Polymer 51 (2010) 6140–6150

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Analysis of poly(ethylene oxide)-*b*-poly(propylene oxide) block copolymers by MALDI-TOF mass spectrometry using collision induced dissociation

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ARTICLE INFO

Article history:
Received 19 July 2010
Received in revised form
12 October 2010
Accepted 13 October 2010
Available online 21 October 2010

Keywords:
Block copolymers
MALDI-TOF mass spectrometry
Collision induced dissociation

ABSTRACT

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was used to analyse the block length of commercially available block copolymers of poly(ethylene oxide) and poly(propylene oxide) (PEO-*b*-PPO) based on the fragmentation behaviour in collision induced dissociation (CID) experiments.

MALDI-CID-TOF^2 analysis is a complex procedure depending on a number of different experimental parameters. Therefore, a step-by-step procedure was used starting with PEG and PPG standards, PEG-PPG blends and endgroup-functionalized PPGs, to understand the fragmentation behaviour of the different species. These results showed that characteristic fragment patterns of the homopolymers and PEG-PPG mixtures can be obtained that facilitate the interpretation of the fragment spectra of PEO-*b*-PPO di- and triblock copolymers. It was found that di- and triblock copolymers can be differentiated by their fragment spectra. In addition, the sequence of monomer units in the diblock copolymers could be determined.

1. Introduction

In this work poly(ethylene oxide)-poly(propylene oxide) block copolymers (PEO-*b*-PPO) were investigated by mass spectrometry (MS). In these materials the PEO and PPO blocks provide hydrophilic and hydrophobic properties, respectively, making them amphiphilic molecules that find wide applications in the chemical industry as nonionic surfactants [1–3].

In general, alkylene oxide block copolymers with surfactant properties find applications as lubricants, dispersants, foam control agents, antistatic agents and solubilizers and in numerous other applications in the pharmaceutical and cosmetic industry [3,4]. To understand the correlation between the molecular structure and the amphiphilic properties it is necessary to analyse these amphiphilic copolymers in detail and to determine the block sequence and block length, the identity and structure of end groups and possible homopolymer impurities. PEO-PPO block copolymers have been characterized using many different analytical methods including liquid chromatography, infrared and raman spectroscopy, viscosimetry, calorimetry, and NMR spectroscopy, compiled in detailed reviews by Kalinoski [5], Chu [3,6] and van Rooij [4]. These methods, however, yield only average information on specific structural features and cannot be used for the characterization of the individual components or molecular weight and chemical composition distributions.

For the analysis of complex polymers mass spectrometry offers the advantage of the possible investigation of single oligomers. In combination with soft ionization techniques which minimize the fragmentation of analyte molecules during the ionization, mass spectrometry can provide information on individual components and their distributions [7]. In particular, matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS), introduced by Tanaka et al. [8] and Karas and Hillenkamp [9] in 1988, has developed into the most successful desorption and ionization method for the analysis of large proteins, peptides, oligosaccharides and synthetic polymers [10,11]. The first MALDI-MS studies of synthetic polymers with molecular weights above 100,000 Da were discussed in detail already in 1992 [12,13]. By coupling the MALDI technique with time-of-flight (TOF) mass spectrometers, samples could be analyzed over a large mass range with high sensitivity, a mass accuracy of typically 0.1% and oligomeric mass resolution [14].

MALDI-TOF-MS enables in polymer analysis the determination of polymer types, endgroups, molecular weights [15], but the sequence distribution in copolymers and the precise structure (isomerism) of terminal groups cannot be determined. To obtain

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doi:10.1016/j.polymer.2010.10.031

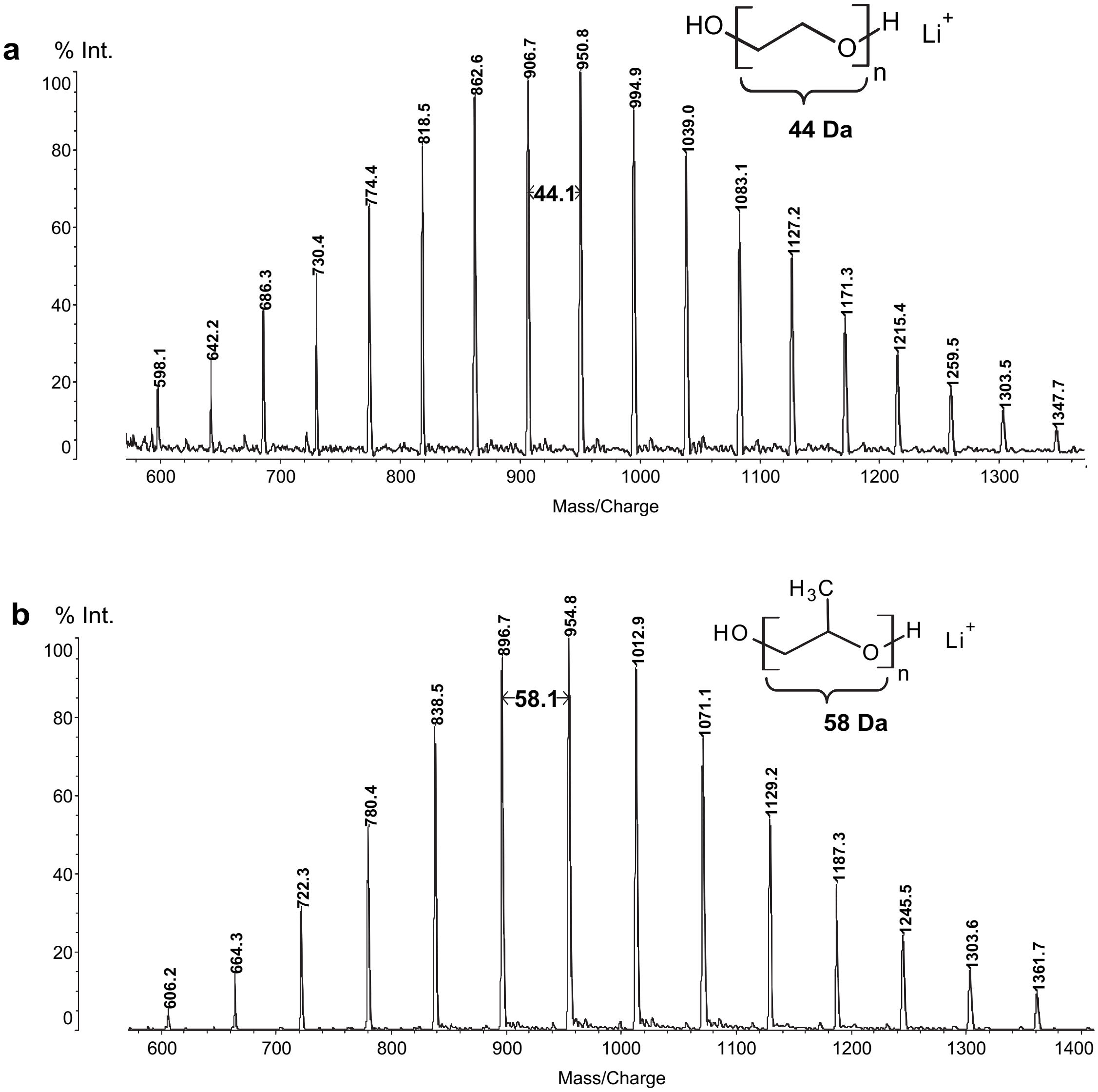


Fig. 1. MALDI-TOF mass spectra of the standards PEG (a) and PPG (b).

additional structural information on individual oligomers of complex polymers Collision Induced Dissociation (CID) has been introduced [16]. In CID the combination of MALDI-TOF-MS with a collision cell leads to fragmentation of selected molecular ions by collision with noble gas atoms. The obtained fragment spectra can provide information on endgroups [17–23], structural isomerism, copolymer compositions and block length distributions.

