



Application Note # ET-25

ESI-Q-TOF MS/MS study of poly(2-oxazoline)s

Electrospray ionization quadrupole time-of-flight mass spectrometry (ESI-Q-TOF-MS) has been used for the detailed characterization of poly(2-oxazoline)s. The ESI-Q-TOF MS/MS studies were performed to evaluate this method as structural characterization tool for poly(2-oxazoline)s. Possible fragmentation mechanisms such as 1,4-hydrogen and ethene elimination, as well as McLafferty rearrangement, were proposed for the obtained fragmentation products. Side group elimination was observed depending on the chemical structure of the repeating units.

Introduction

Electrospray ionization mass spectrometry (ESI-MS) [1] has become an important tool for the characterization of macromolecules in recent years. ESI-MS allows the ionization of various macromolecules with little or no fragmentation, enabling accurate molar mass determination by making the unfragmented structure amenable to mass separation. Combining ESI-MS to high-resolution mass analyzers such as quadrupole-time-of-flight (Q-TOF) instrument provides exact molar masses for the polymers analyzed with mass accuracies in the ppm region. Therefore, valuable information on the chemical constitution of the macromolecule can be derived. The

interfacing of this soft ionization method with collision-induced dissociation (CID) presents a powerful technique for the detailed structural characterization of polymers. In the presented study, the aim was to characterize different poly(2-oxazoline)s by using ESI-Q-TOF MS and MS/MS to obtain structural information about these polymers and investigate fragmentation pathways in detail.

Experimental

Instrumentation

ESI-Q-TOF-MS measurements were performed with a microTOF-Q II (Bruker Daltonics) mass spectrometer equipped with an automatic syringe pump from KD Scientific for sample injection. The ESI-Q-TOF mass spectrometer was running at 4.5 kV at a desolvation temperature of 180 °C. The mass spectrometer was operating in the positive ion mode. For the MS/MS mode argon was used as a collision gas. The standard electrospray ion (ESI) source was used to generate the ions. The ESI-Q-TOF-MS instrument was calibrated in the m/z range 50-3000 using an internal calibration standard (Tunemix solution) which is supplied from Agilent. Data were processed via Bruker Data Analysis software version 4.0.

Sample preparation

Polymer samples were prepared with the concentration of 10 $\mu\text{g/mL}$ and they were injected using a constant flow rate (3 $\mu\text{L/min}$). The solvent was a chloroform/acetonitrile mixture. There was no salt addition prior to analysis, but ionization occurred readily from the sodium content that is naturally present in the glass [2-3].

Results

The synthesis of poly(2-oxazoline)s have been performed using the microwave-assisted living cationic ring-opening polymerization (CROP) [4-5]. By using this technique, polymerization reaction occurs in a well-controlled sequence of initiation, propagation and termination steps, in which the end group functionality can be controlled during these steps. A methyl starting group and a hydroxyl end group were chosen for the synthesis of poly(2-oxazoline)s to study the fragmentation mechanism. In this application note, poly(2-(1-ethylpentyl)-2-oxazoline) [p(EPOx)] is explained in detail as the representative example for poly(2-substituted-2-oxazoline)s. The ESI-Q-TOF mass spectrum of the p(EPOx) is presented in Figure 1a and the spectrum shows the expected signal spacing for

the repeating unit of p(EPOx) ($\Delta m/z=169.14$). The main distribution was the desired polymer structure in the ESI-Q-TOF mass spectrum with the chemical composition of $(\text{CH}_3(\text{C}_{10}\text{H}_{19}\text{NO})_n\text{OH} + \text{H})^+$. There is a second distribution, which can be explained by the chain-transfer reactions that take place during the polymerization of 2-oxazolines leading to hydrogen initiated polymer chains $(\text{H}(\text{C}_{10}\text{H}_{19}\text{NO})_n\text{OH} + \text{H})^+$. In Figure 1b, the ESI-Q-TOF MS data are presented showing an inset with the comparison of the calculated and the experimental isotope patterns for the investigated polymer with 10 repeating units $(\text{CH}_3(\text{C}_{10}\text{H}_{19}\text{NO})_{10}\text{OH} + \text{H})^+$, which was also selected as a parent peak for tandem MS analysis to investigate the fragmentation patterns. Elemental compositions were determined by accurate mass measurements and the deviations from the theoretical values were calculated by using Smart Formula Calculator.

