Comparative study for characterization of fatty alcohol alkoxylate copolymers by MALDI-(TOF)MS and NMR

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Introduction

The class of fatty alcohol alkoxylates describes surfactants that are synthesised by reaction of fatty alcohols with alkoxides like ethylene oxide (EO) or propylene oxide (PO) respectively a combination of both as copolymers.These products are used as nonionic surfactants in home and industrial cleaning and washing agents and also in a broad range of applications at chemical industry.

The type of starter, the degree of alkoxylation (e.g. EO/PO) and the sequence of building blocks (random or block polymerisation) deeply influence the application behaviour. The analysis of these kind of products is challenging due to a high polydispersity, high figures of isomers and additionally the higher molecular range (up to 10000 Da).

NMR is a suitable method for the analysis of EO/PO adducts [1, 2] and is widely used in industrial labs. In addition to NMR techniques matrix-assisted laser desorption ionisation (MALDI) mass spectrometry is a powerful tool to analyse technical polymers. Polymer ions up to about 5000 Da can be fragmented via MALDI collision-induced dissociation (CID) and resulting fragment ions can be obtained e.g. by a reflectron time-of-flight (TOF) instrument [3-5].

Here we present a comparative study for characterization of fatty alcohol alkoxylate copolymers by MALDI-CID-(TOF)MS and NMR in order to gain the maximum of information about the composition of these technical polymers.

Results

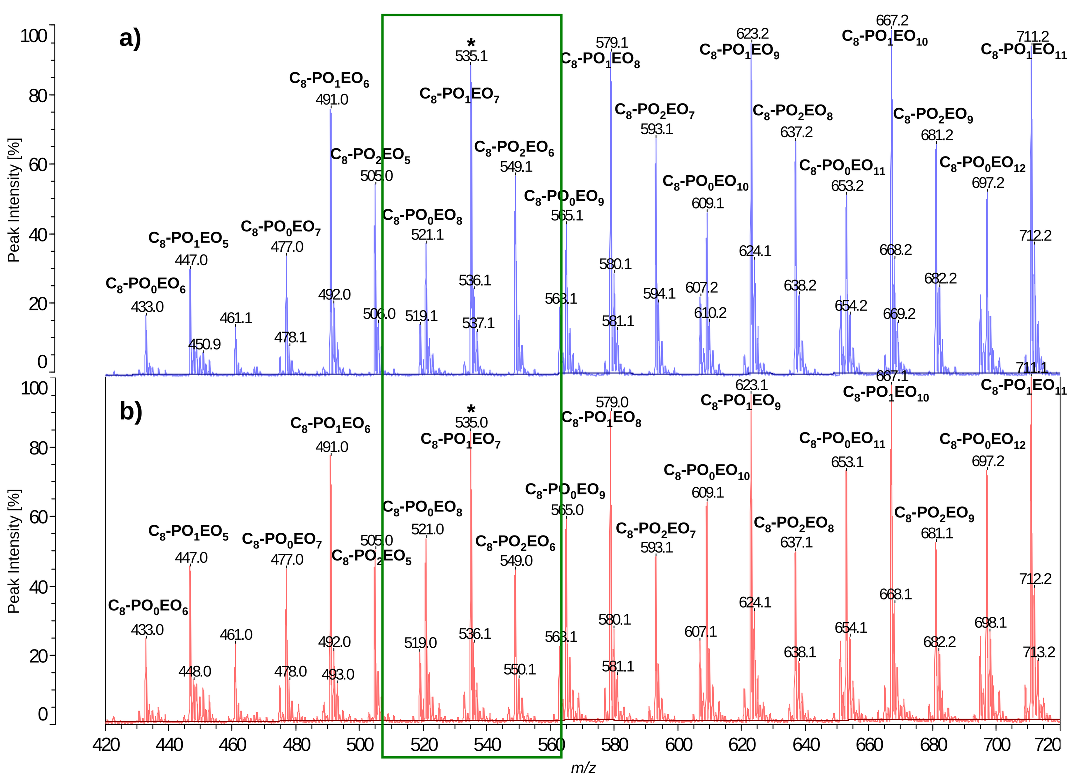

Figure 1
MALDI-(TOF) mass spectra of a octanol initiated poly-propylene-glycol (PPG) / poly-ethylene-glycol (PEG) copolymer built in a random polymer (a) and as a block (b)
PO_x = numbers of propylene-glycol units
EO_y = numbers of ethylene-glycol units

Figure 1 shows an extracted part of MALDI-(TOF) mass spectra of an octanol initiated poly-propylene-glycol (PPG) / poly-ethylen-glycol (PEG) copolymer as a random (a) and a block polymer (b). The differences in relative signal intensities (green box) indicate the different distribution of the single components. Hereof conclusions could be drawn concerning the copolymer type (random or block) based on probability of formation of different components by reaction.

