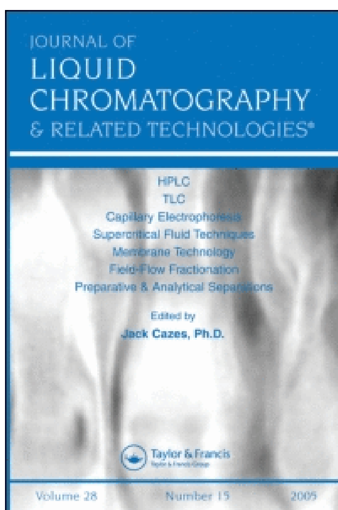
This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Chromatographic Investigations of Macromolecules in the Critical Range of Liquid Chromatography. VIII. Analysis of Polyethylene Oxides

H. Pasch[a]; I. Zammert[a]
[a] Deutsches Kunststoff-Institut, Darmstadt, Germany

To cite this Article Pasch, H. and Zammert, I.(1994) 'Chromatographic Investigations of Macromolecules in the Critical Range of Liquid Chromatography. VIII. Analysis of Polyethylene Oxides', Journal of Liquid Chromatography & Related Technologies, 17: 14, 3091 — 3108
To link to this Article: DOI: 10.1080/10826079408013193
URL: http://dx.doi.org/10.1080/10826079408013193

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

JOURNAL OF LIQUID CHROMATOGRAPHY, 17(14&15), 3091-3108 (1994)

CHROMATOGRAPHIC INVESTIGATIONS OF MACROMOLECULES IN THE CRITICAL RANGE OF LIQUID CHROMATOGRAPHY. VIII. ANALYSIS OF POLYETHYLENE OXIDES

H. PASCH AND I. ZAMMERT
Deutsches Kunststoff-Institut
Schloßgartenstraße 6
64289 Darmstadt, Germany

Downloaded At: 07:53 25 January 2011

ABSTRACT
Alkyloxy and aryloxy terminated polyethylene oxides are analyzed with respect to their terminal groups by liquid chromatography at the critical point of adsorption. The molar mass distribution of the main functional fraction is determined by a modified size-exclusion chromatography technique using matrix assisted laser desorption/ionization mass spectrometry as an additional detector. The results are correlated with data obtained by supercritical fluid chromatography and mass spectrometry.

INTRODUCTION

Polyethylene 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 molar mass and the chemical structure of the terminal groups the amphiphilic properties change, thus influencing the surface activity.

Copyright © 1994 by Marcel Dekker, Inc.

The chemical structure of alkyl/aryloxy PEO's is characterized by distributions in molar mass and functionality. Due to the different initiation, chain transfer and chain termination mechanisms and possible impurities in the reaction mixture, species having different terminal groups bound to the polyethylene oxide chain are formed. To elucidate the structure-property relationships of these products, it is important to know the chemical structure and the number of these terminal groups in addition to the molar mass distribution (MMD).

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]. In brief, every chromatographic process is associated with the distribution of the solute between the mobile and the stationary phase. The distribution coefficient K_d relates to a change in free energy, ΔG, of the monomer unit when the solute molecule passes from the mobile into the stationary phase. ΔG depends on the energy of interaction of the monomer unit and the stationary-phase surface, and starting with a certain critical potential of interaction, ε_c, adsorption of the macromolecule takes place in the pore of the stationary phase. Therefore, if $\varepsilon > \varepsilon_c$, then the macromolecule is adsorbed and vice versa, such that $\varepsilon < \varepsilon_c$, then the macromolecule is unadsorbed and remains in the mobile phase. When $\varepsilon = \varepsilon_c$, the interaction energy is exactly compensated by the entropy losses. Corresponding to these three cases are the three modes of liquid chromatography of macromolecules: adsorption, exclusion, and critical. These modes relate to the different sequences in which macromolecules of various sizes elute. At the critical point, ΔG is zero, irrespective of the size of the macromolecule and all macromolecules elute within one retention time. The retention depends exclusively on the inhomogeneities of the polymer chain; that is, the nature and number of functional groups, grafts, blocks, or branches [2-4].

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 reaction mixture with respect to functionality, the functionally homogeneous fractions may be subjected to SFC or SEC, delivering the MMD of each fraction [5,6].

In the present report a number of technical polyethylene oxides is investigated. The separation with respect to functionality is carried out using liquid chromatography at the critical point of adsorption, whereas MMD is determined by a modified SEC procedure and mass spectrometry.