PEO-PPO copolymers have been analyzed previously by MALDI-TOF-MS [4,24–26]. Terrier et al. [24] determined the copolymer composition of the triblock copolyethers PEO-PPO-PEO, PPO-PEO-PPO and a random copolymer P(EO-PO) by MALDI-TOF-MS using a novel software that allowed to calculate monomer ratios from the mass spectra. They analyzed spectra of triblock copolymers as a function of the MALDI-TOF experimental parameters such as the number of laser shots, the relative proportions of polymer/salt and the nature of the matrix. Investigations on the determination of block length distributions of PEO-PPO triblock copolymers of the Pluronic type were performed by van Rooij et al. using MALDI coupled with Fourier transform ion cyclotron resonance-MS (FTICR-MS) [4]. Weidner et al. [26] investigated various PEO-*b*-PPO mono-n-butylether copolymers by coupling of chromatography and MALDI-TOF-MS techniques. Using the software tool “MassChrom2D” the copolymer composition of each fraction could be calculated from the mass spectra and was visualized in 2D plots. The procedure is based on the comparison of observed and calculated masses in a matrix formed by both monomer units, the normalization and the subsequent correction by chromatographic intensity information. In addition an MS/MS fragmentation was performed for the assignment of a copolymer composition to a given precursor ion.

The aim of the present study is the development of a MALDI-CID-TOF MS method to describe block structures and the block lengths of PEO-*b*-PPO block copolymers from the fragmentation pattern of selected parent ions.

To understand the fragmentation behaviour of PEO-*b*-PPO block copolymers in a first step the homopolymers PEG and PPG were investigated. The influence of the ratio PEG/PPG and the ionizing adduct on the fragmentation behaviour was analyzed using PEG-PPG blends with different compositions and adding different salts. In comparison to PEO-*b*-PPO block copolymers, endgroup-functionalized PPGs were investigated as model compounds. Finally PEO-*b*-PPO diblock and triblock copolymers in complex mixtures were analyzed by MALDI-CID-TOF-MS.

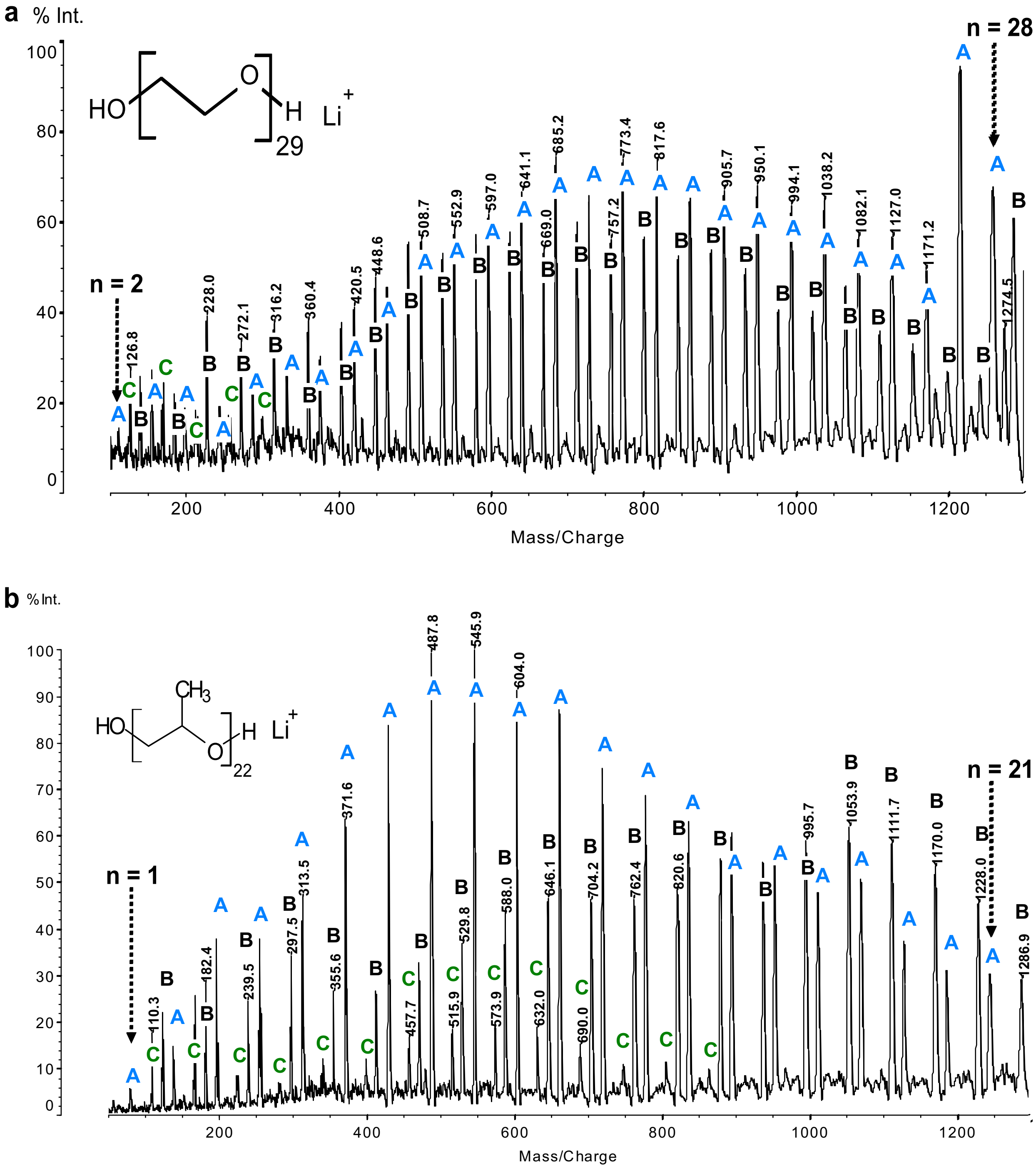


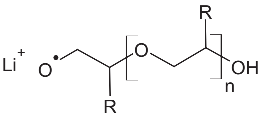
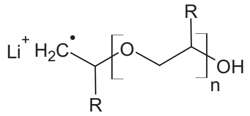
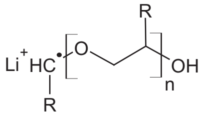
Fig. 2. MALDI-CID mass spectra of EO_{29} at 1303.5 Da (a) and PO_{22} at 1303.3 Da (b).

2. Experimental

2.1. Mass spectrometry

The MALDI-TOF-CID experiments were performed on an Axima-TOF^2 spectrometer (Shimadzu Biotech, Manchester, UK), equipped with a nitrogen laser (337 nm), a high-resolution ion gate for the selection of the parent ions and a collision cell. The width of the window for selecting the parent ion ranged from 2 to 10 Da. Argon was used as the collision gas at a pressure of 8×10^{-6} mbar. The pulsed extraction ion source accelerated the ions with an acceleration voltage of 20 kV. All measurements were performed in the positive reflectron mode with an accumulation of 441 scans per spectrum. The calibration of the reflectron mode measurements was carried out using PEG standards to yield an average mass accuracy of 0.5 Da in a mass range up to 2000 Da. The data acquisition, evaluation and generation of the spectra were performed with the software MALDI-MS Shimadzu Biotech Launchpad 2.7.2.20070105 (Kratos Analytical LTD. 2007). The software ACD/MS fragmenter V10.1 (Advanced Chemistry Development, Inc., Toronto, Ontario, Canada supported) was used for the interpretation of the fragment spectra.

