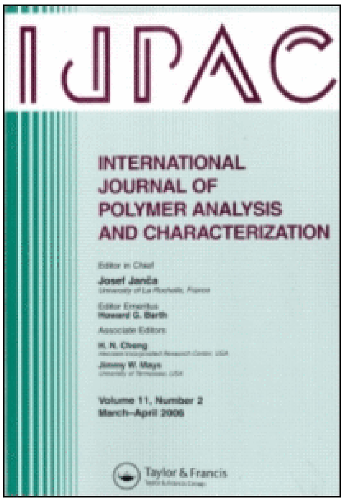

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Pasch, H. , Zammert, I. and Just, U.(1995) 'Matrix-Assisted Laser Desorption/ lonization Mass Spectrometry of Synthetic Polymers; Analysis of Poly (Ethylene Oxides)', International Journal of Polymer Analysis and Characterization, 1: 4, 329 — 338

To link to this Article: DOI: 10.1080/10236669508233885

URL: http://dx.doi.org/10.1080/10236669508233885

Int. J. Polymer Analysis & Characterization
1995, Vol. 1, pp. 329–338
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Gordon and Breach Science Publishers SA
Printed in Malaysia

Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry of Synthetic Polymers; Analysis of Poly (Ethylene Oxides)

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(Received July 22, 1994; in final form December 5, 1994)

Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) is a useful new technique for the determination of the chemical structure and the molar mass distribution of poly(ethylene oxides). Investigating different alkyloxy and aryloxy polyethylene oxides, we have shown that MALDI-MS gives accurate molar masses, provided that the oligomer masses are above 400 g/mol. Below 400 g/mol, mass discrimination effects have to be taken into account. A perfect fit of MALDI-MS with data, determined independently by supercritical fluid chromatography and high performance liquid chromatography, was obtained.

KEY WORDS MALDI-MS, Polyethylene Oxides, Molar Mass Distribution, Functionality Type Distribution, Liquid Chromatography at the Critical Point of Adsorption

INTRODUCTION

Poly(ethylene oxides) (PEO) are important intermediates in organic and polymer chemistry. In particular, alkyloxy and aryloxy terminated PEO's are in widespread use as surfactants. Depending on the length of the polymer chain and the chemical structure of the terminal groups, the amphiphilic properties change, thus influencing the surface activity.

The chemical structure of alkyl/aryloxy PEO oligomers is characterized by distributions in molar mass and functionality. As a result of different initiation, chain propagation and termination mechanisms, species of different terminal groups bound to the poly(ethylene oxide) chain are formed. To elucidate the structure-properties relationships of these products, it is important to know their molar mass distribution (MMD) as well as the chemical structure and number of the terminal groups.

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It has been shown previously that the functionality type distribution (FTD) of PEO may be determined by liquid chromatography at the critical point of adsorption [1]. The determination of FTD and MMD of functional polyethers is possible by using two-dimensional chromatographic techniques, where liquid chromatography at the critical point of adsorption is carried out in the first dimension. After separating the sample with respect to functionality, the functionally homogeneous fractions may be subjected to supercritical fluid chromatography (SFC) or size exclusion chromatography (SEC) to obtain the MMD of each fraction [2,3].

Mass spectrometry (MS) has become an interesting alternative for the characterization of low-molar-mass synthetic polymers. Different from other methods, absolute molar masses can be determined precisely and data on the sequence of repeat units, polymer additives and impurities can be obtained [4]. The main obstacle for MS of high-molar-mass polymers, caused by their low volatility and thermal lability, has been overcome to a considerable extent by the development of soft ionization techniques. Secondary-ion mass spectrometry in combination with time-of-flight mass analysers has been used for molar mass determination of polymers in the mass range m/z 500–10,000 g/mol [5,6]. However, besides desorption of intact oligomer ions, fragmentation of the polymer chain is observed. Other ionization techniques, such as field desorption [7,8], fast atom bombardment [9], plasma desorption [10] and electrospray ionization [11] are also of considerable interest for polymer characterization.

