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Application News

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AXIMA Performance MALDI-TOF

Analysis of Polymers by MALDI-TOF Mass Spectrometry

- Analysis of synthetic polymers by MALDI-TOF MS
- Polymer Analysis software for the characterisation of polymers and co-polymers using MALDI data
- Automatically generate useful information (e.g. monomer mass, residual mass (end groups), polymer statistics, etc.) regarding the sample

Analysis of Polymers by MALDI-TOF Mass Spectrometry

Introduction

Synthetic polymers are widespread in everyday life. Whether they are used as containers for household products and foodstuffs to the construction of car components and electronic devices, plastics now play important roles in our day-to-day activities.

Matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS) is becoming increasingly popular for the analysis of synthetic polymers. The Polymer Division of the National Institute of Standards and Technology (NIST) is dedicated to gathering information regarding methods used in the analysis of polymers. One of the resources of the Polymer Division includes a collection of sample preparation methods specifically for samples which are to be analyzed by MALDI-TOF mass spectrometry, (http://polymers.msel.nist.gov/maldirecipes/index.cfm), highlighting the importance of MALDI in polymer analysis.

The word polymer is derived from the Greek for 'many parts' and is used to describe any material which is composed of repeating subunits ('monomers'). In synthetic polymers, if the repeating units are identical (e.g. $(CH_2CH_2O)_n$), the polymer is referred to as a homopolymer. Alternatively, the polymer can consist of different monomer units (e.g. $(C_2H_4O)_m(C_3H_6O)_n$), in which case the polymer is referred to as a copolymer.

The synthesis of polymers can be difficult to precisely control. Typically, a polymer sample will not contain molecules with the exact same number of monomer units, but rather will contain polymer chains of differing lengths which were formed during the synthesis. Analysis of such a sample results in the detection of a polymer distribution (see Figure 1), which is typical in the analysis of polymers. For a homopolymer, adjacent peaks in the polymer distribution differ in length by one monomer unit. If the peaks are sufficiently resolved, it may be possible to calculate the mass of the monomer units. If the sample contains a copolymer, the spectrum can quickly become very complex due to the overlapping nature of the various chain compositions and chain lengths that may be present in the sample. In such cases, polymer analysis tools which can process the large number of peaks and identify the species which are present are essential.

In this application note, we present results obtained following the analysis of two polymer samples. The examples shown include MALDI spectra obtained for a homopolymer (PEG) and a more complex copolymer sample. Results are presented demonstrating the Polymer Analysis tools for processing MALDI polymer data.

Methods

PEG 2000 sample:

All solutions were prepared in 50/50 acetonitrile/0.1% TFA. Polyethylene glycol (average molecular weight = 2000) was prepared at a concentration of 10 mg/mL. Sodium trifluoroacetate (NaTFA) was prepared at 10 mg/mL. 20 µL of PEG 2000 solution and 20 µL of NaTFA solution were mixed together with 160 µL of 50/50 acetonitrile/0.1% TFA.

Equal volumes of polymer sample and matrix solution (α-cyano 4-hydroxycinnamic acid; 5 mg/mL in 50/50 acetonitrile/0.1% TFA) were mixed and 1 µL was deposited onto a stainless steel MALDI target and allowed to air-dry.

EO-PO sample:

The EO-PO sample was provided by Day International (Irlam, Manchester (UK)) and was used as supplied. Equal volumes of sample solution, matrix solution (dithranol; 35 mg/mL in THF) and sodium trifluoroacetate (10 mg/mL in THF) were mixed and 1 µL was deposited onto a stainless steel MALDI target and allowed to air-dry.

Samples were analyzed using an AXIMAPerformance™ MALDI-TOF MS (Shimadzu Corp.) in positive-ion reflectron mode. The pulsed extraction (P.Ext) value was set to 2000 i.e. delay time optimized for mass 2000 Da.

Results

The results of the Polymer Analysis software demonstrate how it is possible to calculate and report/visualize distribution information (in polymer distribution analysis mode) or identify components of different copolymers (in copolymer analysis mode), present in a sample.

The PEG 2000 example (Figure 1) shows a typical MALDI spectrum obtained during analysis of a synthetic homopolymer sample. Adjacent peaks differ in mass by one monomer unit. Measuring the mass difference between adjacent peaks of the same series gives the mass of the monomer unit. In the case of Figure 1, the observed mass difference is 44.03, consistent with the expected monomer mass (calc. = 44.03).