Table 1
Representation of the assigned structures of the fragmentation series of PEG ($R = H$) and PPG ($R = CH_3$), n = number of repeat units.

Series	Assigned structures	$[M + Li]^+$ (Da)
A		$R = H$: $16 + 28 + 44 \times n + 17 + 7(Li) = 68 + 44 \times n$ $R = CH_3$: $16 + 28 + 58 \times n + 17 + 7(Li) = 68 + 58 \times n$
B		$R = H$: $28 + 44 \times n + 17 + 7(Li) = 52 + 44 \times n$ $R = CH_3$: $28 + 58 \times n + 17 + 7(Li) = 52 + 58 \times n$
C		$R = H$: $14 + 44 \times n + 17 + 7(Li) = 38 + 44 \times n$ $R = CH_3$: $14 + 58 \times n + 17 + 7(Li) = 38 + 58 \times n$

2.2. Samples

2-Methoxyethanol and 2-Ethoxyethanol were purchased from Sigma–Aldrich (Taufkirchen, Germany). These alcohols were used as starters in the propylene oxide polymerization to form $MeOEO_1PO_n$ and $EtOEO_1PO_n$ polymers. The syntheses have been conducted at BASF AG Ludwigshafen, Germany.

The commercially available samples of PEO-*b*-PPO di- and triblock copolymers were obtained also from BASF AG. The syntheses procedure was already reported [27]. The PEG and PPG standards were purchased from BASF AG and Sigma–Aldrich, respectively.

2.3. MALDI sample preparation

The PEO-*b*-PPO block copolymers and the standards PEG and PPG were dissolved in H_2O with a concentration of 4 mg mL^{-1}. 10 μL of the sample solution was mixed with 5 μL of a salt solution (10 mg mL^{-1} in H_2O) and 15 μL of a matrix solution of 1,8,9-trihydroxyanthracene (dithranol) dissolved in dioxane (10 mg mL^{-1}). 5 μL of the mixture was placed on a steel target using the dried droplet method [9,11]. Dithranol was purchased from Sigma Aldrich. All spectra were checked on reproducibility.

3. Results and discussion

3.1. Analysis of the homopolymers PEG and PPG

The MALDI-TOF mass spectra of the standards polyethylene glycol (PEG) and polypropylene glycol (PPG) presented in Fig. 1 show intense mass peaks at constant mass increments of 44 Da corresponding to the ethylene oxide (EO) repeating unit (Fig. 1a) and 58 Da corresponding to the propylene oxide (PO) monomer unit, respectively (Fig. 1b).

In order to study the fragmentation behaviour of these samples a precursor ion with a defined composition was selected for each polymer. The MALDI-CID mass spectra of the precursor ion of PEG with 29 repeating units at 1303.5 Da (Fig. 2a) and of PPG with 22 repeating units at 1303.3 Da (Fig. 2b) are presented in Fig. 2.

In both MALDI-CID mass spectra three fragment ion distributions are observed, which are assigned to the series A, B and C. Within a given series the peak-to-peak mass increment corresponds always to a repeating unit of 44 Da for PEG and 58 Da for PPG, respectively. The A series shows the highest signal intensity which indicates that this type of bond cleavage occurs most frequently. Based on the molecular masses of the fragments the related chemical structures of the fragments were assigned (Table 1).

The fragments A and B are caused by bond cleavage between a carbon and an oxygen atom. These fragments differ by 16 Da. This

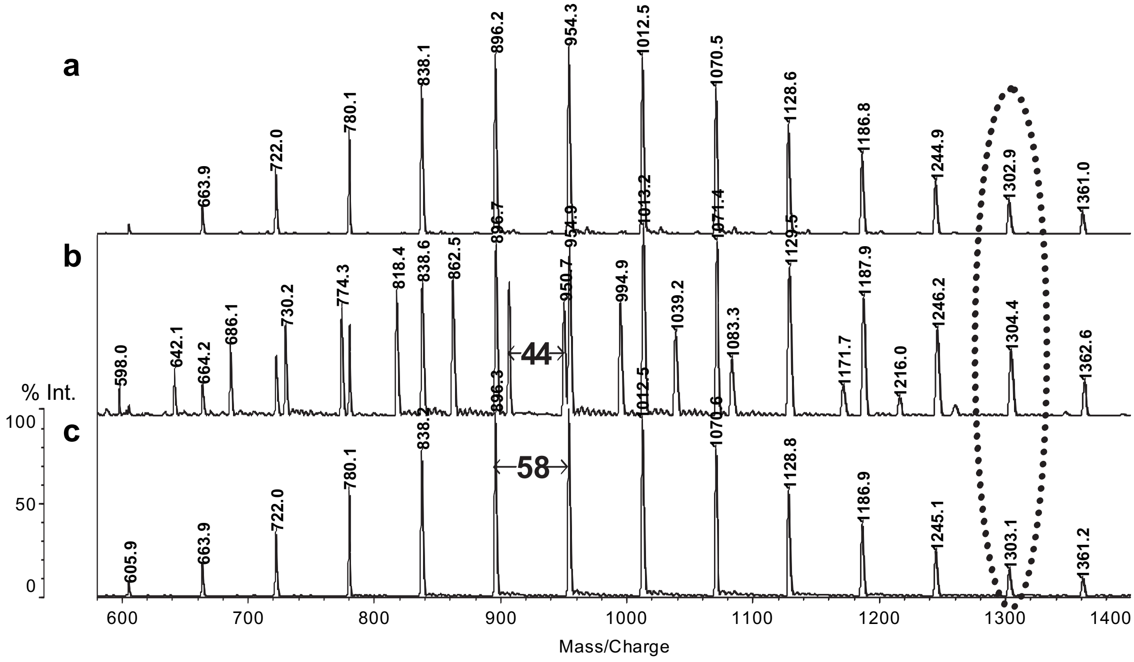


Fig. 3. Overlay of the MALDI-TOF mass spectra of PEG-PPG blends with mass ratios of 1:1 (a), 10:1 (b) and a PPG standard (c).

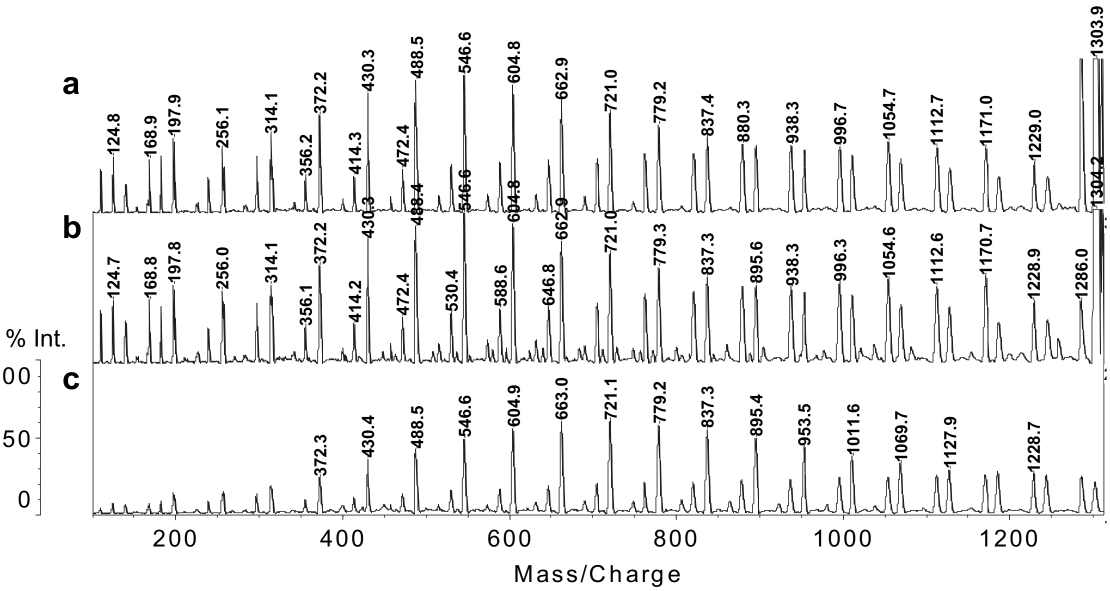


Fig. 4. Overlay of the MALDI-CID mass spectra of PEG-PPG blends with mass ratios of 1:1 (a), 10:1 (b) and a PPG standard (c).

