



End-group Identification of Structural Isomeric Polymers by CID-LIFT MS/MS



Abstract

CID (collision induced dissociation) is a common technique in mass spectrometry where ions are accelerated and collide with neutral gas molecules, causing the ions to dissociate into smaller fragments. By determining the mass of these fragments, structural information about the initial molecule can be obtained. This application note highlights an example where the structural isomers of polyethylene glycol methacrylate, methyl ether acrylate, and diglycidyl ether are analyzed and differentiated by the Bruker autoflex maX MALDI mass spectrometer using CID. It highlights the potential of CID-MS/MS to easily distinguish isomeric species for an improved and confident structural elucidation of synthetic polymers.

Introduction

Matrix Assisted Laser Desorption Ionization (MALDI) mass spectrometry provides highly specific chemical information for polymer structural analysis, copolymer composition, complex polymer mixtures, and surface imaging, making it invaluable in various polymer analysis applications. This technique is widely recognized for the characterization of synthetic polymer samples and is used to calculate average molecular weights and identify end-groups. MALDI is a very easy way of applying mass spectrometry to various challenging applications. No chromatographic separation is required, polymers are analyzed as a whole in a simple workflow. Results can be obtained in seconds to a few minutes. The needed training for using MALDI-MS is minimal, and the large variety of matrices enables the analysis of polymers with very different chemical characteristics like solubility, size or polarity. A clear benefit of MALDI is the easy observation of information that is difficult to obtain with analytical methods that acquire just average results for complex mixtures.

Keywords:

Polymers, MALDI, autoflex maX, PolyTools, MS/MS, Kendrick Mass Defect (KMD)

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When determining end groups, individual polymer distributions can be analyzed independently and directly within a mixture if the molecular weights of the individual end-groups are different and observed as separated peaks in the mass spectrum. However, if the polymer sample is expected to have structural isomers, these structures cannot be distinguished by molecular mass alone. Then MS/MS can provide valuable insight into the molecular structure by analyzing the mass of fragment ions resulting from the controlled dissociation of the initial, intact molecule. These fragment ions usually

contain a single end-group only. It is important to note that it is helpful for this approach to understand the polymer's specific fragmentation mechanism.

In this application note, polyethylene glycol methacrylate, methyl ether acrylate, and diglycidyl ether, which are structural isomers with equal oligomer masses, were identified by MALDI-CID-MS/MS. End-group analysis by MS is based on the total mass of both end-groups, but MS/MS has the advantage of being able to identify each end-group individually.

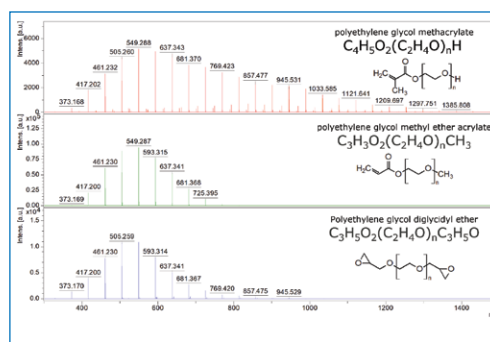


Figure 1
Mass spectra measurements for three polyethylene glycol variants with a base peak at m/z 549.288.

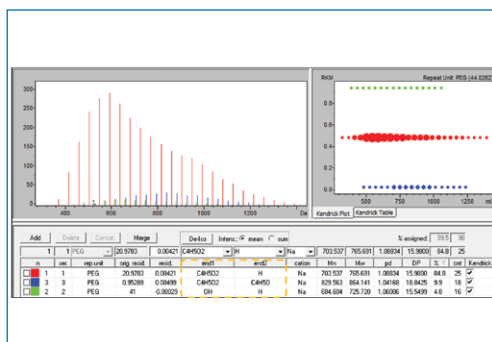


Figure 2
End group assignment of a polyethylene glycol methacrylate sample by PolyTools. The yellow dotted frame indicates the observed end groups.

Methods

A Bruker autoflex maX mass spectrometer was used in both positive reflector MS and CID-MS/MS modes. The initial calibration was conducted using a PMMA mixture (fleXstandard Polymers, Bruker). The acquired data was processed using the software tools flexanalysis and PolyTools 2.0. PolyTools can process peak lists from different mass spec sources and automatically identifies structural elements present in the mass spectrum. It handles monoisotopic and average mass resolved spectra and calculates essential parameters, including end group determination. The KMD (Kendrick Mass Defect) plot feature of the software allows to differentiate individual peak series, which is