A new, most promising technique for the separation of large molecules according to their molar mass has been introduced recently. Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS), developed by Karas and Hillenkamp in 1988 [12], has been successfully used to determine the mass of large biomolecules and synthetic polymers [13]. In principle, the sample to be investigated and a matrix solution are mixed in such a ratio that matrix separation of the sample molecules is achieved. After drying, a laser pulse is directed onto the solid matrix to photo-excite the matrix material. This excitation causes the matrix to explode, resulting in the expulsion and soft ionization of the sample molecules without fragmentation. Once the analyte is ionized it is accelerated and analyzed in a time-of-flight (TOF) mass spectrometer. As a result, the analyte is separated according to molar mass of its components and in the case of heterogeneous polymers a molar mass distribution may be obtained. In some first applications of MALDI-MS, the analysis of poly(methyl methacrylate), poly(styrene sulfonic acid) and poly(acrylic acid) has been described [14,15]. In a recent paper it was shown by us that epoxy resins may be separated into their oligomers according to the degree of polymerization and the type of functional groups [16]. One major advantage of the method is that minimum quantities of the magnitude of a few ng are sufficient for analysis.

So far, little is known about the accuracy of molar mass determinations by MALDI-MS. In particular, comparative studies using MALDI-MS and chromatographic methods would be desirable. An interesting study on poly(dimethyl siloxane) was carried out by Hagenhoff et al., [17] comparing SFC and time-of-flight secondary ion mass spectrometry (TOF-SIMS). The results obtained fit well up to masses of about 3000 g/mol, whereas remarkable differences occur for higher masses due to mass discrimination effects.

In the present report a number of technical PEO samples is investigated. With MALDI-MS, SFC, and liquid chromatography at the critical point of adsorption, the samples are fractionated with respect to molar mass and functionality. The MMD and functional heterogeneities are determined and comparing the data from different methods the accuracy of MALDI-MS is evaluated.

EXPERIMENTAL

Samples

All samples are technical products. They were purchased from BASF Aktiengesellschaft Ludwigshafen, Germany. The following average structures were given by the manufacturer:

Sample	Average Structure
C_{10}-PEO	i-$C_{10}H_{21}(OCH_2CH_2)_7OH$
C_{12}-PEO	n-$C_{12}H_{25}(OCH_2CH_2)_7OH$
C_{13}-PEO	i-$C_{13}H_{27}(OCH_2CH_2)_8OH$
C_{13},C_{15}-PEO	i+n-$C_{13}H_{27}$,$C_{15}H_{31}(OCH_2CH_2)_7OH$
Octylphenol-PEO	$C_8H_{17}C_6H_4(OCH_2CH_2)_6OH$
Nonylphenol-PEO	$C_9H_{19}C_6H_4(OCH_2CH_2)_{10}OH$

MALDI-MS

The MALDI-MS investigations were conducted on a Kratos Kompact MALDI 3 (Urmston, UK). The samples were dissolved in THF or the HPLC solvent and mixed with the matrix 2,5-dihydroxybenzoic acid. After drying the mixture of the sample and the matrix on the sample holder, the measurements were carried out using the following conditions: polarity-positive, flight path-reflection, mass-high (20 kV acceleration voltage), 100 shots per sample.

SFC

The SFC experiments were conducted on a Dionex SFC 600D instrument (Lee Scientific, Sunnyvale, CA, USA) using a 10 m × 50 μm i.d. biphenyl SB-30 capillary column (Lee Scientific, Sunnyvale, CA, USA). The mobile phase was carbon dioxide (Scott, Plumsteadville, PA, USA). Flame ionization detection (FID) at 380°C was used. Timed split injection was carried out using a Valco injection valve (0.2 μL). All samples were injected as 30% solutions in methylene chloride. The density program was as follows: initial density 0.25 g/mL, then increase density to 0.55 g/mL with a ramp rate of 0.007 g/mL·min, followed by increasing the density to 0.67 g/mL with a ramp rate of 0.0064 g/mL·min, and hold for 40 min.

HPLC

The HPLC experiments are described in detail in a previous report.[18]

RESULTS AND DISCUSSION

In a first set of experiments, a well-characterized calibration standard of poly(ethylene glycol) PEG 600 was analyzed by MALDI-MS and SFC. The MALDI-MS spectrum consists of peaks of high intensity, having a peak-to-peak mass increment of 44 g/mol, i.e. of one ethylene oxide unit. These peaks represent the M+Na$^+$ molecular ions of the PEG oligomers, whereas the peaks of low intensity are due to the formation of the corresponding M+K$^+$ molecular ions, see Figure 1A. The intensity of the peaks is assumed to characterize the relative abundance of the oligomers in the sample and from these the molar mass distribution is calculated. When calculating the molar masses the cationization has been taken into consideration.

