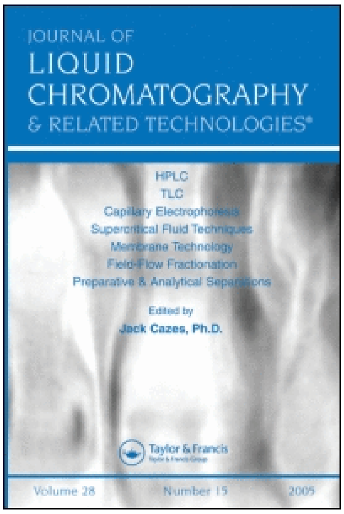

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ANALYSIS OF POLYETHERS BY ISOCRATIC HPLC WITH UNIVERSAL DETECTORS. I. OPTIMIZATION OF CHROMATOGRAPHIC CONDITIONS

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Summary:

Polyethylene glycols, their mono- and dimethyl ethers, and polypropylene glycols were analyzed by LAC with coupled density and RI detection on a C-18 column in methanol-water. Depending on the composition of the mobile phase, PEGs up to molecular weights of 3000 and PPGs up to molecular weights of 1000 could be separated. Peaks were identified using monodisperse oligomers as internal standards. Critical conditions for PEG were found at a mobile phase composition of MeOH:H_2O 80:20, which allowed a good separation of PPG.

Introduction:

In the analysis of polyethers one has to take into account, that samples typically consist of chains with a different number of repeating units, with different end groups (sometimes also cycles), and - in the case of copolymers - with different chemical composition.

It is obvious, that these three distributions cannot be obtained from a single chromatographic technique; only a combination of different analytical tools can provide the desired informations.

Basically, there are two different effects which can be utilized to separate a polymer: Exclusion and adsorption.

Size exclusion chromatography (SEC) separates according to molecular dimensions. End groups and composition play a minor role, their influence on the calibration lines must, however, be taken into account in order to obtain accurate results[1-5]. As SEC is always performed under isocratic conditions, a combination of density and refractive index (RI) detection can be used, which provides additional informations on the chemical composition[6-8]. Complete resolution of higher oligomers can, however, only be achieved with very long columns [1].

Adsorption chromatography separates as well according to chemical composition and chain length, albeit in a different extent.

(In liquid chromatography under "critical conditions" [9-12], which can be regarded as a limiting case, the effects of exclusion and adsorption of the repeating units compensate one another, hence separation occurs only according to the end groups, regardless how long the chains are. This technique provides an excellent tool for the determination of functionality distribution[11,12].)

Different types of adsorption chromatography can be applied to the analysis of polymers and oligomers: While GC is only suitable for the lowest oligomers[13,14], which are sufficiently volatile, Supercritical Fluid Chromatography (SFC)[15,16], Thin Layer Chromatography (TLC)[2,14] and Liquid Adsorption Chromatography (LAC) [16-19] can also be applied to polymers.

Despite its excellent separation efficiency[15,16] SFC is not yet in widespread use, because the equipment is very expensive.

HPLC instruments are comparatively cheap, but as usually gradients are used (as well in normal as in reversed phase), detection can be problematic in the analysis of aliphatic polyethers. Some authors have applied low wavelength UV-detection[16] (with all its problems), or the evaporative mass detector[17], the linearity of which is, however, rather poor.

Because of the importance of polyethyleneoxides, their derivatives, and their (block) copolymers for many applications [19,20] there was a strong need for a simple and reliable chromatographic method, preferrably under isocratic conditions, which would allow the use of universal detectors (such as RI and density). In this case, combination of density and RI detection could provide additional informations.

As has been shown by Eisenbeiß and Ehlerding[18], PEGs can be separated very well on a RP 8 column in methanol-water under isocratic conditions, which allowed the use of a refractive index detector. With an appropriate mobile phase composition even PEG 1000 could be separated into the oligomers almost to the baseline. This excellent resolution would allow to determine the MWD of a sample with much better accuracy than from SEC, if all peaks could be assigned a molecular weight.For low molecular weight samples this is rather easy, as long there are pure oligomers available, which can be used as internal standards. In the case of PEGs the oligomers up to the heptamer are commercially available, and from samples with overlapping MWDs one can identify higher oligomers.