mass difference corresponds to an oxygen atom, i.e. the bond cleavage takes place within the polymer chain before or after the oxygen atom. In the low mass region a further fragment series with signals of low intensity is observed. This C series is formed by a C—C bond cleavage. The difference in mass between A and C fragments is 30 Da which corresponds to the abstraction of a CH_2O-group.

Based on the obtained results it can be expected that samples containing PEG or PPG segments (blends or copolymers) should also show these three distributions A, B and C in the fragment produced by MALDI-CID spectra. These fragments should then be used to determine the exact composition and block lengths of the blends or block copolymers.

3.2. Analysis of PEG-PPG blends

Mixtures of PEG and PPG standards with average molar masses of 1000 g mol^{-1} were prepared with a mass ratio of 1:1 (Fig. 3a) and 10:1 (Fig. 3b). Lithium chloride was added as ionizing agent. An overlay of the MALDI-TOF spectra of these blends in comparison to the PPG standard (Fig. 3c) is shown in Fig. 3.

Contrary to the expectation that the spectra of the PEG-PPG blends present an overlay of the PEG and PPG distributions with signals of equal intensities, it can be clearly seen that under the given conditions a preferential ionization and detection of PPG takes place. For the analysis of the fragmentation behaviour of blends made of PEG and PPG with different compositions (Fig. 4a,b) the signal at roughly 1303 Da was selected, which can be assigned to an overlay of PEG with 29 monomer units and PPG with 22 monomer units (Fig. 4).

The MALDI-CID mass spectra of the blends (Fig. 4a,b) in comparison to the MALDI-CID mass spectrum of the PPG standard (Fig. 4c) show that the fragment ion signals are very similar. Although in the MALDI-TOF mass spectrum of the PEG-PPG blend with a tenfold excess of PEG (Fig. 3b) the signals of PEG and PPG

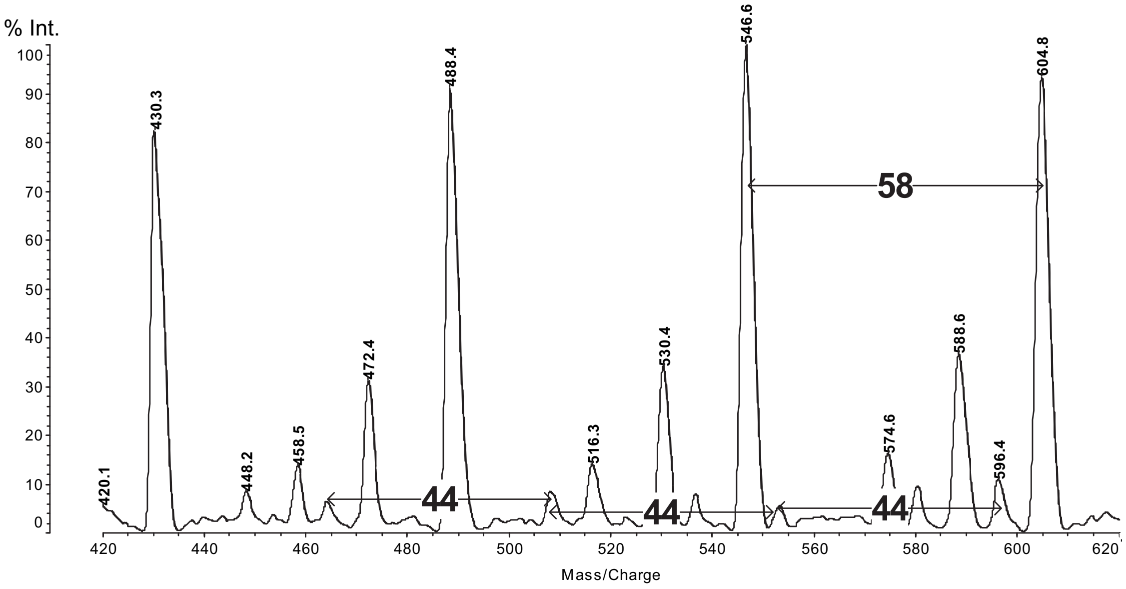


Fig. 5. Zoomed part of the MALDI-CID mass spectrum of PEG-PPG blend (10:1, see Fig. 4), mass range from 420 Da to 630 Da.

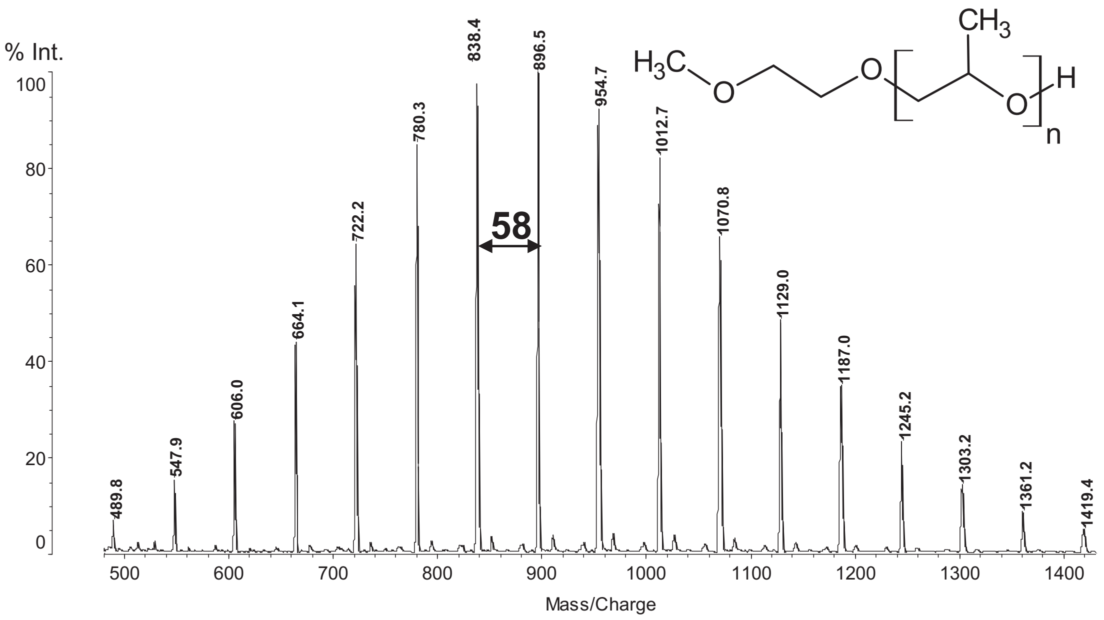


Fig. 6. MALDI-TOF mass spectrum of $MeOEO_1PO_n$.