Similarly, SFC separates the sample into single oligomers, see Figure 1B, however, quantification is more complicated. In SFC, as well as in gas chromatography, where a flame ionization detector (FID) is used, the detector signal does not only depend on the amount of the eluted component but also on its composition and chemical structure. In general, the number of carbon atoms and the types of linkages determine the signal intensity of the FID. In a number of cases, namely for homologous series, the FID response

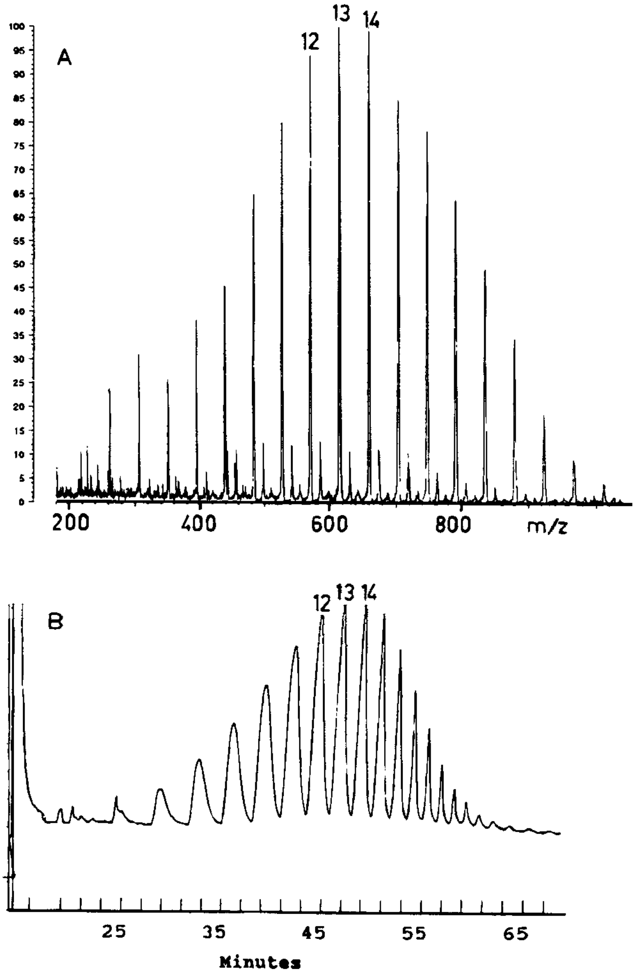

FIGURE 1 MALDI-MS spectrum (A) and SFC chromatogram (B) of poly(ethylene glycol) PEG 600, numbers at peaks indicate degree of polymerization.

may be calculated using increment methods. A detailed description of this procedure was given in a previous report [2]. The assignment of the peaks in the SFC chromatogram was based on comparison with model diethylene and triethylene glycols. The corrected molar mass distribution curves for SFC and MALDI-MS are shown in Figure 2. As can be seen, both curves overlap nearly completely, indicating that the determined distributions are equal. This is in agreement with the calculated molar mass values:

	M_N	M_W	M_W/M_N
MALDI-MS	590	640	1.08
SFC	580	610	1.05

For the following experiments small amounts of LiCl were added to the sample. As a consequence, only the M+Li$^+$ molecular ions were formed, therefore obtaining only one peak for one oligomer in the MALDI-MS spectrum.

Excellent agreement was obtained for the technical octylphenol-terminated PEO. In addition to the SFC and MALDI-MS data, molar masses were obtained by liquid chromatography [18] and the results are shown below.

	M_N	M_W	M_W/M_N
manufacturer's data	470		
MALDI-MS	450	480	1.07
SFC	450	470	1.04
HPLC	440	460	1.04

The MMD curves are given in Figure 3, showing excellent agreement, as expected.

The investigation of the nonylphenol-terminated PEO reveals that the starting nonylphenol was not a pure compound but a mixture of different isomers. While the MALDI-MS spectrum gave the expected oligomer distribution, the SFC chromatogram

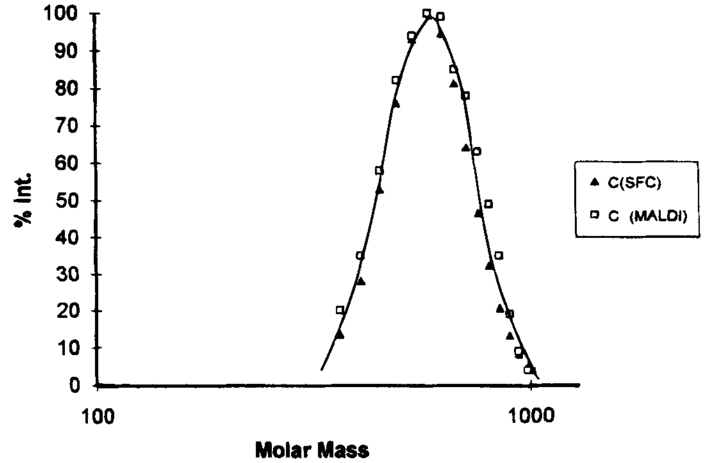

FIGURE 2 Molar mass distribution of PEG 600, determined by SFC and MALDI-MS.