For PEGs with higher molecular weights, however, a mobile phase composition is required, which doesn't allow a separation of the low oligomers, hence one will have to use a well defined standard with an appropriate degree of polymerization. Such samples can be prepared by a Williamson ether synthesis[21-22].

In this paper we describe a method, which allows a separation of polyethyleneglycols (up to molecular weights of 3000), the corresponding mono- and dimethylethers, and polypropyleneglycols under isocratic conditions.

Experimental :

For these investigations, a density detection system DDS 70 (commercially available from A.PAAR KG, Graz, Austria) was used, which has been developed in our group. It was combined with a Bischoff 8110 RI detector, and connected to a MS-DOS computer for data acquisition and processing. The entire system has already been described in full detail in previous communications [23-25]. Data acquisition and processing was performed using the software package CHROMA, which has been developed for the DDS 70.

LAC measurements were performed on a Spherisorb ODS 2 column (5 μ, 250 * 4.6 mm) in isocratic mode using methanol-water (30:70 - 90:10 V/V) as mobile phase at a flow rate of 0.5 ml/min, which was maintained by a JASCO 880 PU HPLC pump, the solvents used were

HPLC grade (Merck LiChroSolv). Samples were injected using a Rheodyne injection valve equipped with a 50 µl loop, the concentration range was 2 - 8 g/l.

Polyoxyethylene and polyoxypropylene samples (diols, mono- and diethers), and the lower oligomers (DP 2 to 6) were purchased from FLUKA and used without further purification. The higher ethylene oxide oligomers were prepared by a Williamson ether synthesis[21,22] and purified by preparative SEC.

Results and discussion:

In the first step of these investigations, we varied the composition of the mobile phase in order to find appropriate conditions for each molecular weight range of PEG and and its mono- and dimethylethers.

The following figures show some typical chromatograms of polyethylene glycols. In the lower molecular weight range peaks could be identified by adding a monodisperse oligomer to the low molecular sample and by comparing chromatograms of samples with overlapping MWD.

Fig.1 shows a chromatogram of PEG 400 obtained in methanol-water 30:70 as mobile phase.

In Fig.2 and Fig.3 chromatograms of PEG-550-monomethylether and PEG-500-dimethylether, obtained in the same mobile phase, are shown. In the analysis of higher molecular weight samples, the composition of the mobile phase did not allow a separation of low oligomers, hence the peaks were identified by spiking with (almost) monodisperse higher oligomers (n = 18, 30, and 54), which were prepared by a Williamson ether synthesis[21-22].

In Fig.4 a chromatogram of PEG 1000 is shown, which was obtained in methanol-water 40:60. The peaks were identified by comparison with the 18-mer, a chromatogram of which is shown in Fig.5.

In Fig.6 a chromatogram of PEG 3000 is shown, which was obtained in methanol-water 55:45 with the 30- and 54-mer of ethyleneoxide as internal standards.

From these data we could assign each oligoethyleneglycol up to n = 75 an elution volume.

In Fig.7 the elution volumes of PEG-oligomers are plotted as a function of the degree of polymerization for different mobile phase compositions.