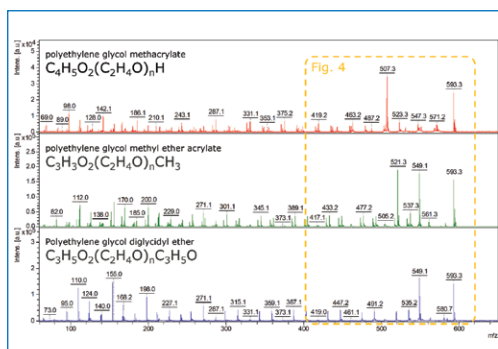
particularly useful for complex mixtures. Three types of polyethylene glycol were purchased from Sigma-Aldrich and prepared as 20 mg/mL solutions in THF (tetrahydrofuran): methacrylate (M_n : 500), methyl ether acrylate (M_n : 480) and diglycidyl ether (M_n : 500). They were mixed with the matrix solution (20 mg/mL DCTB in THF) and an ionizing agent solution (2 mg/mL sodium trifluoroacetate in THF) at a ratio of sample/matrix/salt of 2:10:1. 0.5 μ l of the mixture was applied to the target plate (Bruker MTP 384 Ground Steel) and dried at room temperature. For CID-MS/MS, argon was used as collision gas at a purity of 99.99% and the pressure in the ion source was adjusted to 6×10^{-6} mbar.

Results

Fig. 1 contains the mass spectra collected for the three polyethylene glycol samples: polyethylene glycol methacrylate (red), methyl ether acrylate (green), and diglycidyl ether (blue). All 3 samples have a base peak at m/z 549.288. The mass spectra exhibit consistent masses for the primary constituents but display subtle differences in the polymer distribution width. However, it is not possible to determine the microstructure of the samples from the MS spectra alone.

The PolyTools end-group analysis of the PEG methacrylate variant is given in Fig. 2. The interpreted series of the acquired MALDI-TOF spectrum are displayed in the upper left corner, followed by the KMD (Kendrick Mass Defect) plot on the right side. The detailed analysis of the three components is tabulated below the 2 plots which includes average

molecular weights, M_n and M_w , as well as the observed end groups (yellow dotted frame). The KMD plots reveals three different peak series for this single polymer. A component that can be assigned to dimethacrylate (end-groups $C_4H_5O_2$ and C_4H_5O , shown in blue) was detected as a minor component, indicating that the major component (mono) methacrylate (end-groups $C_4H_5O_2$ and H, shown in red) is not 100% pure. Another minor peak series was found representing the masses of the unmodified PEG (end-groups OH and H, shown in green). Due to the clear mass differences in the MS spectra, it was possible in this case to estimate the end-groups of the main component as $C_4H_5O_2$ and H and those of the low intensity by-products as $C_4H_5O_2$ and C_4H_5O . However, it is not possible to decide if other isomeric compounds are mixed for this sample.



The MS/MS analysis shown in Fig. 3 and 4 provides direct and more detailed information for the three PEG isomers. Here, the molecular ion at m/z 593.3 was isolated and fragmented for each sample. In the MS/MS spectra, the fragment signals just below the

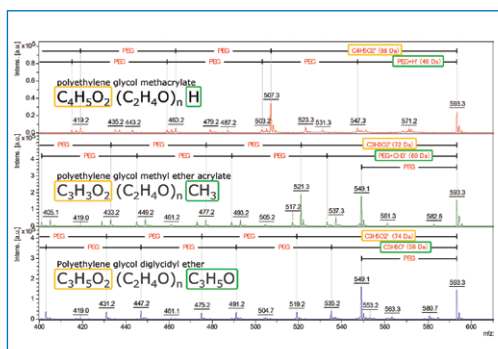
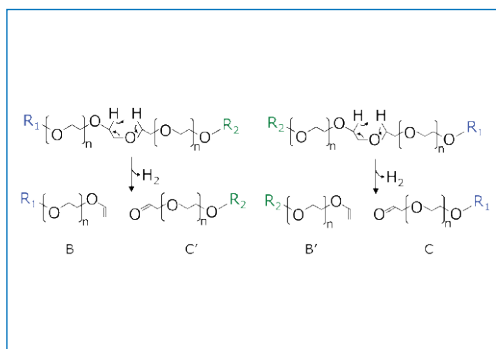


Figure 3
CID-MS/MS spectra of three polyethylene glycol variants. The MS/MS fragments just below the precursor mass of m/z 593.3 (yellow frame) reveal clear end group differences.

Figure 4
Expanded view of the CID-MS/MS spectra of three polyethylene glycol variants. All three variants show the PEG repeat unit. The two fragment series in each spectrum reveal the two individual end groups of each variant.

precursor ion of m/z 593.3 reveal the mass of both end-groups independently and allow to assign each end-group individually for a much more reliable identification compared to the information from the MS spectra alone.

Knowledge about the fragmentation pathway of these polymers can highly support the direct and confident peak assignment. According to the well-known fragmentation pathway of polyethylene glycol¹⁾ shown in Fig. 5, four types of fragment ions have the same end-group of C₂H₃O, while the other observable end group is R₁, OR₁, R₂ or OR₂.



E.g., for polyethylene methacrylate, R₁ corresponds to C₄H₅O and R₂ corresponds to H. PolyTools can be conveniently used for the peak assignment of MS/MS spectra as shown in Fig. 6, where all four types of fragment ions are clearly assigned (different color coding in the spectra and KMD plot as well as in the table below the spectra).