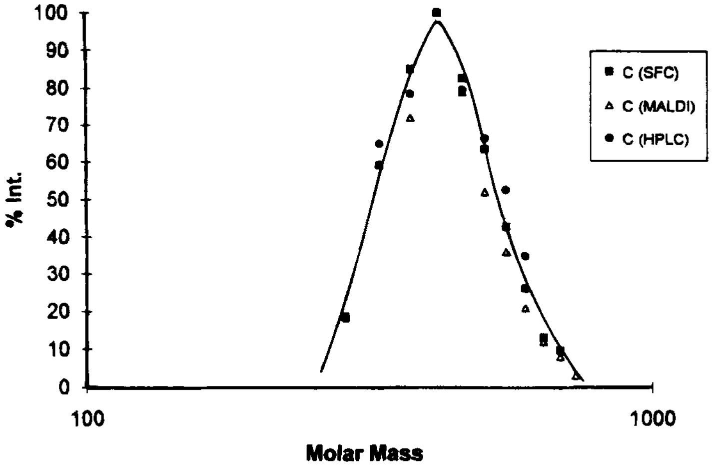

FIGURE 3 Molar mass distribution of octylphenol-PEO, determined by SFC, MALDI-MS and HPLC.

shows overlapping peaks for each degree of polymerization, see Figure 4. As the isomeric composition of the nonylphenol is not known, the MMD cannot be calculated from the SFC chromatogram. For this type of sample MALDI-MS is the method of choice because isomerism does not affect the separation. Again, the calculated MMD is in good agreement with the manufacturer's data:

	M_N	M_W	M_W/M_N
manufacturer's data	600		
MALDI-MS	630	660	1.05

A different behavior is obtained for the dodecyl-terminated PEO, see Figure 5, where significant deviations occur for MALDI-MS as compared to the SFC and HPLC distribution curves. At the high-molar-mass end of the distribution curves, excellent agreement between the three methods was obtained, whereas at the low-molar-mass end the MALDI-MS distribution curve indicates a much lower concentration of the corresponding oligomers. Accordingly, the calculated molar masses show increased numbers for MALDI-MS:

	M_N	M_W	M_W/M_N
manufacturer's data	490		
SFC	480	540	1.12
HPLC	490	530	1.08
MALDI-MS	520	580	1.12

This low-mass-discrimination effect in MALDI-MS was obtained before and was attributed to the high volatility of these oligomers. Obviously, due to the high vacuum in the mass spectrometer, low molar mass oligomers located at the surface of the sample spot, are evaporated, thus decreasing their concentration in the sample.

This discrimination effect is less pronounced for higher mass terminal groups. For a technical PEO, comprising a mixture of a tridecyl- and a pentadecyl-terminated PEO, only