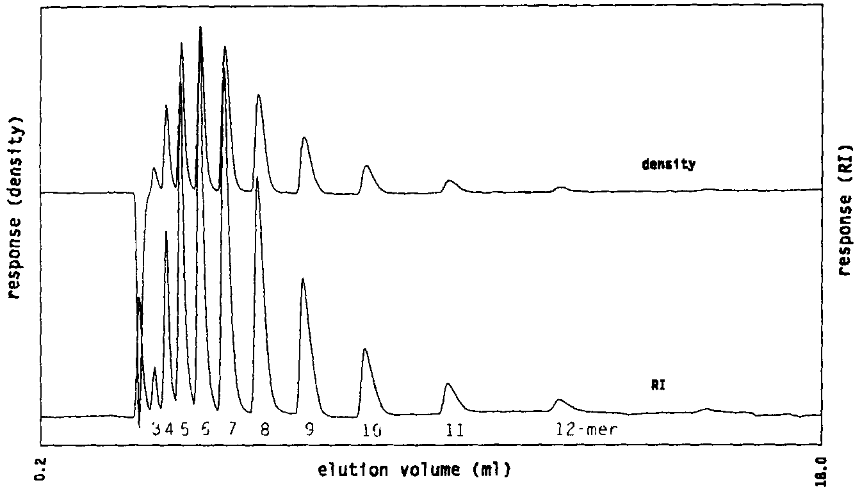

Fig.1: Density and RI trace of a chromatogram of PEG 400 obtained in methanol-water 30:70 as mobile phase

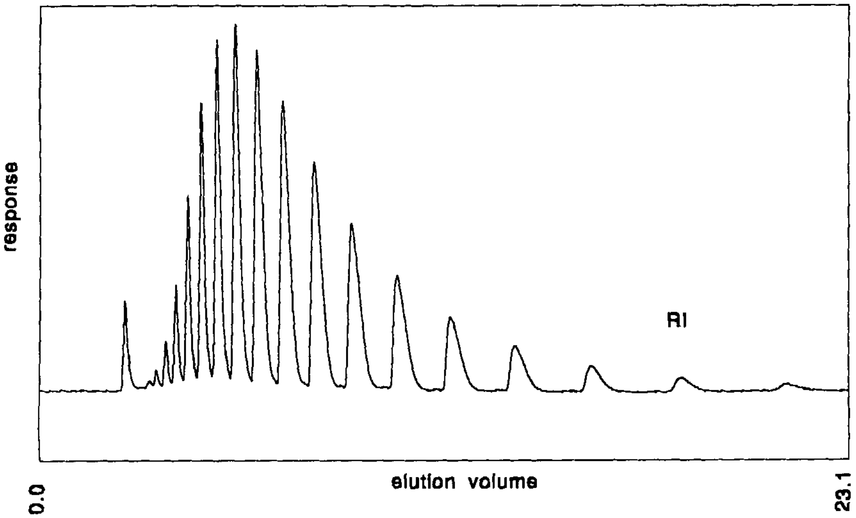

Fig.2: RI trace of a chromatogram of PEG-550-monomethylether obtained in methanol-water 30:70 as mobile phase

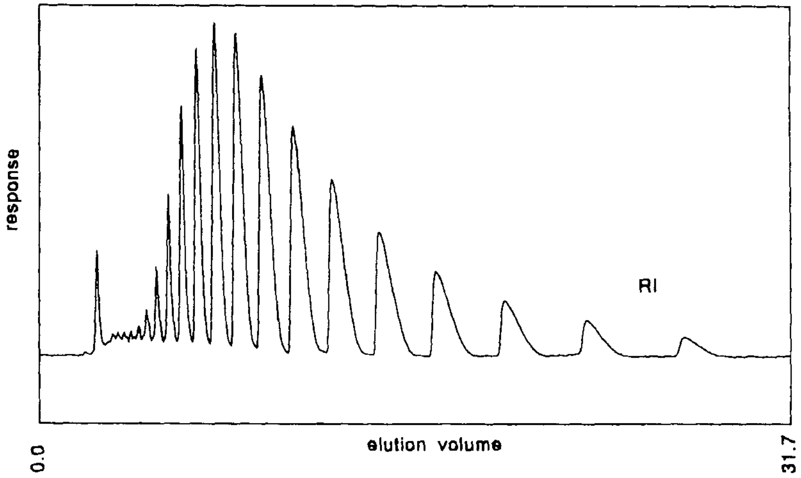

Fig.3: RI trace of a chromatogram of PEG-500-dimethylether obtained in methanol-water 30:70 as mobile phase