Downloaded At: 07:53 25 January 2011

MATERIALS AND METHODS

The polyethylene oxide samples were technical products of BASF, Ludwigshafen (Germany). The following average structures were given by the manufacturer:

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

Downloaded At: 07:53 25 January 2011

Liquid chromatography at the critical point of adsorption and modified SEC were carried out on a modular HPLC system, comprising a Waters model 510 pump, a Waters differential refractometer R401, a Knauer u.v./vis filter photometer, a Rheodyne six-port injection valve and a Waters column oven, keeping the temperature for all experiments at 25°C. The columns used were Macherey-Nagel Nucleosil RP-18 or RP-8, 125x4mm I.D. or 60x4mm I.D. Some preparative separations were carried out on a Nucleosil RP-18, 250x20mm I.D, column.
All solvents were Ferak HPLC grade.
The MALDI-MS investigations were conducted on a Kratos Kompact MALDI 3. The samples were dissolved in THF or the HPLC solvent and mixed with the matrix 2,5-dihydroxy benzoic 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 (20kV acceleration voltage), 100 shots per sample.
The detailed description of the SFC experiments will be given in a forthcoming publication [10].

RESULTS AND DISCUSSION

In agreement with previous investigations, the separation of the functional PEO's according to functionality was carried out on a stationary phase RP-18 and

acetonitrile-water as the mobile phase [1]. However, using a column length of 250 mm or 125 mm, very strong retention of the functional PEO's was observed at the critical point of PEO due to the long hydrophobic chain end. To avoid irreversible adsorption on the stationary phase, a shorter column or a packing material of lower hydrophobicity was used.

The critical diagram M vs. retention time for a RP-18 column of 60 mm length is shown in Figure 1. At acetonitrile concentrations >47% by volume in the solvent mixture, the retention time decreases as the molar mass of the PEO calibration sample increases; per definition retention corresponds to a size-exclusion mode. The reverse behaviour is obtained at acetonitrile concentrations <45% by volume, where the retention time increases with increasing molar mass. At a solvent composition of acetonitrile-water 46:54% by volume, the retention time does not change with molar mass, and at this "critical point of adsorption" separation is accomplished exclusively with respect to functionality regardless of the molar mass.

The critical chromatograms of functional PEO's with different terminal groups at the critical point of adsorption of PEO are shown in Figure 2. As can be seen for the C_{10}- and C_{12}-PEO's, two distinctively different fractions are obtained, resulting in a very sharp peak at a retention time of about 35 s and a broad peak at higher retention times. For the Octylphenol-PEO RI and UV detection was used and the first peak appears only in the RI detector. By comparison with a standard sample the first peak was identified as polyethylene glycol, which is known to be formed as an unwanted by-product. In the case of the Octylphenol-PEO two additional peaks at retention times of 154 s and 303 s are detected, when UV detection at a wavelength of 280 nm is used. By comparison with the pure compound the peak at 154 s is found to be octylphenol. The second peak at 303 s is assumed to consist of Alkyphenol-PEO with a smaller alkyl substituent, which might have been formed due to impurities in the starting octylphenol.

The quantitative determination of the PEG fraction is carried out using a calibration curve amount PEG vs. refractive index response. The PEG content of the samples is in the magnitude of 1-3% by weight, which is typically for this type of commercial products, see Table 1.

In agreement with the expected behaviour for a reversed-phase column, the retention time of the samples increases with increasing hydrophobicity of the terminal group. Therefore, the elution order with respect to the terminal group is

Downloaded At: 07:53 25 January 2011

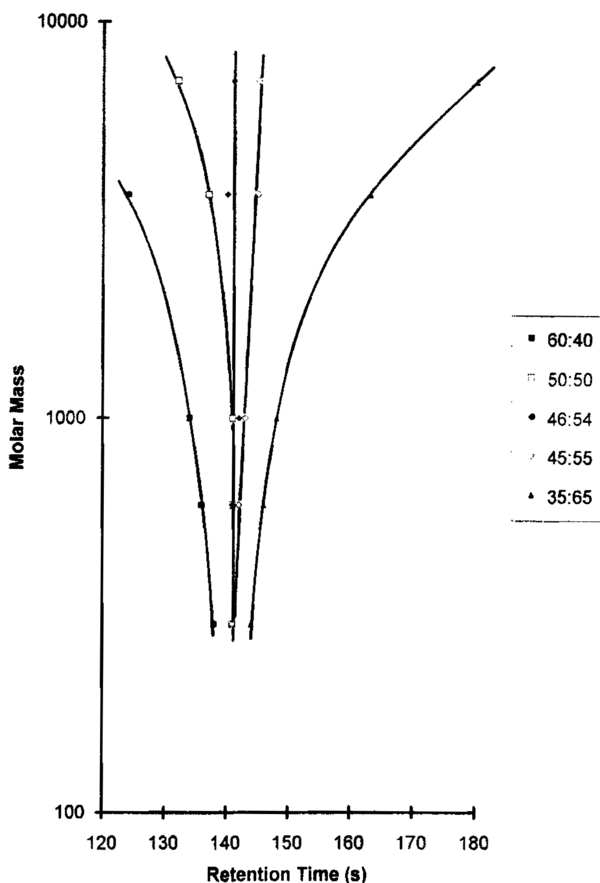


FIGURE 1 Critical diagram molar mass vs. retention time of polyethylene glycol, stationary phase: Nucleosil RP-18, 60x4mm I.D., solvent: acetonitrile-water

OH (PEG) << $C_{10}H_{21}$ < $C_{12}H_{25}$ < $C_{13}H_{27}$ < $C_{15}H_{31}$. The change of the retention times with changing the composition of the solvent mixture is given in Figure 3. The dramatic increase of the retention times near the critical point suggests, that PEO's with alkyloxy end groups greater than C_{13} may not be eluted from the column in reasonable times. In fact, it was found for C_{15}-terminated PEO and all following, that they do not elute from the column within 60 min.