Analysis of the MALDI data using the Polymer Analysis software (in distribution analysis mode; Figure 2) generated the results shown in Figure 3. The Polymer Analysis software automatically detected a single distribution (in the mass range 1431 to 2713 m/z). The average calculated monomer mass (calculated by the software) is 44.03, consistent with the PEG monomer. In addition, the residual mass calculated by the software (see Figure 3) is 18.0, consistent with H- and -OH as endgroups

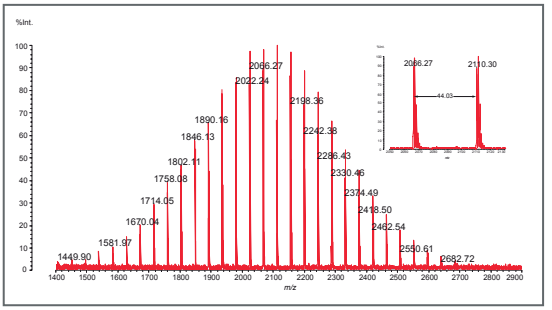

Figure 1: MALDI-MS spectrum obtained for polyethylene glycol (PEG), average molecular weight = 2000. The sample was prepared in CHCA with the addition of NaTFA. Inset: Zoom view showing expanded mass range (2050 - 2130 m/z) of the spectrum. The mass difference between adjacent peaks gives the mass of the monomer unit (for PEG, $\Delta M = 44.03$ (CH_2CH_2O)).

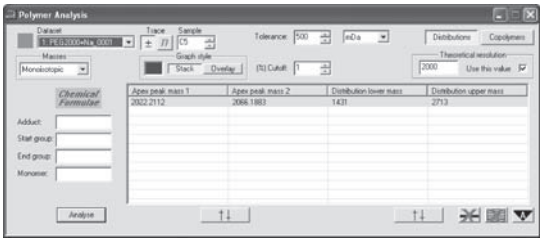

Figure 2: Polymer Analysis *window (distribution mode). The* Polymer Analysis *software is part of the MALDI-MS AXIMA control software and requires a licence key to access this module.*

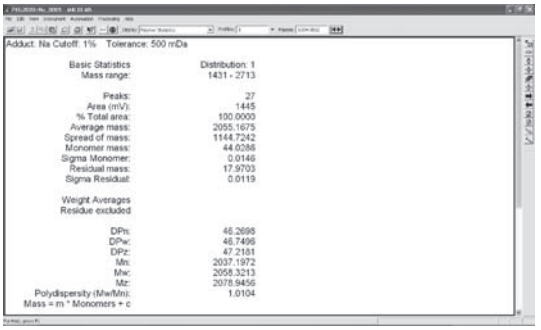

Figure 3: Distribution calculation results following processing (analysis) of the spectrum shown in Figure 1 using the Polymer Analysis *software.*

If the chemical formula of monomer is known, it can be entered, along with the cation/salt used to prepare the sample, into the Polymer analysis software and used to generate a theoretical polymer distribution. This theoretical distribution can then be compared with the experimantally obtained MALDI spectrum (see figure 4)

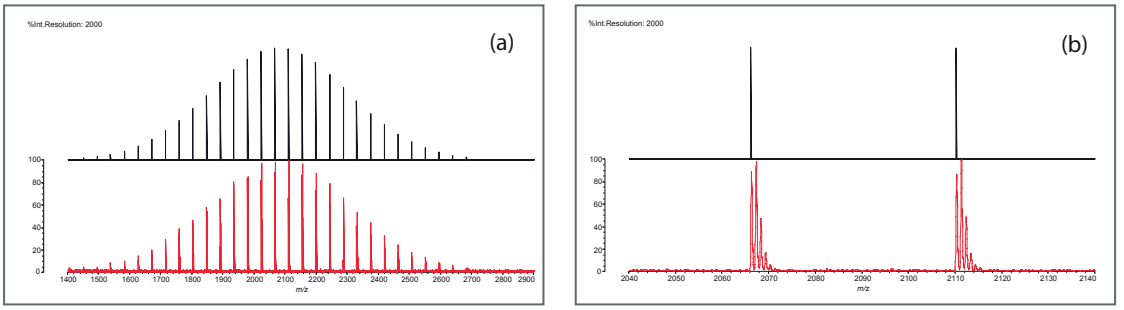

Figure 4: Overlay of theoretical data (black) and experimental spectrum (red). (a) mass range = 1400 - 2900 m/z; (b) mass range = 2040 – 2140 m/z.
In the polymer calculations, the masses were considered as monoisotopic.

The spectrum shown in Figure 5 was obtained during the analysis of a more complex copolymer sample. The zoom view of this spectrum (Figure 6) highlights the complexity of the spectrum compared with that obtained for the homopolymer sample (Figure 1). The increased spectrum complexity arises from the overlapping series corresponding to the different polymer chains present in the sample. Attempting to manually interpret this data would be a challenging and time consuming task. However using the Polymer Analysis software in copolymer analysis mode, the masses of different copolymer combinations can be automatically calculated, facilitating the assignment of peaks (see Figure 8).