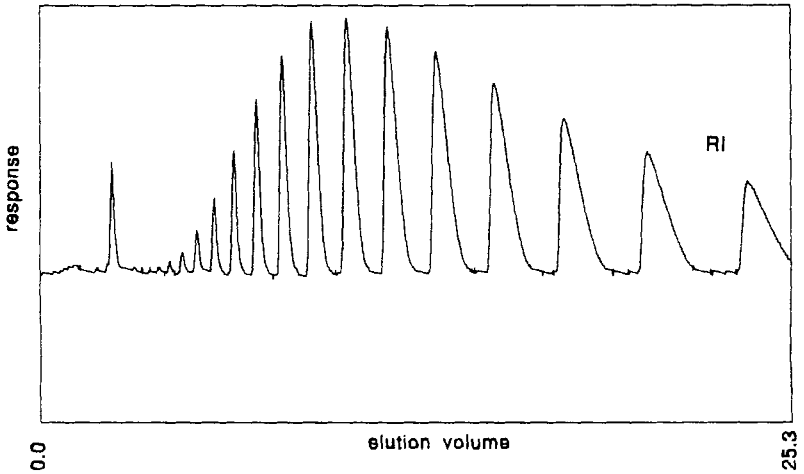

Fig.4: RI trace of a chromatogram of PEG 1000 obtained in methanol-water 40:60 as mobile phase

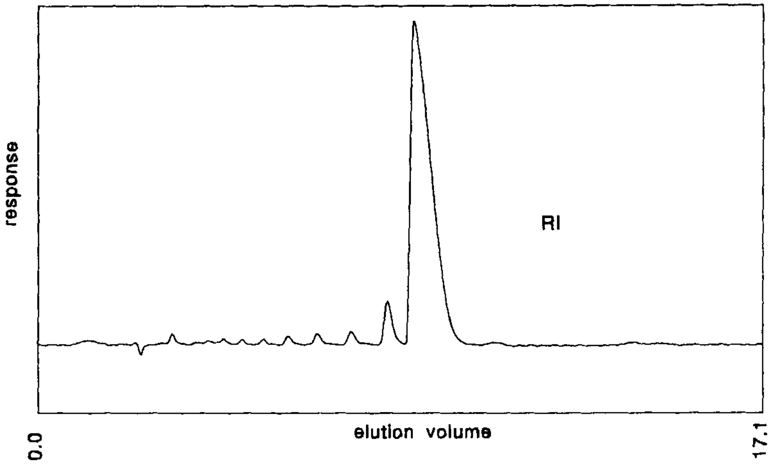

Fig.5: RI trace of a chromatogram of the 18-mer of PEG obtained in methanol-water 30:70 as mobile phase

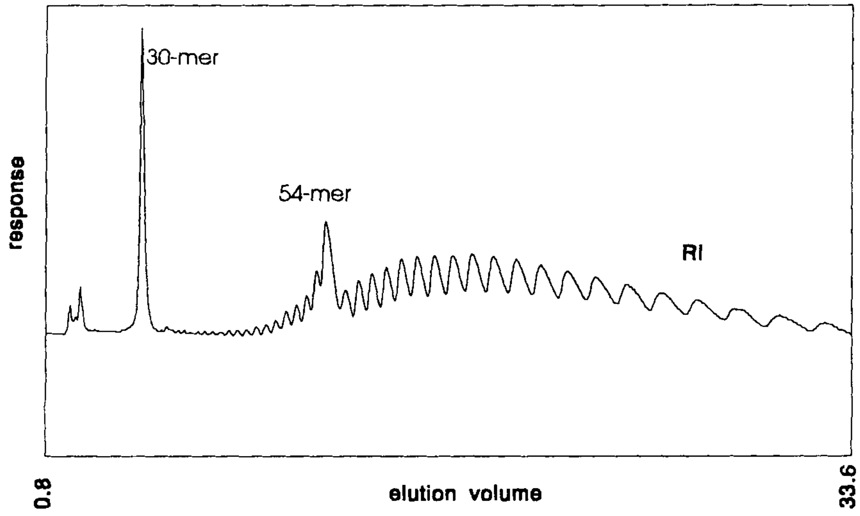

Fig.6: RI trace of a chromatogram of PEG 3000, spiked with the 30-mer and the 54-mer, obtained in methanol-water 55:45 as mobile phase