Downloaded At: 07:53 25 January 2011

Downloaded At: 07:53 25 January 2011

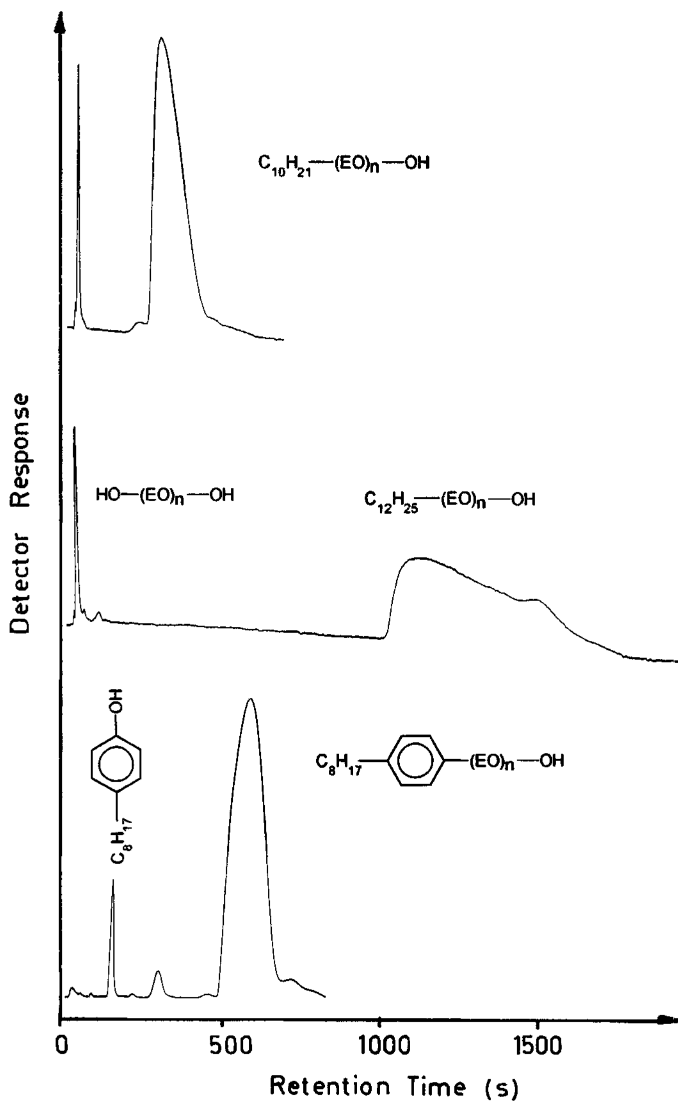


FIGURE 2 Chromatograms of functional PEO's at the critical point of adsorption of PEO, stationary phase: see Fig. 1, solvent: acetonitrile-water 46:54% by volume

Downloaded At: 07:53 25 January 2011

TABLE 1

PEG Content of the Polyethylene Oxide Samples Determined by Liquid Chromatography at the Critical Point of Adsorption

Sample	PEG (% by weight)
C_{10}-PEO	3.27
C_{12}-PEO	2.50
C_{13}-PEO	2.32
C_{13},C_{15}-PEO	1.93
Octylphenol-PEO	1.32
Nonylphenol-PEO	1.58

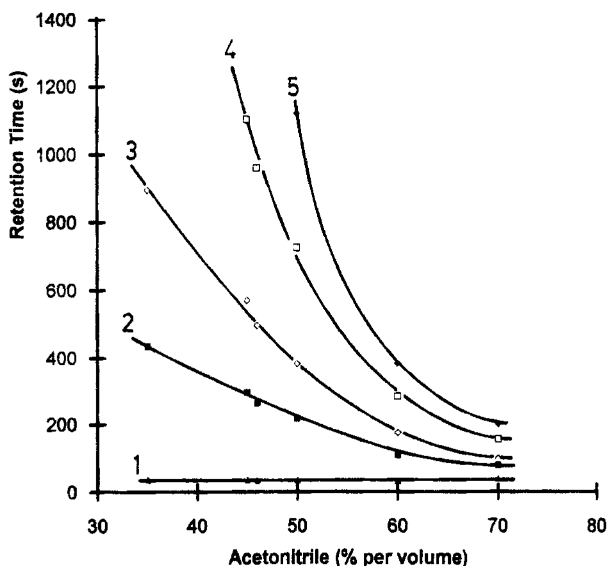


FIGURE 3 Diagram of retention time of the main functional fraction vs. composition of the solvent, stationary phase and solvent: see Fig. 1, samples: PEG (1), C_{10}-PEO (2), Octylphenol-PEO (3), C_{12}-PEO (4), C_{13}-PEO (5)