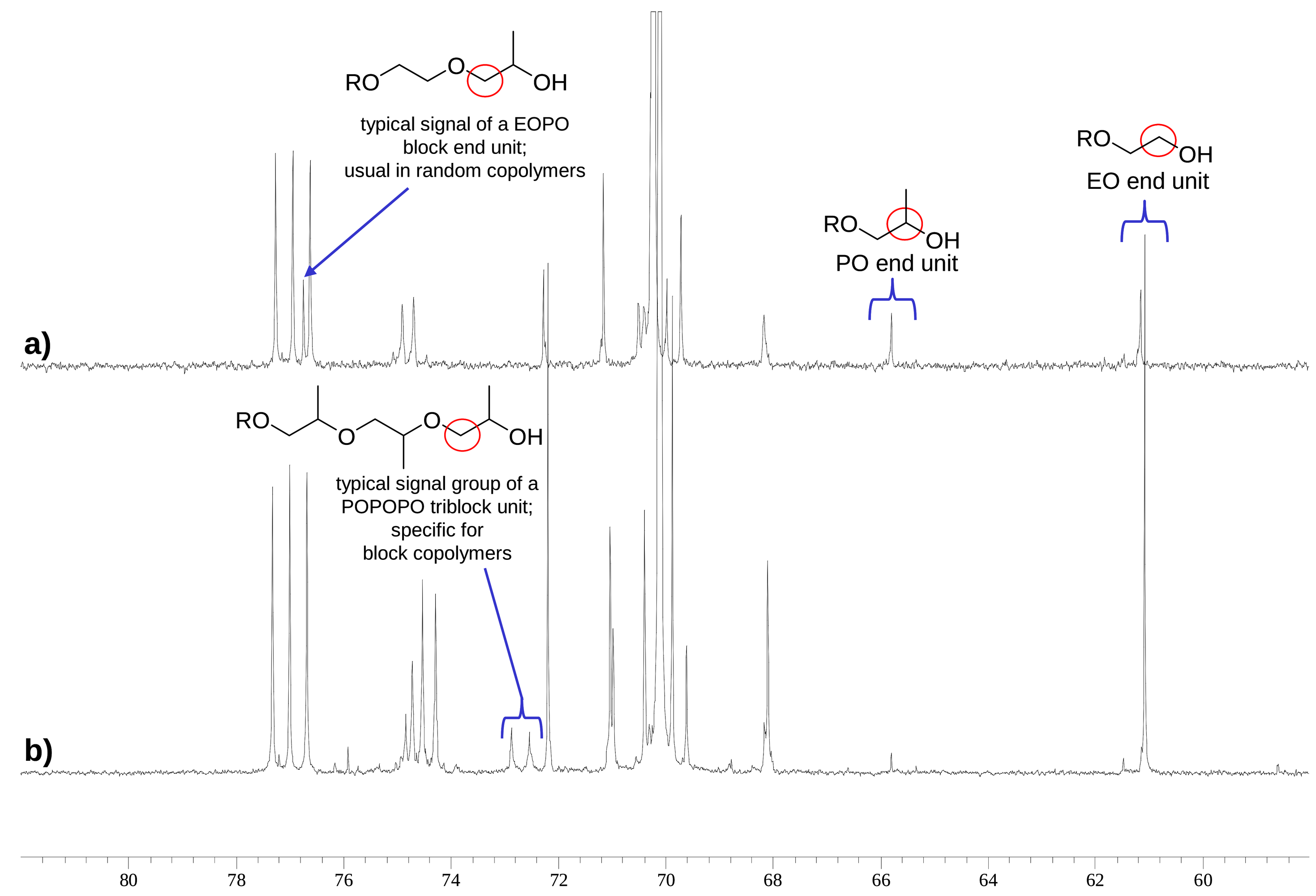

Figure 3
^{13}C NMR spectra of an octanol initiated poly-propylene-glycol (PPG) / poly-ethylene-glycol (PEG) copolymer as a random (a) and a block polymer (b)

The MALDI-CID experiments of a random and a block copolymer (figure 2) shows several fragments of the precursor mass (*m/z* 535, C_8-PO_1EO_7).
Starter and first building block form characteristical fragment ions.
Fragmentation from the terminal group results in a typical mass pattern representing the terminal sequence of EO and/or PO.