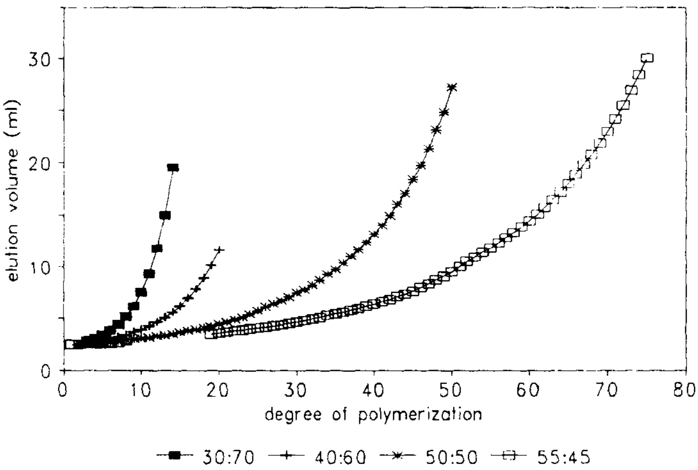

Fig.7: Elution volumes of polyethylene glycols in different mobile phase compositions as a function of degree of polymerization

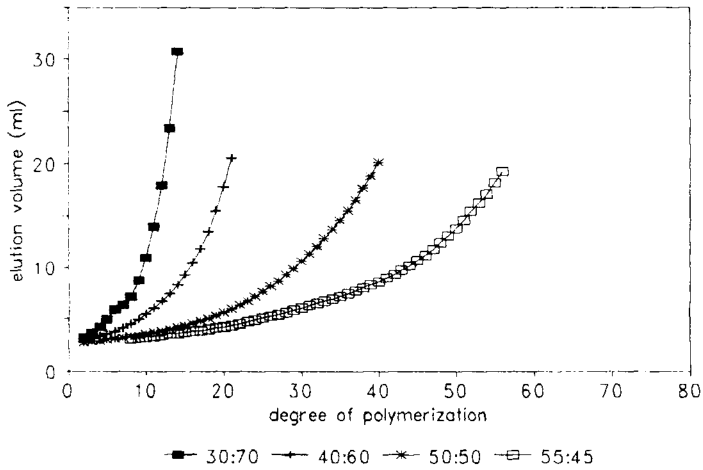

Fig.8: Elution volumes of polyethylene glycol monomethylethers in different mobile phase compositions as a function of degree of polymerization

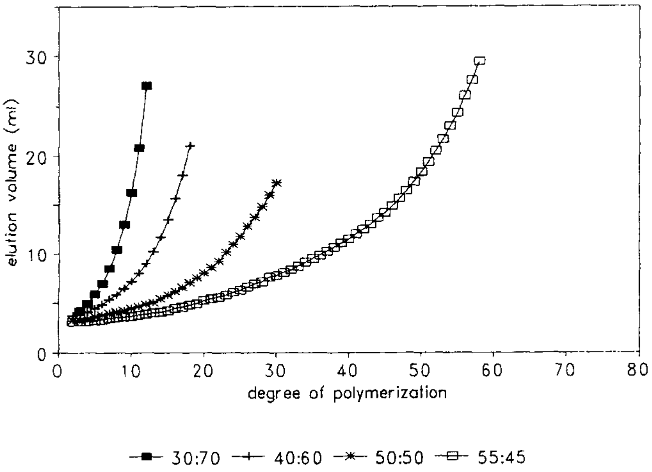

Fig.9: Elution volumes of polyethylene glycol dimethylethers in different mobile phase compositions as a function of degree of polymerization

In Fig.8 the elution volumes of the monomethylethers are plotted as a function of the degree of polymerization for different mobile phase compositions, Fig. 9 shows the same representation for the dimethylethers.

With increasing methanol content of the mobile phase, a separation is achieved at higher molecular weights, and the lower molecular weights appear at the same elution volume.

At a composition of 80:20 critical conditions for PEG are reached, as can be seen from Fig. 10, and at 90:10 the elution order changes to the exclusion mode. Under critical conditions for PEG, the elution volumes of diols, mono- and dimethylethers are quite similar.