In order to decrease the hydrophobicity of the stationary phase and the retention times accordingly, a RP-8 instead of a RP-18 column is used. In this case C_{13}- and C_{15}-terminated PEO's elute from the column at the critical point of adsorption, see Figure 4. In addition to the previously detected peaks, for the aryloxy samples a third functionality fraction was eluted, which obviously corresponds to the α,ω-diaryloxy species. The concentration of this third functionality fraction, however, is very low and can be detected in the reaction mixture only with a 30 fold sensitivity of the UV detector.

As was mentioned before, on a RP-18 stationary phase the retention times of the functional PEO's increase dramatically by approaching the critical solvent composition. On the other hand, the differences in retention times at higher acetonitrile concentrations in the solvent suggest, that even in the size-exclusion region a separation into functionality fractions should be possible (see Figure 3). Assuming a mixed SEC-adsorption separation mechanism, at acetonitrile concentrations of 50-70% per volume at least the separation of the PEG fraction from the functional PEO is expected to occur. In order to increase resolution, a RP-18 column of 125 mm is used for this experiment.

The chromatograms of the samples at a solvent composition of acetonitrile-water 70:30% per volume are summarized in Figure 5. The inspection of the chromatograms reveals a separation into oligomer series for the C_{12}- and the C_{13},C_{15}-PEO's. Unexpectedly, for the C_{10}-, C_{13}- and aryloxy PEO's this type of separation is not obtained. However, regardless of the type of the functional group, in all cases a sufficient separation from the PEG and the diaryloxy fractions is obtained, thus allowing to determine all functionality fractions.

As can be seen from Figure 5, the proposed modified SEC separation technique is still very sensitive towards the chemical structure of the terminal groups. Even an increase of the substituent chain length by one methylene unit in the aryloxy PEO's (from octyl to nonyl) results in a significant increase in retention time. With a difference of two methylene units in the terminal group a complete separation of the functional fractions is obtained, see C_{13}- and C_{15}-fractions of C_{13},C_{15}-PEO in Figure 5.

From PEO chemistry it is known, that fatty alcohols of different structure are used as starting materials. They may not only differ in the length of the alkyl chain but also in the isomeric form (n-alcohol vs. iso-alcohol). From the technical point of view it is often more feasible to use mixtures of different isomers instead of pure

Downloaded At: 07:53 25 January 2011

Downloaded At: 07:53 25 January 2011

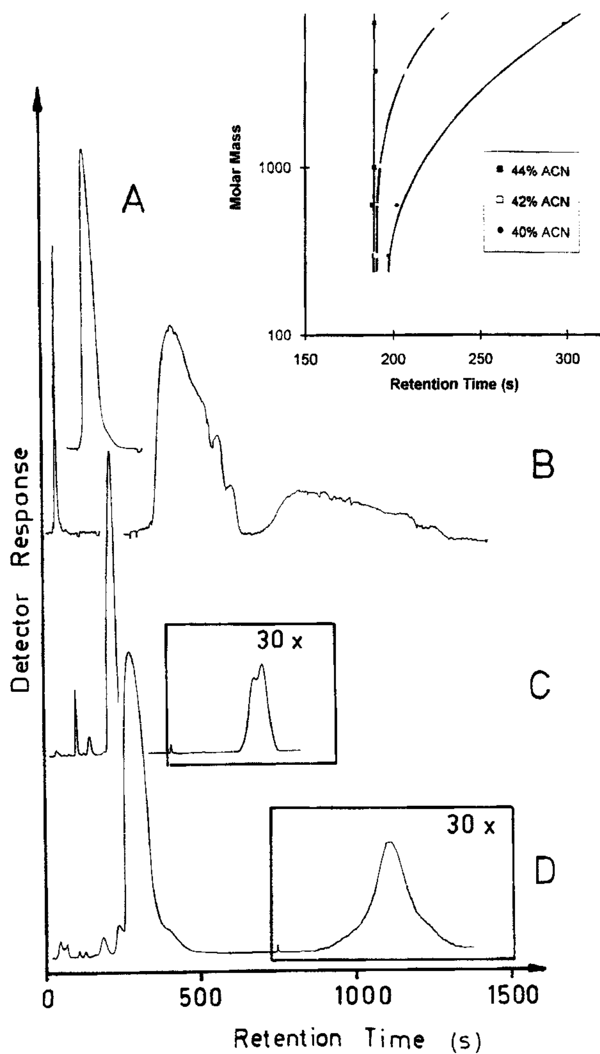


FIGURE 4 Critical diagram molar mass vs. retention time of polyethylene glycol (insert upper right corner) and chromatograms of functional PEO's at the critical point of adsorption of PEO, stationary phase: Nucleosil RP-8, 60x4mm I.D., solvent: acetonitrile-water 44:56% by volume, samples: C_{10}-PEO (A), C_{13},C_{15}-PEO (B), Octylphenol-PEO (C), Nonylphenol-PEO (D)