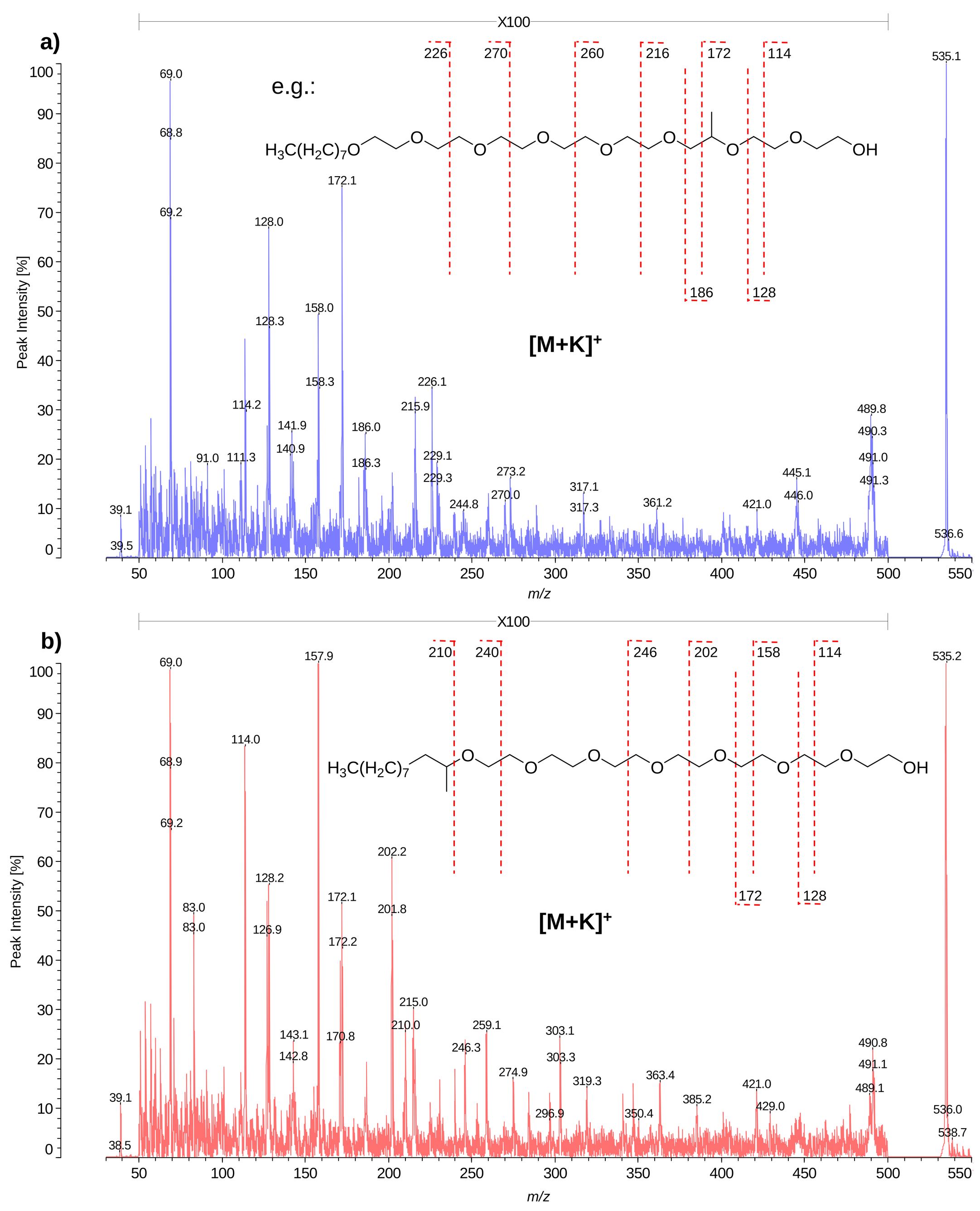

Figure 2
MALDI-CID spectra and different characteristical fragmentation pathways for the random (a) and block (b) polymer of the C_8-PO_1EO_7 precursor ions (*m/z* 535) received from the MALDI spectra in figure 1