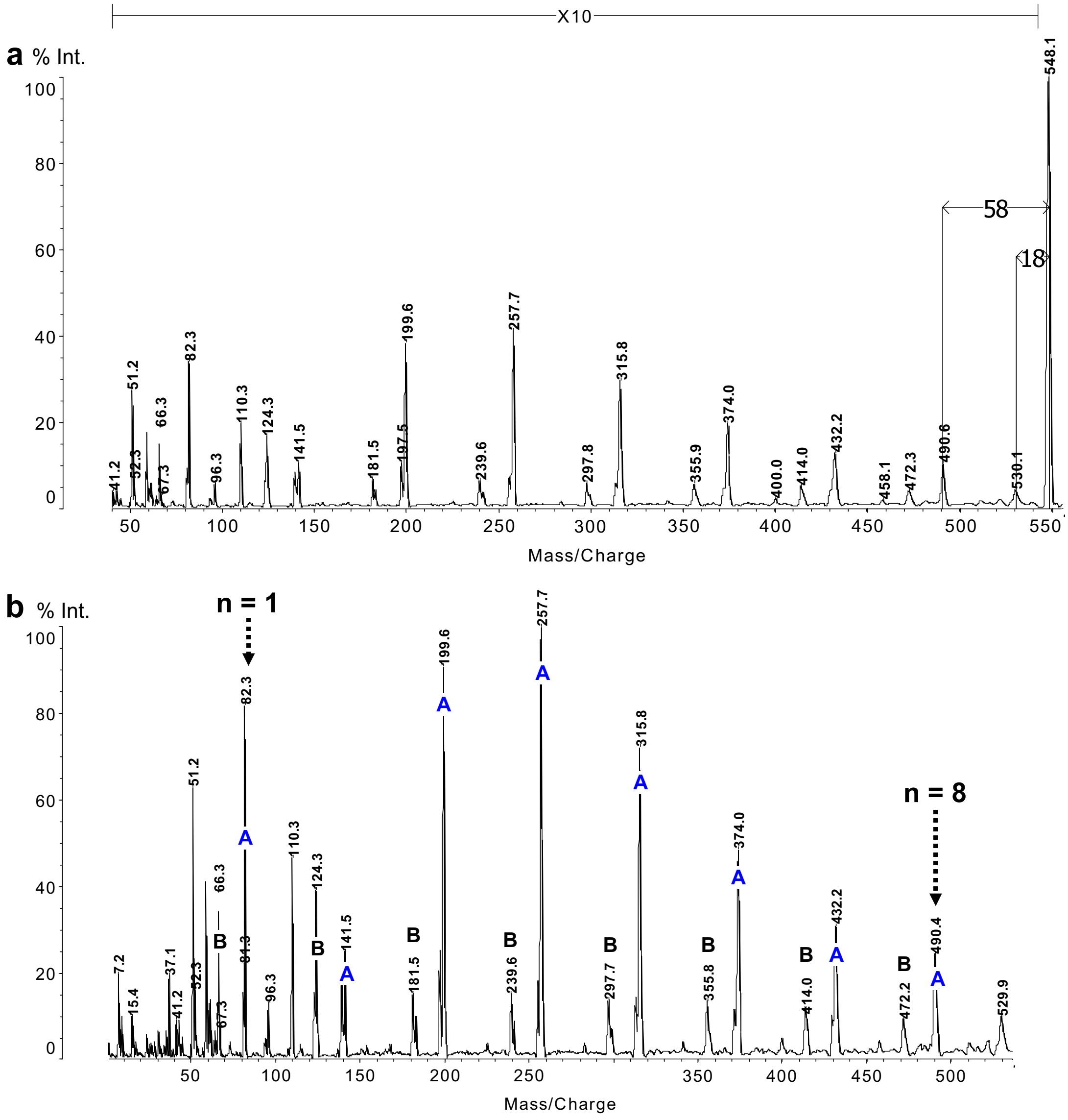


Fig. 7. MALDI-CID mass spectrum of $MeOEO_1PO_n$ (a) and enlargement of the mass region below the parent ion peak at 548 Da (b).

were of approximately equal intensity, the fragment spectrum of this blend (Fig. 4b) shows mainly PPG-fragment ion signals. The PEG fragment ion series A of very low signal intensity is just visible by enlarging a narrow section of the MALDI-CID mass spectrum of the 10:1-blend (Fig. 5). This behaviour can be explained probably by ion bond cleavage taking place preferably at the PPG homopolymer chain additionally to the preferred ionization of the PPG parent ion. This seems to indicate that the PEG segments are more stable against bond cleavage as could be expected.

These present measurements show that the experimental conditions (mass ratio of homopolymers, salt) have a significant influence on the observed peak intensities of parent ions. Under the present conditions PEG fragment ions of low intensity can be seen in the fragment spectrum only when PEG is present in excess in the PEG-PPG blend. For the investigation of PEO-*b*-PPO block copolymers it can be assumed that the CID mass spectra also will show fragment series that preferentially correspond to the PPG-fragment ions with or without the PEG block.

3.3. Analysis of ROEO$_1$PO$_n$ copolymers

In preparation of the studies on the PEO-*b*-PPO block copolymer fragmentation a sample with the simplest composition REO$_1$PO$_n$ (R = MeO, EtO) was analyzed by MALDI-TOF-MS. These investigations can lead to the information about the fragmentation behaviour of the PPG chain with different endgroups. The MALDI-TOF spectrum of the methoxy-EO-functionalised polypropylene glycol MeOEO$_1$PO$_n$ is shown in Fig. 6.

As expected, the spectrum of MeOEO$_1$PO$_n$ shows a single distribution with a peak-to-peak mass increment of 58 Da corresponding to the PO unit. For the MALDI-CID analysis the parent ion at roughly 548 Da was selected which can be the polymer MeOEO$_1$PO$_8$ (Fig. 7).

The first step in the fragmentation mechanism is the loss of a H_2O molecule from the parent ion at 548 Da and the formation of a signal at 530 Da. In this step probably a vinyl group is formed at the polymer chain end. The next signal at 490 Da may be obtained after the elimination of CH_3OCH_2CH (58 Da) from the one side of the polymer chain as well as of a PO (58 Da) unit of the PPG block from the other side. As can be seen in Fig. 7 two fragment series are observed in the spectrum, which are assigned to the fragment ion series A and B. Within a series the peak-to-peak mass increment is 58 Da corresponding to a PO monomer unit, i.e. the degradation takes place at the PPG block. The fragments of series A have the highest signal intensity which means that the bond cleavage occurring here is most frequent. Considering the copolymer ROEO$_1$PO$_x$ with the possible bond cleavages presented in Fig. 8 it must also be noted that two types of fragment ions can be produced. The fragment ions A und B contain a hydroxyl-group and A′ and B′ an alkoxy-group as an endgroup.

Based on the fragmentation experiments the molecular masses of the fragments were determined and the related structures were assigned (Table 2). The molecular mass differences of 1–2 Da can be explained by a hydrogen shift. Details about hydrogen shifts are given in Ref. [28].

The fragment ions A and B show a similar intensity as the fragment ions of the PPG homopolymer. In contrast the intensity of the C series decreased compared with the fragment spectra of the PPG homopolymer. As can be seen from Table 2 the series A and B′ as well as B and A′ have the same molar masses. That is why the observed signals are probably an overlay of these series. In order to verify the nature of these signals it was necessary to investigate the fragmentation behaviour of an EO-functionalised PPG with another endgroup, in this case EtOEO$_1$PO$_n$. The advantage of the measurement of the copolymer EtOEO$_1$PO$_n$ is that the molecular masses of the fragment ions are not identical with the proposed structures in Table 2 and the shift of the series has to be observed due to the mass difference of the endgroups, i.e. 14 Da for the additional CH_2-group.