Downloaded At: 07:53 25 January 2011

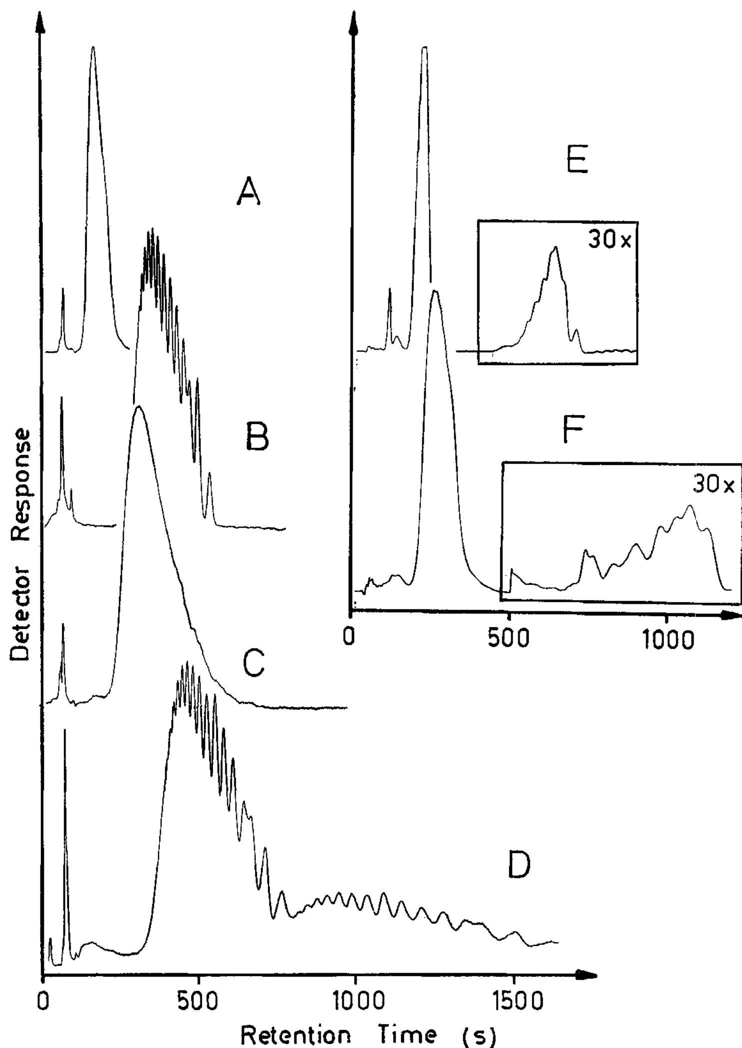


FIGURE 5 Chromatograms of the functional PEO's in a modified SEC mode, stationary phase: Nucleosil RP-18, 125x4mm I.D., solvent: acetonitrile-water 70:30% by volume, samples: C_{10}-PEO (A), C_{12}-PEO (B), C_{13}-PEO (C), C_{13},C_{15}-PEO (D), Octylphenol-PEO (E), Nonylphenol-PEO (F)

alcohols. The chromatographic behaviour of PEO's having isomeric structures as the terminal group is supposed to be different from that of uniform structures. Thus, an oligomer separation may be expected for uniform but not for isomeric terminal groups. With respect to retention, a higher retention time is expected for n-alkyl groups compared to branched iso-alkyl groups due to corresponding differences in hydrophobicity.

Considering these differences in retention behaviour with respect to the terminal group, the different chromatographic behaviour of the samples may be explained. For the C_{12}- and C_{13},C_{15}-PEO's, where oligomer separation takes place, a uniform n-alkyl terminal group may be assumed. The C_{10}- and C_{13}-PEO's are assumed to have iso-alkyl terminal groups. This explanation is in agreement with the lower retention time of the C_{13}-PEO compared to the C_{13}-fraction of the C_{13},C_{15}-PEO.

After separating the PEG fraction from the other functional species, and obtaining an oligomer separation for the main functional fraction, it should be possible to determine the molar mass distribution of the main functional fractions in the C_{12}- and C_{13},C_{15}-PEO's. Knowing the degree of polymerization or the molar mass at each oligomer peak in the chromatogram, a calibration curve log M vs. retention time may be obtained, thus allowing to calculate the M_n and M_w values. The molar mass at each oligomer peak may be determined by preparatively separating the samples into oligomer fractions and determining the molar masses of the individual fractions by an independent method. As this is rather time-consuming, a different approach was developed.