It is remarkable, that in a plot of log(k') vs. the degree of polymerization the linear range reaches up to very high values of n, as can be seen from Fig. 11.

In the next step we tried to separate PPG oligomers and polymers using mobile phase compositions close to those of the critical conditions for PEG.

Fig. 12 - 13 show typical chromatograms of PPG samples, and in Fig. 14 the elution volumes of PPG-oligomers are plotted as a function of the degree of polymerization for different mobile phase compositions.

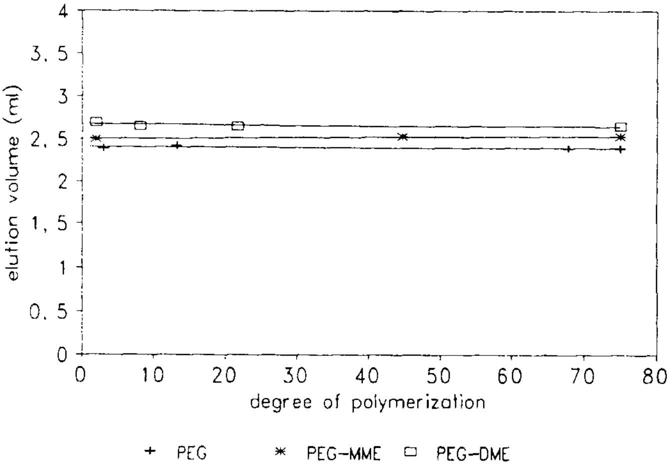

Fig.10: Elution volumes of polyethylene glycol derivatives in methanol-water 80:20 (critical conditions for PEG) as a function of degree of polymerization

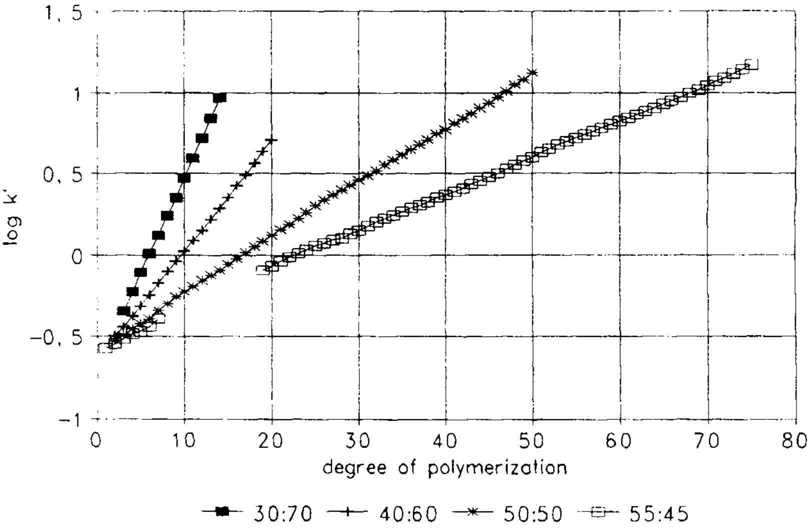

Fig.11: log(k') of polyethylene glycols in LAC on ODS 2 in MeOH-H_2O of different composition.

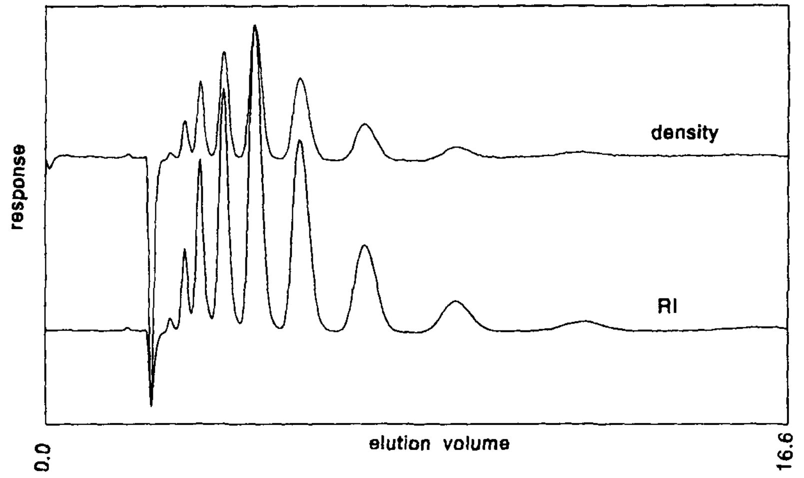

Fig.12: Density and RI trace of a chromatogram of PPG 425 obtained in methanol-water 70:30 as mobile phase