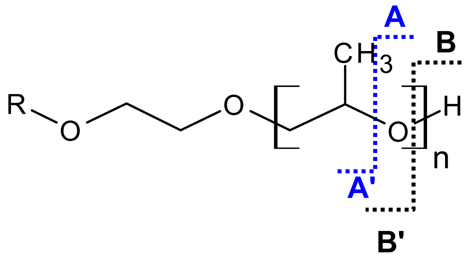


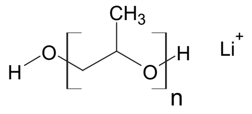
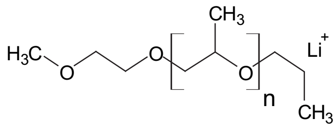
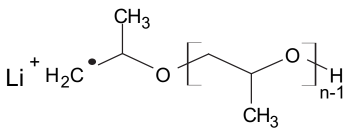
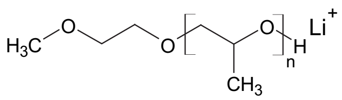
Fig. 8. General structure of ROEO$_1$PO$_x$ with the possible cleavage points and the corresponding fragments A, A′, B and B′; R = CH_3, CH_3CH_2.

An overlay of the MALDI-CID mass spectra of the parent ions of MeOEO$_1$PO$_8$ (Fig. 9a) and EtOEO$_1$PO$_8$ (Fig. 9b) shows that the Series A and B are of approximately equal intensity. That means the distributions can be assigned predominantly to the fragment ions series A and B which do not contain the alkyl oxide endgroup. A comparison of the spectra shows that the fragment spectrum of EtOEO$_1$PO$_8$ contains additional peaks of low intensity which can be seen clearly by enlarging a narrow mass region (Fig. 10) of this spectrum. These signals can be assigned to the series A′ and B′ (Table 2).

Thus, it is possible that there is an overlay of the series A and B′ and B and A′ in the MALDI-CID mass spectrum of MeOEO$_1$PO$_8$ (Fig. 7). But the signals corresponding to the fragment ions A′ and B′ can be neglected caused on the low intensity.

Furthermore, the fragmentation behaviour of MeOEO$_1$PO$_n$ (Fig. 11a–c) and EtOEO$_1$PO$_n$ (Fig. 12a–c) with different PPG block lengths was investigated.

Table 2
Representation of the proposed structures of the fragment signals of MeOEO$_1$PO$_8$, n = number of PO units.

Peak assignement	Calculated structures	$[M + Li]^+$ (Da)
A		18 + 58 × n + 7(Li) = 25 + 58 × n
A′		31 + 44 + 58 × n + 43 + 7(Li) = 125 + 58 × (n−1)
B		58 + 58 × n + 1 + 7(Li) = 67 + 58 × (n−1)
B′		31 + 44 + 58 × n+1 + 7(Li) = 83 + 58 × n

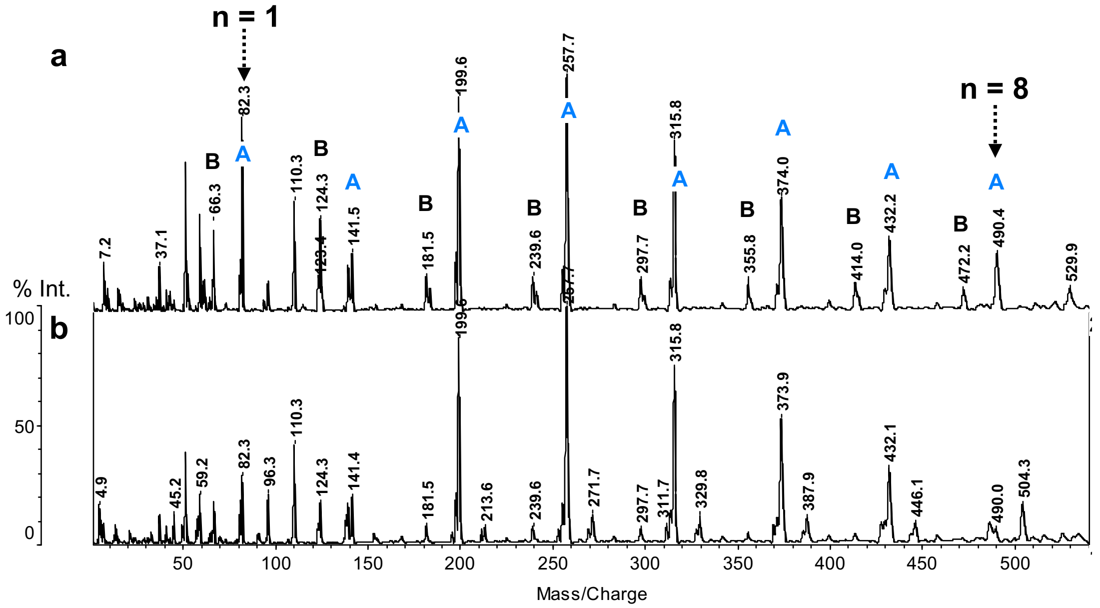


Fig. 9. Overlay of the MALDI-CID mass spectra of MeOEO$_1$PO$_8$ (a) and EtOEO$_1$PO$_8$ (b).

The overlay of the MALDI-CID mass spectra shows that the fragment signals are identical. Regardless of the block length of the PPG block and the nature of the endgroup R the fragment spectra of ROEO$_1$PO$_n$ contain always the Series A and B.

The results of this investigation have shown that high intensity fragment signals were obtained mainly from cleavages in the PPG block. The resulting fragments contain a hydroxyl endgroup. Accordingly, PPG-fragment ions with EO units and the MeO- or EtO-endgroups show signals of very low intensity.

Therefore, it can be expected that fragment spectra of PEO-*b*-PPO block copolymers with different PEG block lengths will show mainly the PPG-fragment series A and B after removal of the PEG block. Consequently it would be possible to determine the block length of the PPG block from the fragment signals and based on the knowledge of the total molar mass of the block copolymer (molar mass of the parent ion) the PEG block length could be calculated.

3.4. Analysis of PEO-PPO copolymers

Based on fragmentation experiments it should be possible to determine if a copolymer is statistical/random or block-like, if it is a diblock or triblock copolymer and what the exact composition of the copolymer is. The sample under investigation is assumed to be a mixture of PEO-*b*-PPO di- and triblock copolymers.