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 [7], has been successfully used to determine the mass of large biomolecules and synthetic polymers [8]. In principle, the sample to be investigated and a matrix solution are mixed in such a ration 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

Downloaded At: 07:53 25 January 2011

polymers a molar mass distribution may be obtained. 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 [9]. One major advantage of the method is, that minimum quantities of the magnitude of a few ng are sufficient for a proper analysis.

In order to assign the oligomer peaks in the chromatograms of C_{12}- and C_{13},C_{15}-PEO's, further chromatographic separations using the analytical RP-18 column are carried out and the oligomer fractions are collected, resulting in amounts of 5-20 ng substance per fraction in an acetonitrile-water solution. The solutions are directly mixed with the matrix solution and subjected to the MALDI-MS experiments. For C_{12}-PEO 14 fractions are collected, fraction 1 being the PEG and fractions 2-14 containing the C_{12}-terminated ethylene oxide oligomers.

The resulting spectra of some of the fractions are shown in Figure 6. The MALDI-MS spectrum of fraction 1 consists of peaks of major intensity, having a peak-to-peak mass increment of 44 Da, i.e. of one ethylene oxide unit. These peaks represent the $M+Na^+$ molecular ions of the PEG oligomers, whereas the peaks of minor intensity are due to the formation of $M+K^+$ molecular ions. The intensity of the peaks characterizes the relative abundance of the oligomers in the sample and from these the oligomer or molar mass distribution of the fraction may be calculated.

Downloaded At: 07:53 25 January 2011

The MALDI-MS spectra of fractions 2-14 show one major peak each, representing the $M+Na^+$ molecular ion of the corresponding oligomer, and some minor peaks of neighbour oligomers due to incomplete separation. In all cases the main peak and its corresponding mass is used to assign a degree of oligomerization to the corresponding peak in the chromatogram. Similarly, the oligomer peaks in the C_{13},C_{15}-PEO sample are collected and subjected to MALDI-MS.

Once all peaks in the chromatograms are assigned to a degree of polymerization, the desired calibration curves log M vs. retention time may be obtained for the C_{12}-, C_{13}- and C_{15}-fractions, see Figure 7. using these calibration curves, the average molar masses and polydispersities are determined. They agree well with data obtained independently by SFC and MALDI-MS in a stand-alone mode, see Table 2. The detailed description of the SFC and MALDI-MS experiments will be dealt with in a separate publication [10].

As is shown in Figure 5, an oligomer separation is not obtained for the C_{10}- and C_{13}-PEO's as well as the aryloxy PEO's. Corresponding experiments using SFC

