



● MALDI-CID Study of Poly(methyl methacrylate)

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was chosen for an in-detail analysis of poly(methyl methacrylate) (PMMA) in order to determine the possible fragmentation mechanism with the help of collision-induced dissociation. Every parent peak yielded four fragmentation series by MS/MS analysis, confirming fragmentation mechanisms already observed under different experimental conditions for PMMA.

Introduction

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) became one of the important

characterization methods for synthetic polymers in the last years. However, from the MS spectrum alone it is only possible to calculate the sum-mass of both end groups. To gain information

on the single end group the oligomeric species have to be selected and fragmented in a CID process. The resulting fragments contain now only a single end group. As soon as

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the fragmentation mechanism of a polymer is understood, unknown samples can be analysed for their single termini. The aim of this study was to characterize poly(methyl methacrylate) by the use of a modern MALDI-TOF/TOF [1], like it was performed for poly(ethylene glycol) (PEG) [2] and polystyrene (PS) [3] earlier.

Experimental

Instrumentation:

An autoflex TOF/TOF, equipped with a collision cell, was used for the analysis. All spectra were measured in the positive mode. A PMMA standard from Polymer Standards Services GmbH (Mainz, Germany) was used for external calibration of the MS spectra. For the MS/MS mode, argon was used as collision gas at a pressure of 5×10^{-6} mbar.

Sample preparation:

For the sample preparation, PMMA 1,900 (5 mg/mL), DCTB(10 mg/mL) and the doping salt sodium trifluoroacetate (0.1 mol/l) were all dissolved in THF. As the determination of average molar masses of the polymer was not the focus of this study, a simple dried droplet preparation could be used [4]. The polymer-, matrix- and salt-solutions were mixed in a ratio 5:25:1 and 0.5 μ l were hand-spotted on a ground steel target plate.

Results

According to the supplier both end groups of the PMMA were referred to be hydrogen. In the MALDI-TOF MS spectrum the oligomer distribution was found in the molar mass range from m/z 600 to 3600 as shown in Figure 1. Due to the fact that the sample preparation results in a very thin and flat film, mass resolutions R of close to 30,000 were reachable with the autoflex as displayed in

Figure 2. The masses of the signals of this main distribution correlate with the chemical composition $H(C_5H_8O_2)_nH + Na^+$. In addition, a second distribution with low intensity was observed, which could be explained by the formation of cyclic products. These side-products are typical for group transfer polymerization (GTP) [5] and, therefore, the way of the synthesis could already be identified from the MALDI-TOF MS spectrum. For the MALDI-TOF MS/MS measurements in general every peak of the MS spectrum could be selected as a parent peak. But only two of them were chosen as representative parent ion peaks at m/z 1,625.84 and 2,226.16 to discuss the possible fragmentation in the high energy CID mode. These are marked with arrows in Figure 1.

Both spectra (Figure 3a and b) showed similar fragmentation behavior with relative high intensities in the monomer, dimer and trimer region. Moreover, four different peak series with a molar mass difference of m/z 100.05 were observed throughout

the MS/MS spectra. The zoom in the mass range of m/z 500 - 600 shows single peaks out of four fragment ion series A, A' and B, B' (Figure 3c). Jackson et al. observed identical series with liquid secondary ion tandem mass spectrometry using collision energies of 4 keV [6] or MALDI CID at 800 eV [7], respectively. The fragments A and A' correspond to the structures C and D, which were found in ref. [6]. The fragmentation mechanism was explained as loss of a carbon

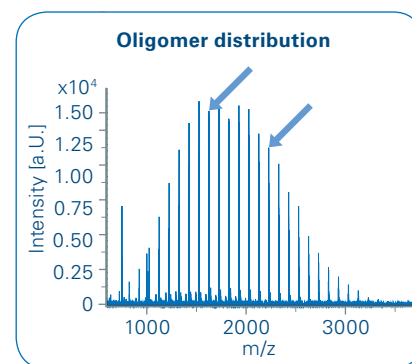


Figure 1: A MALDI-TOF MS spectrum of the PMMA calibration standard (matrix: DCTB, ionization salt: NaTFA). The selected parent peaks (m/z 1,625.84 and 2,226.16) are marked with arrows.

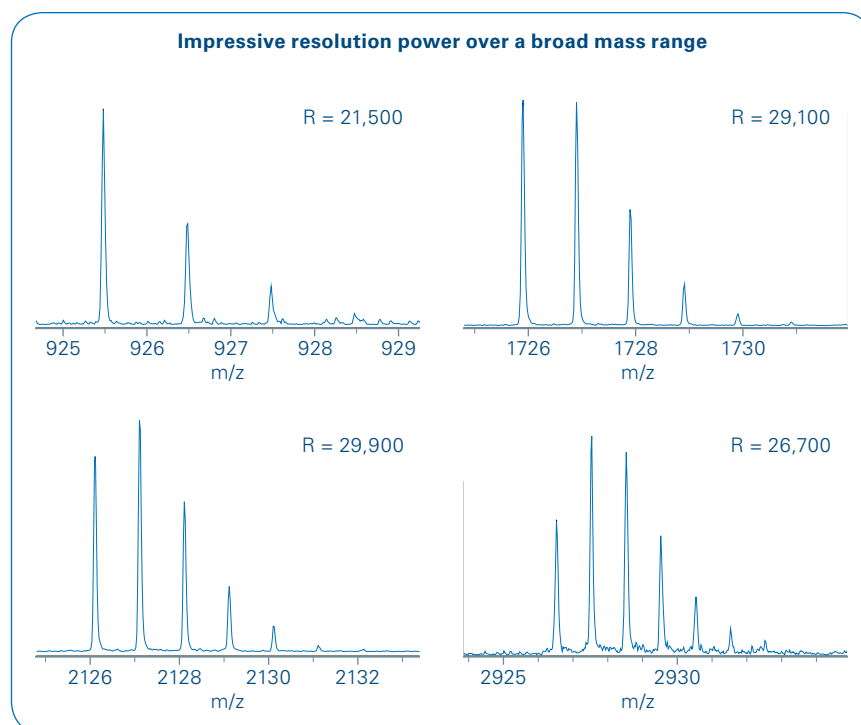


Figure 2: Mass resolution of the PMMA spectrum observed on the autoflex speed.