The studies of PEG-PPG blends have shown that PPG is ionized preferentially by LiCl. Therefore, it is expected that the fragment spectrum of HOEO$_2$PO$_{16}$ contains mainly the PPG-fragment series A, B and C (compare results on PPG homopolymer). The fragmentation

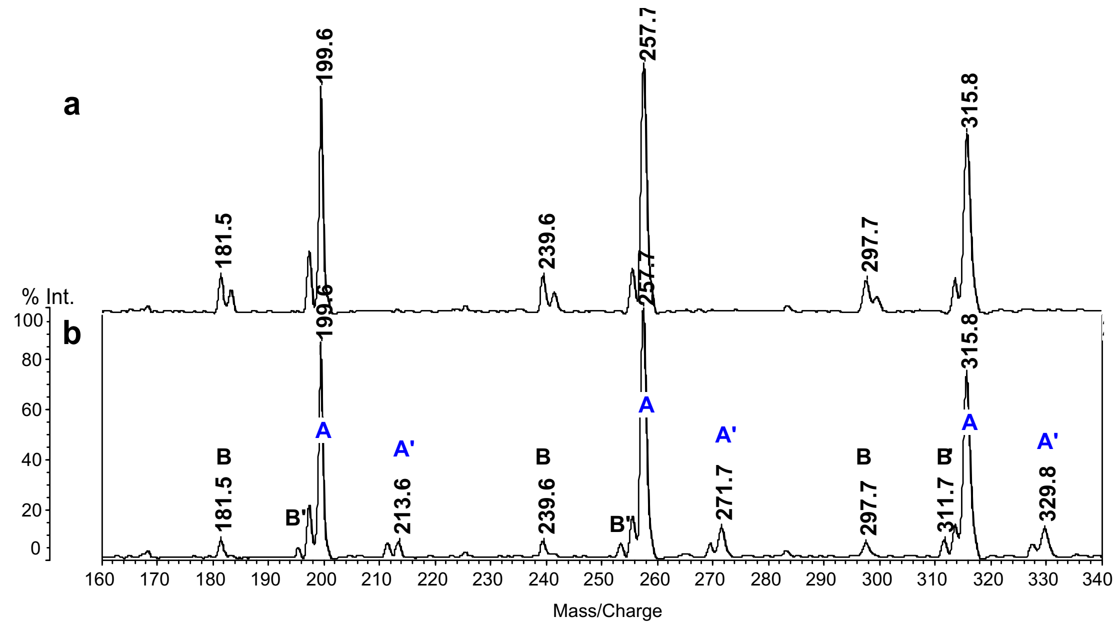


Fig. 10. Enlargement of the mass region from 160 Da to 340 Da.

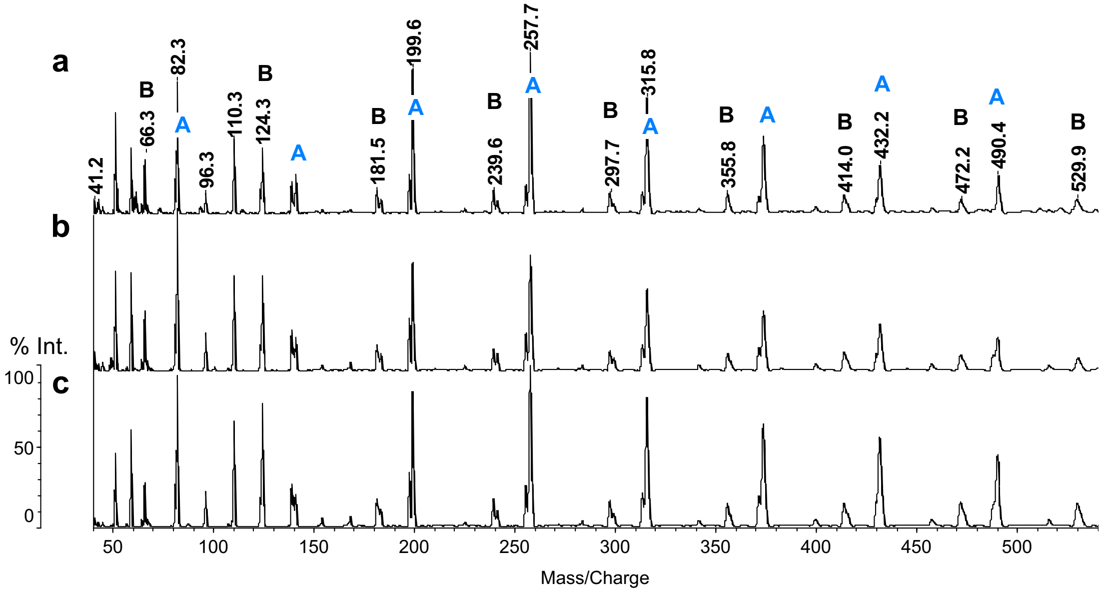


Fig. 11. Overlay of the MALDI-CID spectra of $MeOEO_1PO_n$ with $n = 8$ (a), 9 (b) und 10 (c).

in the PEO block is also possible, but these peaks should be only visible when the fragment ions contain the PPO block.

For the analysis of the fragmentation behaviour of PEO-*b*-PPO copolymers, parent ions were chosen in different mass areas. In Fig. 13 an overlay of the fragment spectra of $EtOEO_1PO_{16}$ (Fig. 13a) and the parent ion at 1042 Da (Fig. 13b), which can be assigned to the formal composition $HOEO_2PO_{16}$, is shown.

The spectrum shows that the fragmentation pattern of this parent ion is in agreement with the characteristic PPG-fragment ion signals of sample $EtOEO_1PO_{16}$. The PPG-fragment ion series A is of highest peak intensity and the series B is of lower intensity. Since the signal intensity of the parent ion is already very low, the signals of the series B are difficult to detect and the series C cannot be detected.

In the spectra 16 consecutive PPG signals until the signal at 953 Da can be observed. Thus, a triblock copolymer $PO_yEO_2PO_{16-y}$ can be excluded. This means that the selected parent ion is a diblock copolymer with a large PPO block of 16 units. Based on the mass of the precursor ion of 1042 Da and the PPO block of 16 units with a molar mass of 953 Da the block length of the PEO-block with 2 units could be calculated. This investigation showed that the fragmentation experiment enables the determination of the diblock copolymer sequence of $HOEO_2PO_{16}$. Furthermore it is evident that there are no PEG fragment ion series. A reason could be that the bonds within the PPO- block are broken preferably compared to the bonds within the PEO- block.

A further investigation was the analysis of the parent ion at 1799 Da which can be assigned to the calculated formal composition $HOEO_{35}PO_4$ and $HOEO_6PO_{26}$. It can be expected that the fragment spectra are more difficult to analyse because an overlay of parent ions belonging to different di- and triblock copolymers with the same molar mass is possible.

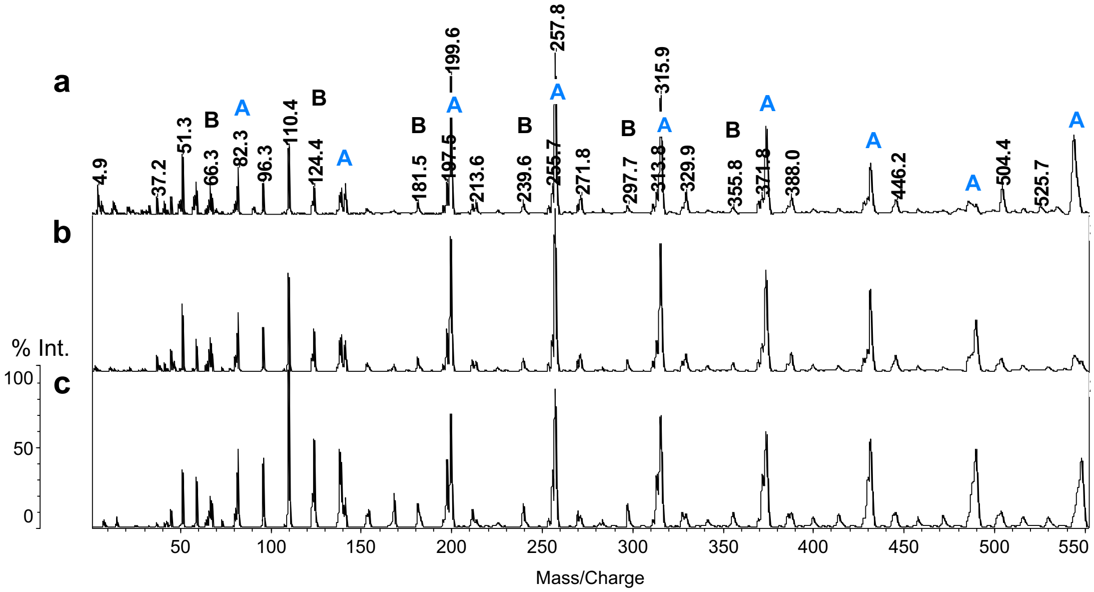


Fig. 12. Overlay of the MALDI-CID spectra of $EtOEO_1PO_n$ with $n = 8$ (a), 9 (b) und 12 (c).