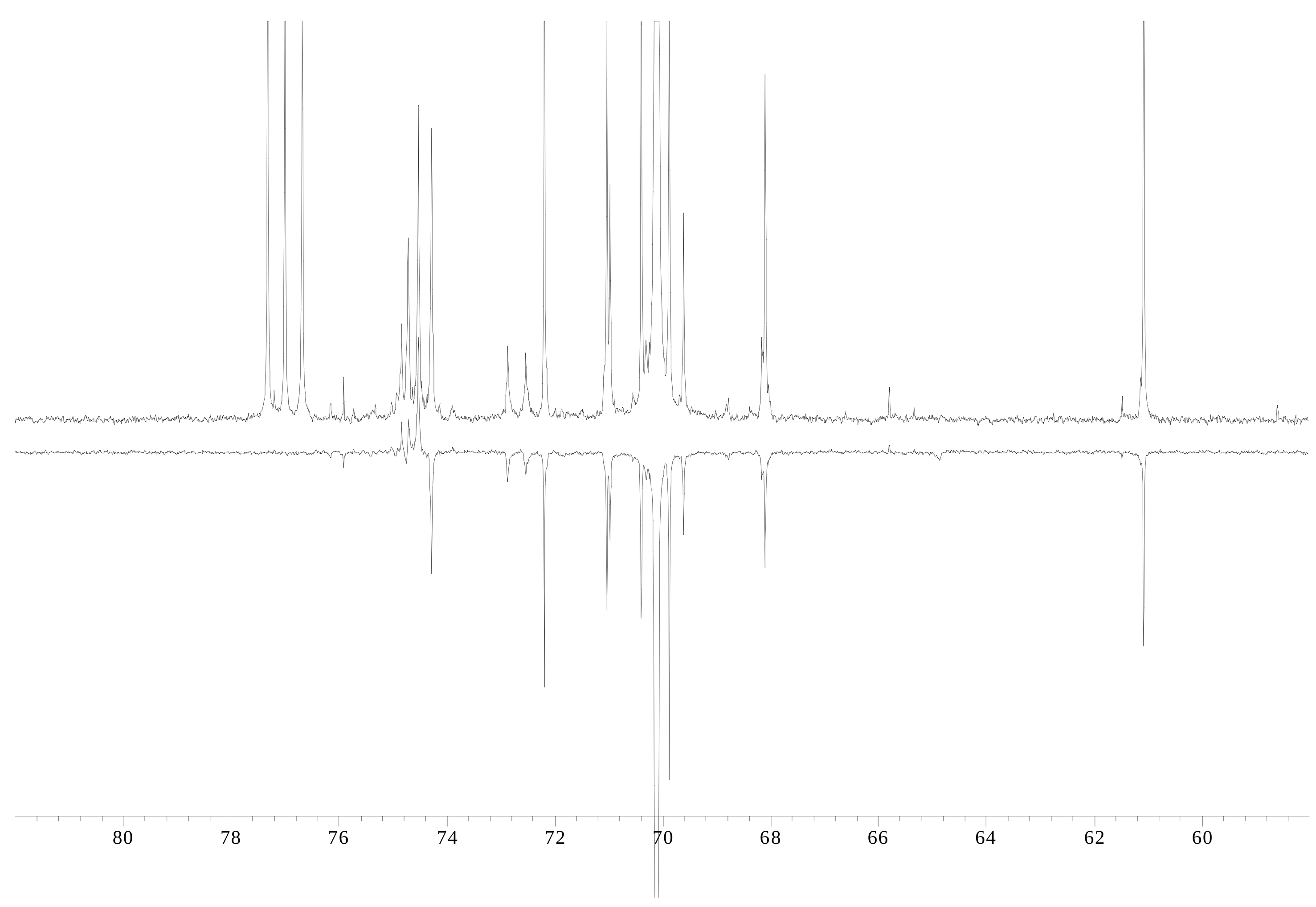

Figure 4
Overlay of ^{13}C NMR and ^{13}C-DEPT NMR spectra of an octanol initiated poly-propylene-glycol (PPG) / poly-ethylene-glycol (PEG) copolymer as a block polymer to prove the structur-signal-correlation shown above

By MALDI-MS and MALDI-CID-MS experiments following information could be achieved:

- Distribution of the molecular masses
- Degree of ethoxylation and/or propoxylation related to a known starter (here: fatty alcohol)
- Information on the first adducted building block
- Arrangement of the building blocks (type of polymerisation: random or block)

By NMR experiments following information could be achieved:

- Mean EO/PO degree and the alkyl chain (^1H NMR)
- Type of terminal building block (^{13}C NMR)
- Sequence of building blocks

Conclusions and Outlook

The applied NMR and MALDI-MS techniques are fully complementary methods which allow a detailed characterisation of such technical and complex polymers like fatty alcohol EO/PO adducts.

By these techniques even complex or high sophisticated structures like random followed by a block polymerisation and vice versa can be analysed.

Methods

MALDI-(TOF)MS and high energy MALDI-CID MS/MS experiments were performed using a MALDI reflectron time of flight mass spectrometer (AXIMA Performance™, Shimadzu Biotech, Manchester, UK). The accelerating voltage used was 20 kV. Helium was used as collision gas. The technical products were provided by Cognis (Düsseldorf, Germany) and diluted in THF to give a concentration of 3 mg/ml. MALDI measurements were performed with Dithranol, 10 mg/ml in THF. The target spot was precoated with 2 µl of a KCl solution (0.1 mol/l). Sample and matrix solutions were premixed in a volume ratio of 1:1 and 0.75 µl were applied onto the MALDI target.

^1H and ^{13}C nuclear magnetic resonance spectra were recorded on a Bruker ARX 400 spectrometer. The shown copolymers (100 mg) were dissolved in $CDCl_3$. Chemical shifts are reported in ppm relative to $CDCl_3$.

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