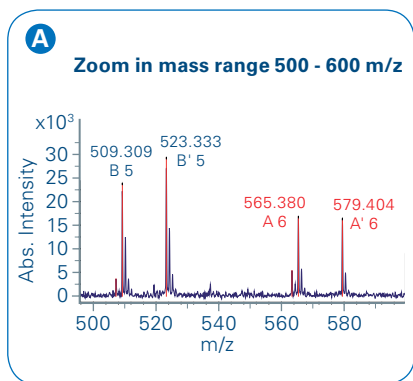
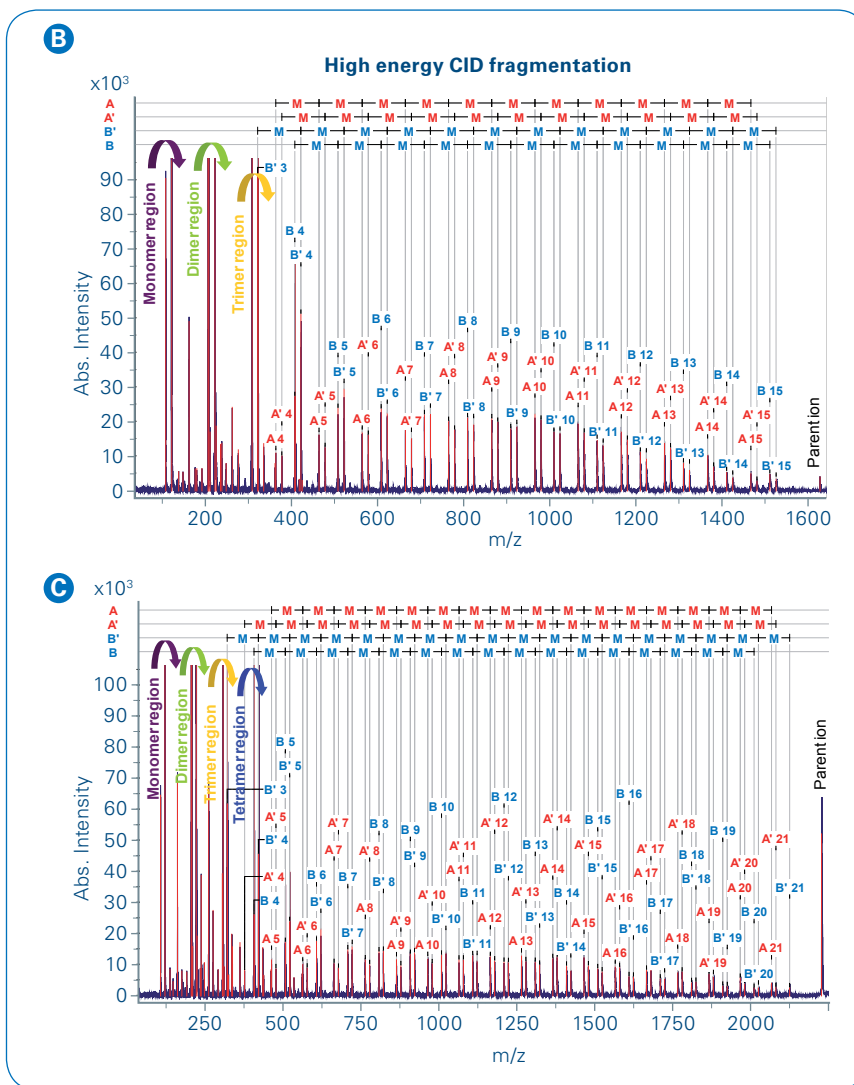


Figure 3: A MALDI-TOF MS/MS spectrum of the selected parent peaks at molar masses of **A** m/z 1,625.84 and **B** m/z 2,226.16. A, A', B and B' indicate four different fragment series with different numbers of monomer M. **C** A zoom of the MALDI-TOF MS/MS spectrum of PMMA 1,900 (region from m/z 500 to 600).

dioxide, along with a 1,5-hydrogen rearrangement [6] or loss of carbon monoxide and methanol [7]. But the fragmentation mechanism A and A' can also be formed by main chain scission and migration of ester side group followed by a β -scission, which can be found in ref. [8]. The series B and B' displayed in Figure 3c can be explained by main chain scission and migration of a methyl group in the backbone followed by a β -scission [8] or by 1,5-hydrogen rearrangement between two methylene carbons of the polymer backbone [6,7], which correspond to the structures A and B [6].

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We wish to acknowledge the Dutch Polymer Institute (DPI, technology area high-throughput-experimentation) and the Thüringer Kultusministerium (grant no. B515-07008) for the financial support of this study.



Conclusion

- A detailed characterization of a defined PMMA sample was demonstrated using MALDI-TOF MS. From the MS spectrum alone it was already possible to gain first information about the polymerization process. In the MS/MS spectrum four distributions were observed. These are in accordance with known fragmentations of PMMA. With this knowledge now also high energy CID on a MALDI-TOF instrument can be used for single end group determination on PMMA.



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