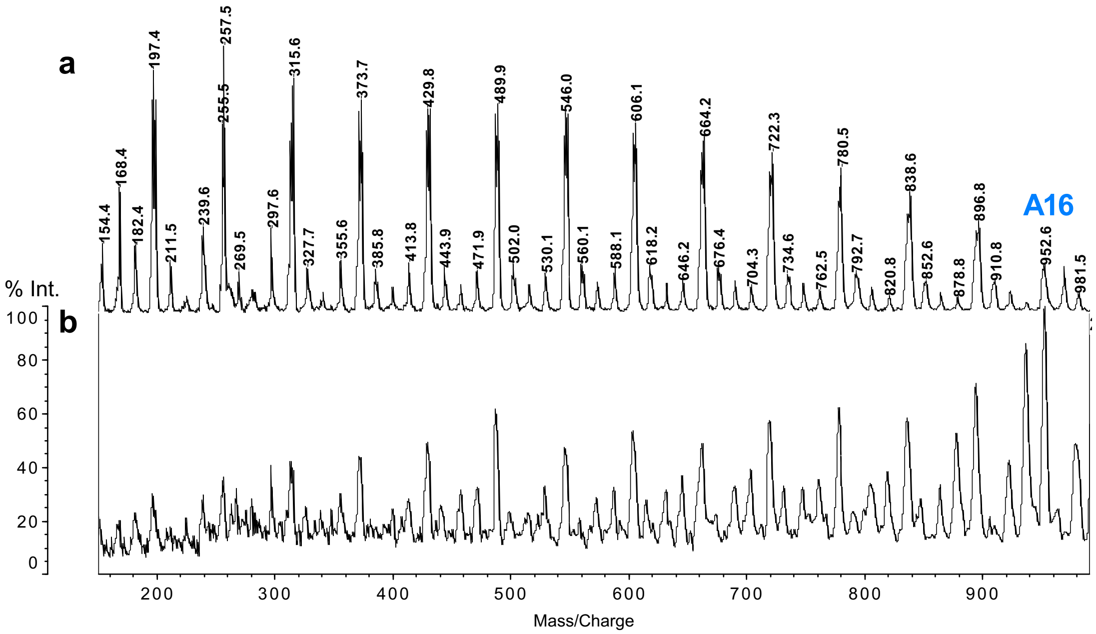


Fig. 13. Overlay of the MALDI-CID spectra of $EtOEO_1PO_{16}$ (a) and $HOEO_2PO_{16}$ at 1042 Da (b).

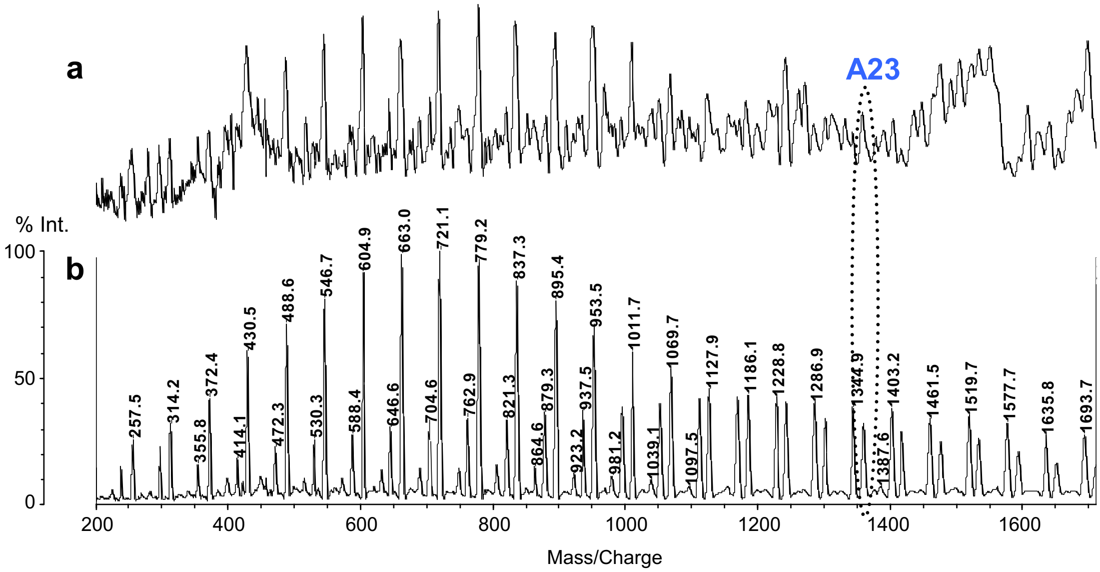


Fig. 14. Overlay of the MALDI-CID spectra of the triblock copolymer $PO_nEO_6PO_{26}$ (a) and a PPG homopolymer (b).

The MALDI-CID spectrum in Fig. 14a shows signals of low intensity. In comparison to the spectrum of a PPG homopolymer (Fig. 14b) the signals can be assigned clearly to the signals of the PPG-fragment series A. The quality of the spectrum is poor but the signals are reproducible, so it can be ensured that these signals were not caused by noise. The fragment spectrum shows 23 consecutive PPG-fragment ion peaks corresponding to series A. This means that a diblock copolymer can be ruled out because the spectrum of the diblock $HOEO_6PO_{26}$ should show 26 consecutive PPG-fragment ion peaks and the spectrum of the diblock $HOEO_{35}PO_4$ only 4 consecutive PPG-fragment ion signals. Consequently, the present sample is a triblock copolymer with the composition $HOPO_3EO_6PO_{23}$. But nevertheless an overlay of triblock copolymers with the composition $HOPO_{3+n}EO_6PO_{26-n}$ is possible because the spectra also show the corresponding number of consecutive PPG-fragment ion signals. So an overlay with the fragment pattern of $PO_3EO_6PO_{23}$ cannot be excluded.

4. Conclusion

It can be concluded that the present investigation showed a characteristic fragmentation behaviour of PEO-*b*-PPO copolymers which could be used for the detailed analysis of these block copolymers. As has been shown, it is possible to distinguish between di- and triblock copolymers and to determine the sequence in diblock copolymers on the basis of their fragment spectra. Although the quality of the spectra of the triblock copolymer was poor it showed reproducible signals.

But the results of measurements by MALDI-MS depend on the experimental conditions. So they are specific and therefore not directly comparable. Weidner et al. have investigated PEO-*b*-PPO mono-n-butylether polymers which showed different fragment behaviour. A fragment spectrum of a PEO-*b*-PPO block copolymer presented PEO and PPO fragment ions of approximately equal intensities using a different matrix. For their MALDI-MS/MS measurements a matrix of *trans*-2-(3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene)malononitrile (DCTB) and sodium trifluoracetate as the salt were selected [26].

Acknowledgement

The authors wish to acknowledge Dr. F. Rittig for his helpful synthesis and cooperation.

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