oligomeric species cannot be separated anymore

Conclusion

The combination of a high-resolution MALDI-TOF MS system and PolyTools provides detailed information on

- Average molecular weight determination
- Automatic detection of monomer
- End-group characterization

together with

- Single end-group analysis using MS/MS [2]
- Copolymer analysis [3]
- Detection of impurities

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