For the ESI-Q-TOF tandem MS (MS/MS) investigations, it is possible to select all ions with good signal intensities within the main distributions as precursor ions. But for this study, one of them was chosen to investigate the fragmentation patterns. The ESI-Q-TOF MS/MS analysis of p(EPOx) can be seen in Figure 2a, which shows different fragmentation series (A, A', B, and B') that are already explained in Lattimer and coworkers' early studies for poly(glycol)s [7-9],

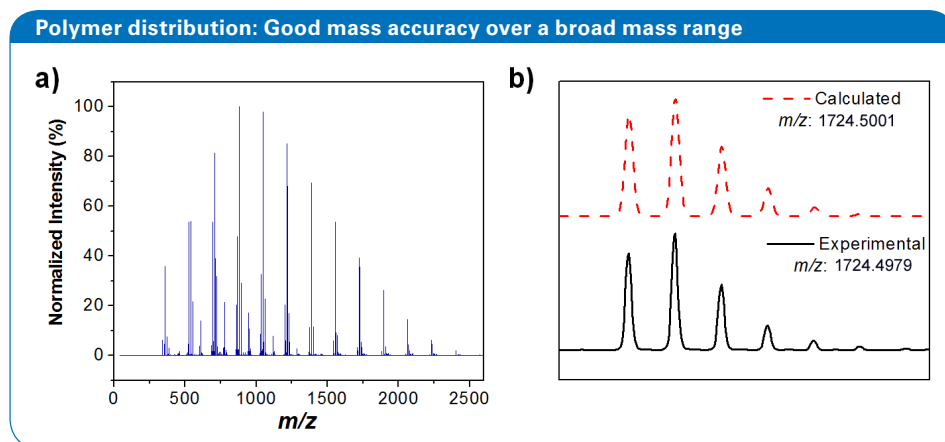


Figure 1: a) ESI-Q-TOF mass spectrum of poly(2-phenyl-2-oxazoline), b) zoom into the isotopic pattern and the calculated isotope pattern of the selected parent peak with 10 repeating units.

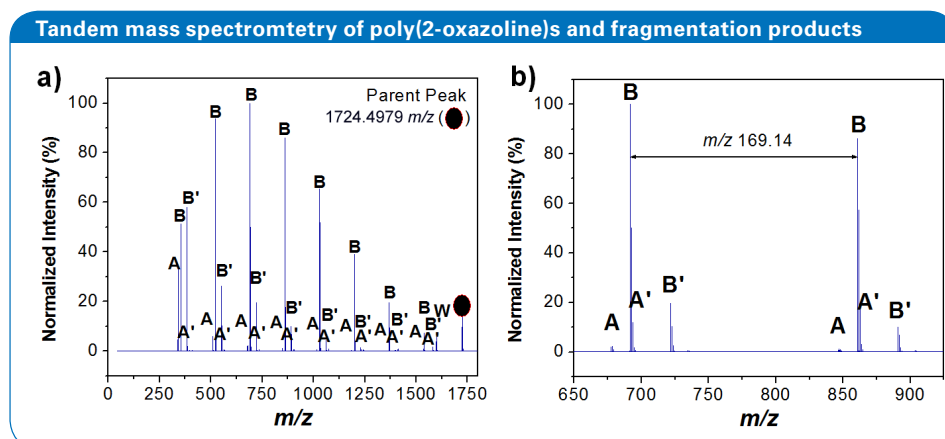


Figure 2: a) ESI-Q-TOF-MS/MS spectrum of the parent peak with 10 repeating units, b) zoom into the MS/MS spectrum in the range between m/z 650 and 925 with the observed fragmentation series marked.

in which the fragmentation products were formed by a 1,4-hydrogen and an ethene elimination mechanisms. Figure 2b shows the zoom into the MS/MS spectrum in the range between m/z 650 and 925 with the observed fragmentation series. Adaptation of these elimination mechanisms to the poly(2-ethyl-2-oxazoline)s explain all four fragment series. There is another possible mechanistic explanation for the fragmentation products obtained via ESI-Q-TOF MS/MS which is the McLafferty rearrangement [10]. McLafferty rearrangement is a β -cleavage with an accompanying transfer of a γ -hydrogen (hydrogen atom in the γ -position to an unsaturated functional group); a scission can take place with the aid of the side group to form a double bond end group. This mechanism is irrespective of the position of the charge. McLafferty rearrangement could be the preferred fragmentation mechanism for these polymers; however, alone it is not sufficient to explain all the other fragmentation products. W products were formed by the side group elimination which occurs in the beginning of the fragmentation of poly(2-alkyl-2-oxazoline)s. However, this mechanism was not observed for poly(2-aryl-2-oxazoline)s.

Conclusion

ESI-Q-TOF-MS has been used for the detailed characterization of poly(2-oxazoline)s. The results obtained from tandem mass spectrometry provided an understanding about the fragmentation mechanism of the poly(2-oxazoline)s. ESI-Q-TOF MS/MS of the poly(2-oxazoline)s revealed the elimination of small molecules such as ethene and

hydrogen in their fragmentation patterns, which are partially dependent on the side groups. Also, a McLafferty rearrangement can be a possible fragmentation route for these polymers. These insights are the preliminary steps toward the construction of a product ion library with fragments and fragmentation pathways for different polymers (similar to proteomic libraries) which will provide necessary knowledge for the future to make a fast and automated identification of these polymers possible. The information gained from this kind of studies will facilitate the structural elucidation of polymers.

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Data Analysis 4.0

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