Downloaded At: 07:53 25 January 2011

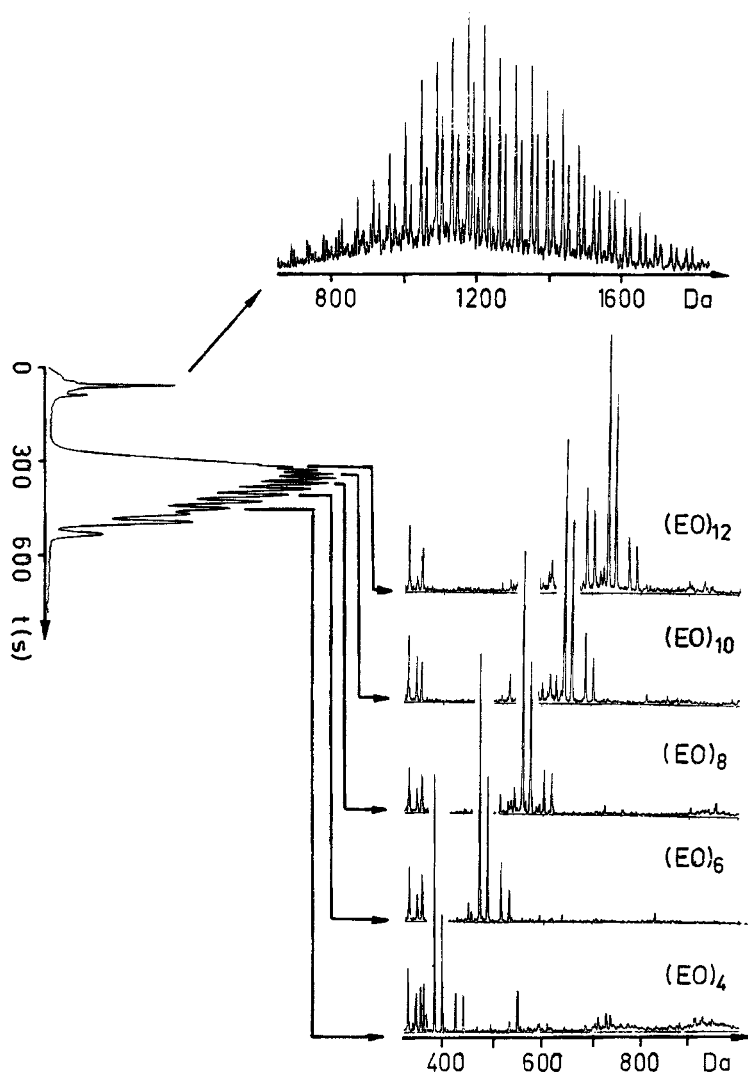


FIGURE 6 Identification of fractions of C_{12}-PEO by MALDI-MS, chromatogram taken from Fig. 5

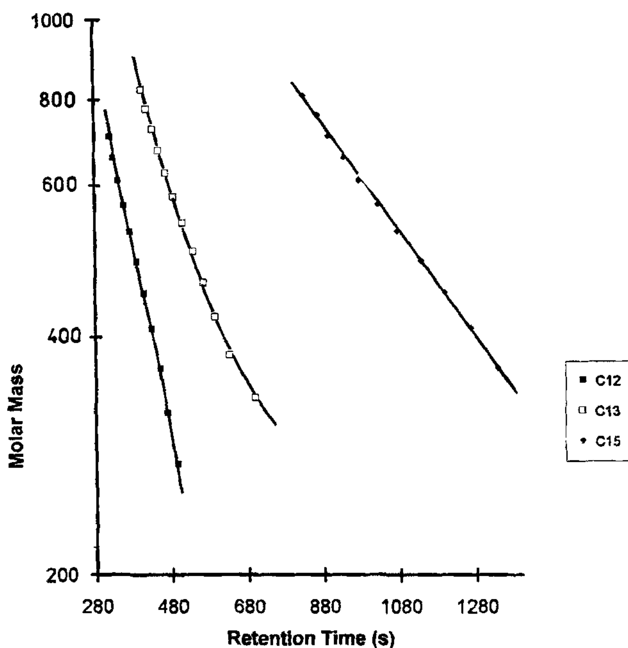


FIGURE 7 Calibration curves molar mass vs. retention time for the main functional fractions of C_{12}-PEO and C_{13},C_{15}-PEO, stationary phase and solvent: see Figure 5

Downloaded At: 07:53 25 January 2011

reveal, that instead of one peak for each degree of polymerization, a number of overlapping peaks is obtained. This is a clear indication for the presence of isomeric structures, as was assumed from the HPLC behaviour. However, for the Octylphenol-PEO this behaviour is not obtained and, therefore, isomeric structures are not likely to be present in the sample.

As MALDI-MS separates exclusively with respect to mass per charge, isomerism does not interfer. Therfore, regardless of the isomeric endgroups the C_{10}-, C_{13}- and Nonylphenol-PEO's are separated with respect to their oligomer distribution and the molar mass can be calculated from the peak intensities, see Table 2.

The Octylphenol-PEO is investigated on a different column in order to obtain an oligomer separation. This is achieved on a preparative column Nucleosil RP-18, 250x20 mm I.D., using a solvent composition of acetonitrile-water 70:30 per

TABLE 2

Molar Masses and Polydispersities of the Polyethylene Oxides Determined by Modified SEC, MALDI-MS and SFC

Sample	SEC			MALDI-MS[1]			SFC[1]		
	M_n	M_w	U	M_n	M_w	U^2	M_n	M_w	U^2
C_{10}-PEO	------------			580	620	0.07	-------------		
C_{12}-PEO	480	530	0.10	520	580	0.11	480	540	0.12
C_{13}-PEO	------------			690	740	0.07	-------------		
C_{13},C_{15}-PEO									
C_{13}-fraction	550	610	0.11	580	620	0.07	540	590	0.09
C_{15}-fraction	480	520	0.08	570	620	0.09	-------------		
Octylphenol-PEO	460	490	0.06	470	490	0.04	500	520	0.04
Nonylphenol-PEO	-------------			630	660	0.05	--------------		

[1] experimental details in [10]

[2] $U = M_w/M_n - 1$

Downloaded At: 07:53 25 January 2011

volume, see Figure 8. Again, the different fractions are subjected to MALDI-MS and the molar mass is determined via a corresponding oligomer calibration curve. As can be seen, the first fraction, which elutes before the main functional fraction, consists of a number of oligomers. From the peak-to-peak mass increment of 44 Da it is clear, that these oligomers represent PEO's. However, the peak masses do not agree with the masses, obtained for Octylphenol-PEO oligomers. Instead, a mass of 131 Da is calculated for the endgroup. This mass agrees well with 133 Da calculated for a butylphenol endgroup and accordingly it is assumed, that the