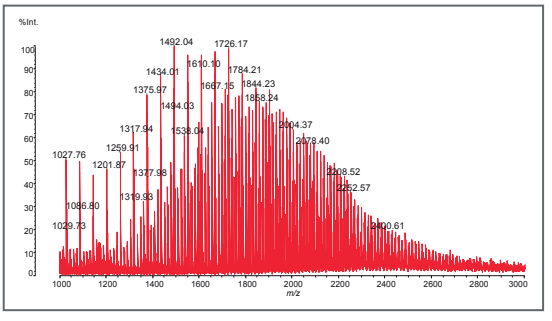

Figure 5: MALDI-MS spectrum obtained for the EO-PO sample. The sample was prepared in dithranol with the addition of NaTFA.

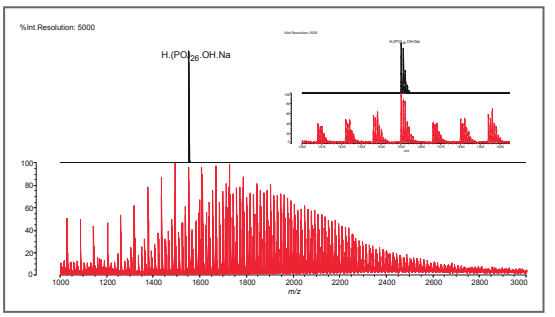

Figure 6: MALDI mass spectrum obtained for the copolymer sample (red trace) and theoretical peak corresponding to H.(PO) $_{26}$*.OH.Na (black trace). Inset: Zoom view showing expanded mass range (1500 - 1605 m/z) of the MALDI-MS spectrum shown in Figure 5 with the calculated distribution for the peak at 1550 m/z. In the polymer calculations, the masses were considered as monoisotopic.*

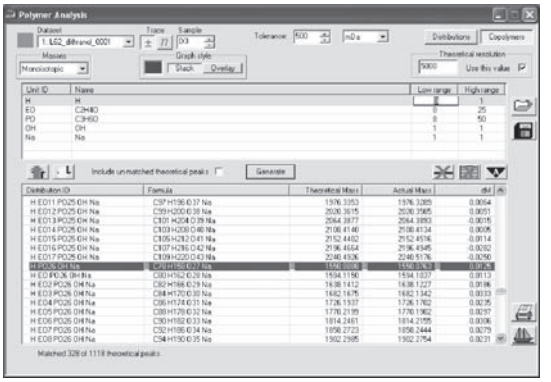

Figure 7: Polymer Analysis *software window showing the calculated distributed IDs, chemical formulae, theoretical and observed masses and errors, calculated within the specified range of values (copolymer analysis mode). The highlighted line corresponds to the distribution shown in the upper trace of Figure 6.*

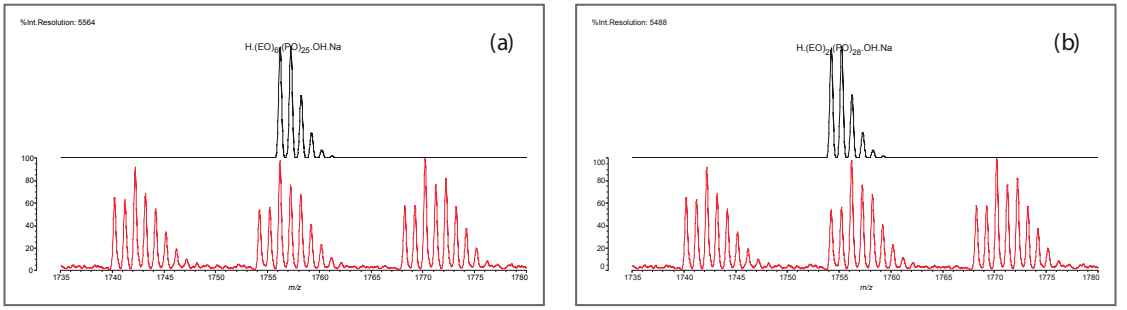

Figure 8: Examples showing assignment of overlapping peaks from a complex copolymer sample. Red trace: MALDI mass spectrum obtained for the copolymer sample; Black trace: theoretical distribution corresponding to (a) peak at 1756.2 m/z (H.(EO) $_{6}$*(PO)* $_{25}$*.OH.Na) and (b) peak at 1754.2 m/z (H.(EO)* $_{2}$*(PO)* $_{28}$*.OH.Na)*

Conclusion

- MALDI-TOF Mass Spectrometry is a valuable tool for the analysis of synthetic polymers
- Polymer Analysis software can be used to facilitate the interpretation of MALDI data derived from polymer samples
- The software can be used to identify polymer distributions or for the analysis of copolymers, facilitating the assignment of peaks or ions belonging to the same series

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