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Mass Spectrometric Characterization of Synthetic Polymers

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Title: MASS SPECTROMETRY OF POLYETHYLENE GLYCOLS

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Abstract:

The polymeric derivatives of ethylene oxide are divided into two classes, namely polyethylene glycols and poly(ethylene oxide). The polyethylene glycols (PEGs) are relatively low in molecular weight having average molecular weights of 200 – 40000 Da. They have found a widespread use as homo- and copolymers in, e.g. cosmetics, lubricants, pharmaceuticals and other polymers.

We have studied a number of PEGs using electrospray ionisation mass spectrometry. A Thermoquest LCQ quadrupole ion trap mass spectrometer equipped with the advanced scan function, which extends the mass range to 4 kDa has been used. The PEGs were ionised by association with appropriate cations in methanol/water.

Mass spectrometry was found to be a versatile analytical technique with a high sensitivity and good reproducibility. The mass spectra reflect semi-quantitatively the average molar mass of the polymer as well as the polymeric distribution. However, it appears that the use of multiple charged ions may lead to a too low estimate of the average molar mass. This aspect will be discussed in detail. The accuracy in mass determination (0.1-0.2 Da) makes the elucidation of end-groups very straightforward.

The MS/MS capabilities enable an in-depth characterisation of a given oligomeric molecule as selected by the first mass analysis. The high order mass spectra, i.e. MS_n are of key-importance when studying ammonia adducts, since the diagnostic ions first appear in the MS/MS/MS spectra or later.

The advanced use of MS/MS will be highlighted by identification the initiator molecule with respect to structure and position in PEGs. It is expected that this strategy will enable differentiation of various synthetic routes to be made. This discussion will be based on a series of novel 1,3-propandiol/polyethylene glycol systems.

Mass Spectrometry of Polyethylene Glycols

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Introduction

The polymeric derivatives of ethylene oxide are divided into two classes, namely polyethylene glycols and poly(ethylene oxide). The polyethylene glycols (PEGs) are relatively low in molecular weight having average molecular weights of 200–20000 Da. The PEGs appear to be moderate sensitive towards oxidation, which may be significant in long-term applications. The stability of PEGs can apparently be enhanced by substitution. However, no methods are apparently available for the analysis of point modifications of the polymers. We demonstrate in this contribution the applicability of mass spectrometry.

Experimental

The PEGs were investigated by using electro-spray ionisation (ESI) mass spectrometry. A Thermoquest LCQ quadrupole ion trap mass spectrometer equipped with the advanced scan function was used. The PEGs were ionised by association with appropriate cations, e.g. by using 25 mM ammonium formate in methanol/ water (1:1). The PEGs were prepared either by base catalysed addition of ethylene oxide to 1,3-propanediols or by reaction of 1,3-propanediol-ditosylate and the pentamer/hexamer ethylene glycolates (sodium) in pyridine.

Results and Discussion

The molar mass distribution of the glycols is reflected in the ESI mass spectrum. However, it should be recalled that this spectrum is sensitive to the efficiency of ionisation, ion transfer and detection, and may, hence, not directly correlate to the distribution of the oligomers. PEGs give frequently rise to multiple charged ions, which in a favourable way extend the mass range. However, it is important to note that a significant error may arise caused by the ability of the oligomer to accommodate the higher charge states. This may easily lead to a slightly too high estimate of the molecular weight based on multiple charged species.

In the zoom scan mode the dynamic resolution is on the order 8000. This enables analysis of the isotopic pattern and absolute determination of charge states. In addition, the high precision in mass assignment facilitates an unambiguous identification of end groups.

Soft ionisation is in combination with MS/MS a powerful method for characterisation of individual species in complex mixtures. In the case of oligomeric mixtures this opens up for the characterisation of individual oligomers. In the present study we have used this strategy to elucidate point modification of PEGs. Thus, PEGs are ionised by cationisation followed by appropriate MSⁿ as illustrated by the MS³ analysis of the product originating from the reaction between ethylene oxide and 1,3-propanediol, cf. Figure 1.

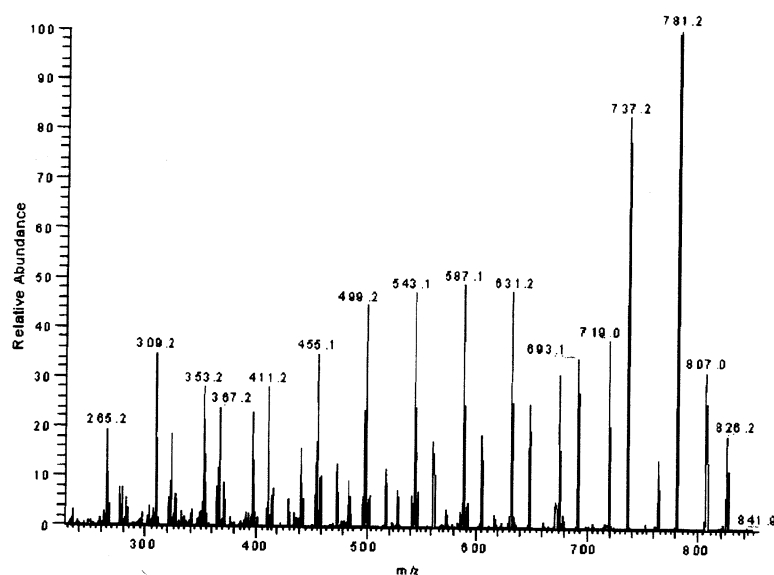


Figure 1. MS/MS/MS spectrum of the oligomer at m/z 842 $[(1,3\text{-propanediol} + 17 \text{C}_2\text{H}_4\text{O units}) + \text{NH}_4]^+$ corresponding to the collision activation spectrum (MS/MS) of the $[[\text{M} + \text{NH}_4]^+ - \text{NH}_3]$ ion m/z 825 $([\text{M} + \text{H}]^+)$.

Two series of ions are observed formally corresponding to $([\text{M} + \text{H}]^+ - n(\text{C}_2\text{H}_4\text{O}))$ and $([\text{M} + \text{H}]^+ - n(\text{C}_2\text{H}_4\text{O}) - \text{H}_2\text{O})$, respectively. The principal position of the 1,3-propanediol unit is at the centre of the oligomer. The moderate randomisation of the 1,3-propanediol unit is attributed to the non-specific synthesis strategy. This phenomenon is therefore observed to lower extent in the specifically synthesised products. Thus, MS/MS strategies may preferentially be used for elucidating point modifications of polyethylene glycols.