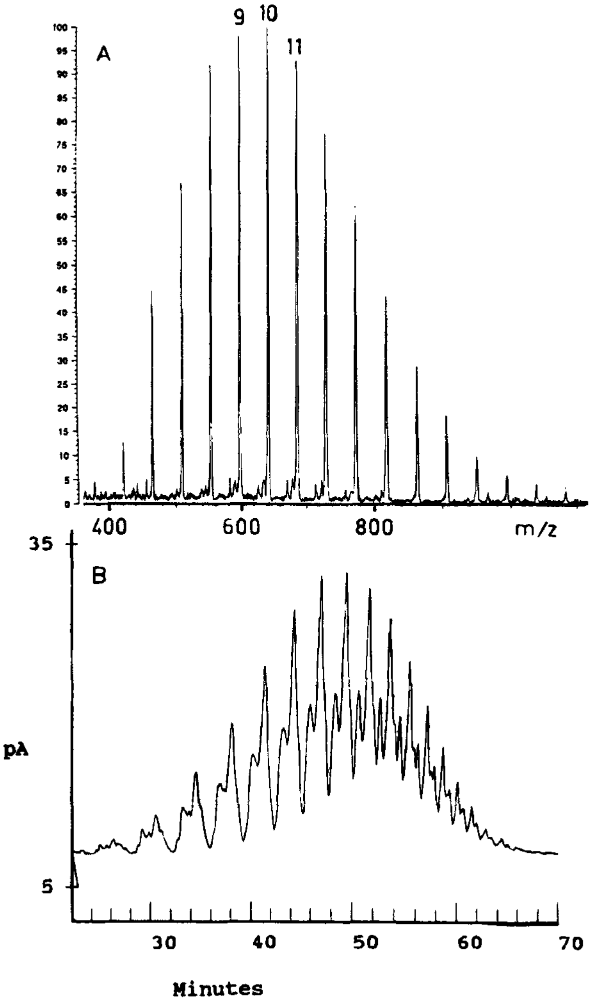

FIGURE 4 MALDI-MS spectrum (A) and SFC chromatogram (B) of nonylphenol-PEO; numbers at peaks indicate degree of polymerization.

the molar mass distribution of the tridecyl-fraction is affected by mass discrimination, see Figure 6, and the calculated numbers are as follows:

	M_N	M_W	M_W/M_N
$C_{13}H_{27}$-fraction			
SFC	540	590	1.09
HPLC	550	580	1.06
MALDI-MS	580	620	1.07
$C_{15}H_{31}$-fraction			
HPLC	570	590	1.04
MALDI-MS	560	580	1.04

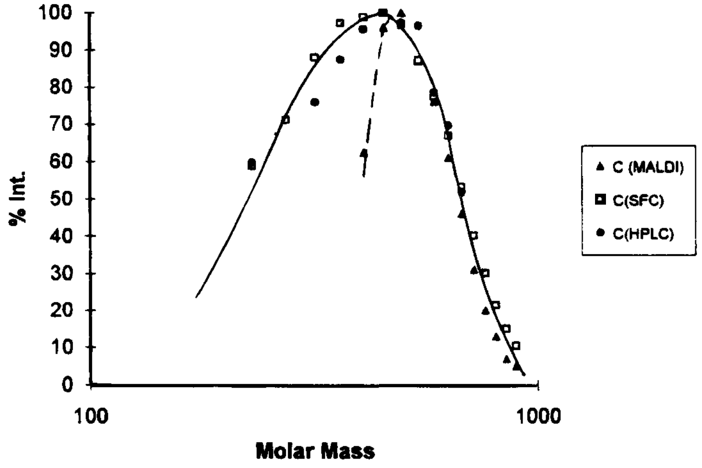

FIGURE 5 Molar mass distribution of dodecyl-PEO, determined by SFC, MALDI-MS and HPLC.

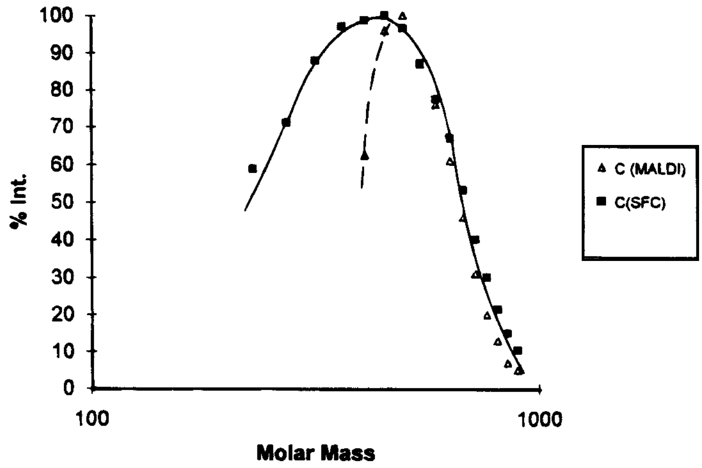

FIGURE 6 Molar mass distribution of the $C_{13}H_{27}$-fraction of a $C_{13}H_{27}$,$C_{15}H_{31}$-PEO, determined by SFC and MALDI-MS.