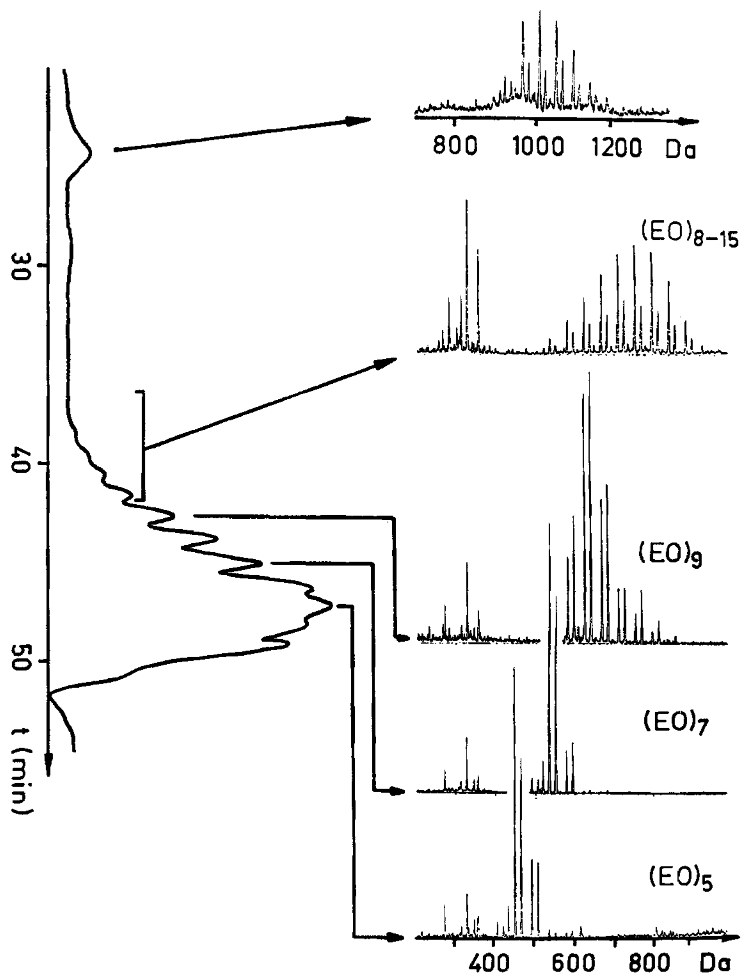


FIGURE 8 Chromatogram of Octylphenol-PEO and identification of fractions by MALDI-MS, stationary phase: Nucleosil RP-18, 250x20mm I.D., solvent: acetonitrile-water 70:30% by volume

Downloaded At: 07:53 25 January 2011

starting octylphenol contained minor amounts of butylphenol. It is interesting, that the average molar mass of this fraction with M_n~1020 is distinctively higher than that of the main fraction.

Figure 5 shows, that in addition to the PEG and the main functional fraction, at higher retention times fractions are obtained, which may be visualized only using a very high UV detector sensitivity. These fractions, which are assumed to consist of α,ω-diaryloxy species, are separated as well. Unfortunately the amount of these fractions is too low for a proper characterization. Therefore, further efforts are necessary to accumulate enough material for analysis.

To summarize, liquid chromatography at the critical point of adsorption and modified SEC near the critical region have been shown to provide useful information on the functionality of alkyloxy and aryloxy polyethylene oxide. Using MALDI-MS as an additional detector, the molar mass distribution of the functional fractions may be determined. The average molar masses agree well with data, obtained independently by supercritical fluid chromatography and MALDI-MS alone.

Downloaded At: 07:53 25 January 2011

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 polyethylene oxide samples.

REFERENCES

1. A.V. Gorshkov, H. Much, H. Becker, H. Pasch, V.V. Evreinov, S.G. Entelis, J. Chromatogr., 523: 91 (1990)

2. S.G. Entelis, V.V. Evreinov, A.V. Gorshkov, Adv. Polym. Sci., 76: 129 (1986)

3. B.G. Belenkii, E.S. Gankina, M.B. Tennikov, L.Z. Vilenchik, J. Chromatogr., 147: 99 (1978)

4. H. Pasch, H. Much, G. Schulz, A.V. Gorshkov, LC-GC International, 5: 38 (1992)

5. H. Pasch, H. Krüger, H. Much, U. Just, Polymer, 33: 3889 (1992)

6. H. Pasch, C. Brinkmann, H. Much, U. Just, J. Chromatogr., 623: 315 (1992)

7. M. Karas, F. Hillenkamp, Anal. Chem., 60: 2299 (1988)

8. R.C. Beavis, Rapid Commun. Mass Spectrom., 3: 233 (1989)

9. H. Pasch, R. Unvericht, Angew. Makromol. Chem., 212: 191 (1993)

10. H. Pasch, publication in preparation

Received: December 1, 1993
Accepted: December 27, 1993

Downloaded At: 07:53 25 January 2011