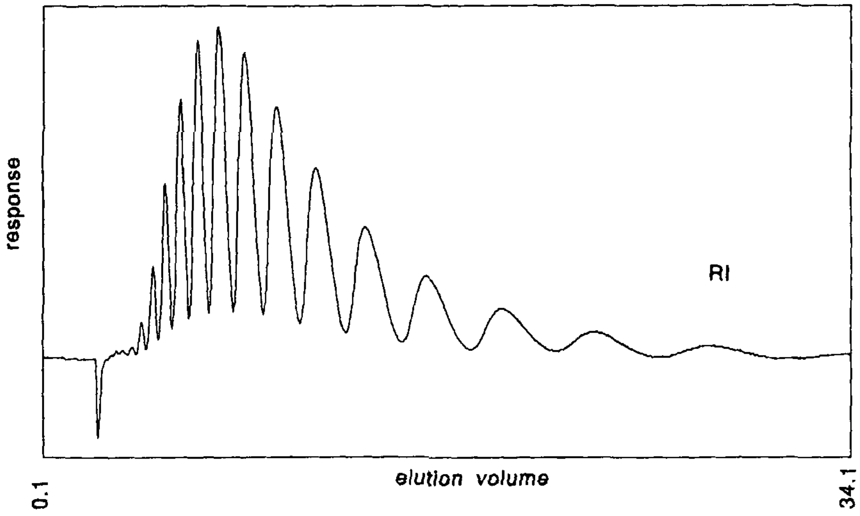

Fig.13: RI trace of a chromatogram of PPG 1000 obtained in methanol-water 80:20 as mobile phase

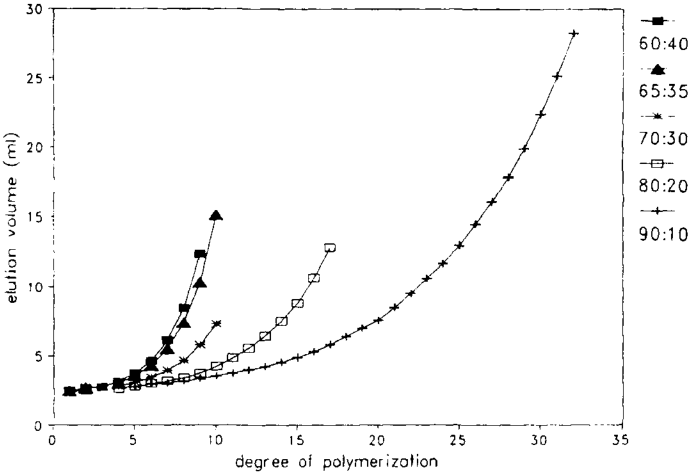

Fig.14: Elution volumes of polypropylene glycols in different mobile phase compositions as a function of degree of polymerization

As can be seen, the separation of PPG oligomers with molecular weights of several hundreds works very well in a mobile phase composition, which corresponds to the critical conditions for PEG. As will be shown in another paper[26], block copolymers of ethylene oxide with propylene oxide can be separated under these conditions according to the number of oxypropylene units.

Conclusions:

LAC with coupled density and RI detection proves to be a more powerful tool than SEC in the analysis of polyethers up to molecular weights of several thousands. Under the conditions presented in this paper, PEG and PPG can be separated with very high resolution. As will be shown in part 2 of this series[27], molecular weight averages can be calculated from LAC with better accuracy than from SEC, provided that the molecular weight dependence of response factors is known. Further investigations shall show the potential of the new method in determining the chemical composition of block copolymers under critical conditions for PEG.

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