As was already discussed for the nonylphenol-terminated PEO, problems in molar mass determination by SFC and HPLC always occur when isomerism affects the separation. The SFC chromatogram of the $C_{13}H_{27}$,$C_{15}H_{31}$-PEO, given in Figure 7B, shows that one single peak is obtained for the $C_{13}H_{27}$-terminated oligomers, whereas for the $C_{15}H_{31}$-terminated oligomers a number of overlapping peaks is formed for each oligomer. These results suggest that pure tridecanol and isomeric pentadecanol were used in the preparation of these samples. The presence of these compounds does not allow us to calculate the MMD for the pentadecyl-fraction from the SFC chromatogram. Even more complex is the SFC chromatogram of a technical tridecyl-terminated PEO, see Figure 7D. In this case it is

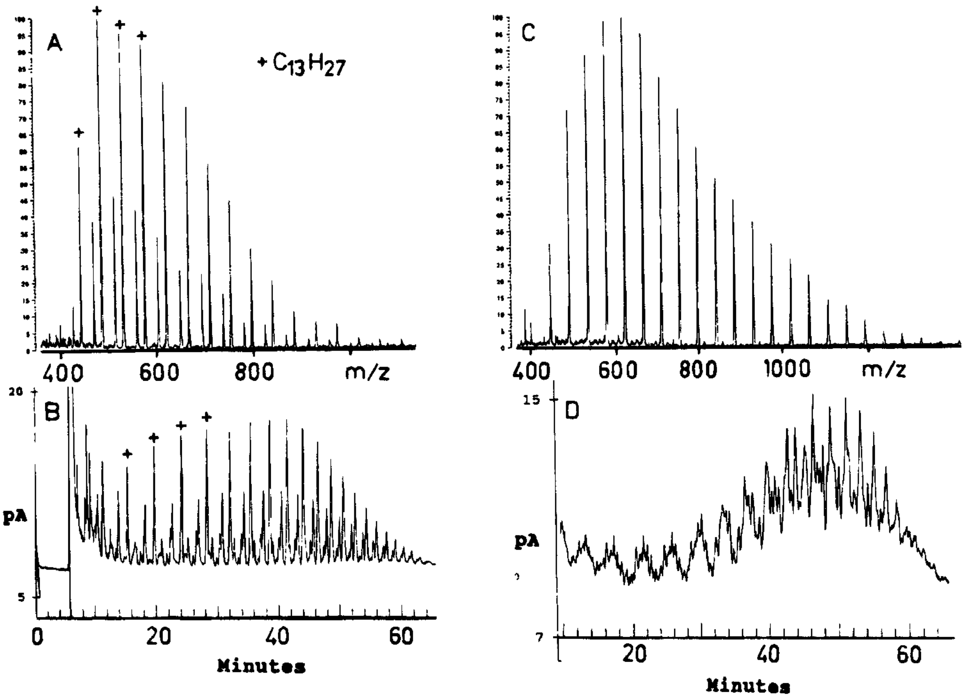

FIGURE 7 MALDI-MS spectra (A,C) and SFC chromatograms (B,D) of a $C_{13}H_{27}$,$C_{15}H_{31}$-PEO (A,B) and a $C_{13}H_{27}$-PEO (C,D).

even impossible to assign the chromatographic peaks to a certain degree of polymerization. For this type of very complex isomeric mixtures, MALDI-MS is the only method for providing a MMD information, see Figure 7C.

Referring to Figure 7A, in addition to the determination of MMD of the tridecyl- and pentadecyl-fractions it should be possible to calculate the relative concentration of both fractions.

With the equations

$$m(C_{13}) = \Sigma A_i(C_{13})/\Sigma A_i(C_{13}) + \Sigma A_i(C_{15}) \bullet 100\%$$

$$m(C_{15}) = 100 - m(C_{13})$$

with A_i being the relative intensity, the following compositions are calculated from MALDI-MS and HPLC data:

	$C_{13}H_{27}$-PEO	$C_{15}H_{31}$-PEO
MALDI-MS	73 Mol.-%	27 Mol.-%
HPLC	74 Mol.-%	26 Mol.-%

The data fit perfectly, thus showing the applicability of the approach.

In conclusion, MALDI-MS has been shown to be a useful new technique for the determination of the chemical structure and the molar mass distribution of poly(ethylene oxides). Depending on the mass range of the oligomers, mass discrimination may adversely affect the MALDI-MS determinations. Above masses of about 400 g/mol these discrimination effects may be neglected.

Acknowledgment

Financial support from the Bundesminister für Wirtschaft through the Arbeitsgemeinschaft Industrieller Forschungsvereinigungen e.V. (AIF) is gratefully acknowledged (project No. 9287).

The authors are grateful to BASF, Ludwigshafen, for providing the samples, and to Shimadzu Europe GmbH, Duisburg, for supporting the MALDI-MS experiments.

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