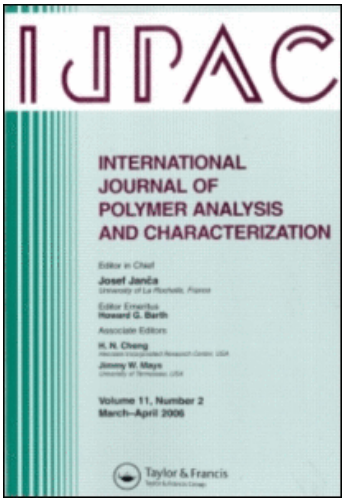

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Analysis of Polyethers by Isocratic HPLC with Universal Detectors IV. Comparison of Size Exclusion Chromatography and Liquid Adsorption Chromatography for the Analysis of Poly(propylene glycols)

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Liquid adsorption chromotography (LAC) on an analytical scale, as well as on a semi-preparative scale is used for the analysis of poly(propylene glycols), (PPG), and its performance for the determination of molecular mass distributions was compared with that of size-exclusion chromatography (SEC). Semi-preparative LAC provides monodisperse standards of PPG up to a molecular mass of 1400, which are used to establish an accurate SEC calibration. The influence of preferential solvation in LAC is studied and a correction method using two universal detectors (density and refractive index) is presented.

KEY WORDS Size exclusion chromotography, HPLC of polymers, density detector, liquid adsorption chromatography, poly(propylene glycol)

INTRODUCTION

In the analysis of polyethers, various chromatographic techniques are used, which yield different information. Depending on the molecular mass of the samples, capillary gas chromatography (CGC), [1–4] supercritical fluid chromatography (SFC), [4–7] liquid adsorption chromatography (LAC), [5, 6, 8–15] or size [exclusion chromatography (SEC), [16–23] can be applied. SEC separates according to molecular dimensions (not to molecular mass, as often assumed); the other methods also separates according to chemical composition. A special modification of liquid chromatography is called "LC at the critical point of adsorption" or "liquid chromatography under critical conditions (LCCC)" [24–27]. In this case, all members of a homologous series elute at the same elution volume, regardless how long the chains are, which means, that the main chain (or, in the case of block copolymers, one block) becomes "invisible," and the separation occurs exclusively according to the end groups (or the other block). This allows a separation into pure homologous series, which can be analyzed by SEC to yield a three-dimensional map of a polymer [26, 27]. Even if the sample to be analyzed consists of one homologous series, there are still several problems in the analysis of low-molecular-weight samples.

In the case of SEC, the following sources of error have to be taken into account [28–30]:

1. Calibration curves are different for different polymers, and often also for different end groups [19]. The concept of universal calibration is, however, not a solution to this problem for low-molecular-weight samples, [31] because the sensitivity of a viscosity detector for oligomers is very low.
2. Flow rate changes can cause severe errors, which can be reduced, but not eliminated by the use of an internal standard. If the flow rate changes within a chromatogram, this approach does not work.
3. Overloading effects may influence the elution volumes.
4. Peak spreading, unless corrected, will result in overestimated polydispersities [30].
5. The assumption of a continuous molecular mass distribution is problematic on the low molecular side of the MMD, where the oligomers are partially resolved [32, 33].
6. The quality of the baseline also limits the accuracy of the results.
7. The response factors of the commonly used refractive index (RI) detector typically depend on molecular mass (and, in the case of copolymers, on the composition) [10, 16, 23, 31]. The evaporative light scattering detector (ELSD), [6, 34] has a poor linear range, and its response factors for homologous series are not yet clear.
8. Preferential solvation, which can even occur in "pure" mobile phases (due to moisture, a stabilizer, or other impurities) may also depend on molecular mass [35].

In the case of LAC, errors 1 to 5 are not relevant, provided that the oligomers can be sufficiently separated and identified. There remain, however, still questions 6 to 8.

Recently we have shown [36, 37] that the MMD of poly(ethylene glycols) (PEG) can be determined by LAC (on an ODS2 column in methanol-water) with much better accuracy than by SEC. The peaks could be identified using (almost) monodisperse oligomers, which had been prepared by condensation reactions. The response factors of both the density and the refractive index (RI) detector showed a very small molecular mass dependence, for which could be easily compensated. Preferential solvation seemed to be negligible, too, as the solvent peak ("vacant" peak) was typically very small. A comparison with SEC data showed good agreement of the results. It was also shown that poly(propylene glycols) (PPG) can also be separated on the same column, but with a different composition of the mobile phase [36]. For PPG, the synthesis of pure standards is not so easy, hence we have chosen a different approach for these investigations.

In this paper, we describe a method to determine the MMD of PPGs by LAC. Monodisperse oligomers of PPG up to molecular masses of 1400 (obtained on a semi-preparative column) were used as markers for LAC and to establish a SEC calibration, which considerably improved the accuracy of SEC. The influence of preferential solvation in LAC was studied, and the results were compared with those from SEC.

EXPERIMENTAL

These investigations were performed using a density detection system DDS70 (commercially available from CHROMTECH, Graz, Austria), which has been developed in our group. This instrument has been described in full detail in previous communications [38–40]. In SEC measurements, it was combined with a SICON LCD 201 RI detector, in LAC with a Bischoff 8110 RI detector. Each system was connected to a MS-DOS computer via a serial port. Data acquisition and processing were performed using the software package CHROMA, [40] which has been developed for the DDS 70. Integration data from LAC were written to ASCII-files, which were imported to a spreadsheet to calculate molecular mass distributions.

SEC measurements were performed in chloroform (HPLC grade, Rathburn) at a constant flow rate of 1.0 mL/min, which was maintained by a Gynkotek 300C HPLC pump. Samples were injected using a VICI injection value equipped with a 100-μL loop, the concentration range was 4–8 g/L. A column set of four Phenogel columns, (2 × 500 Å), 30 cm each, was used for all chromatographic separations. The SEC calibrations were obtained using pure oligomers of PO, which were obtained from semi-preparative LAC and identified from overlapping chromatograms of samples with different MMD.

In LAC, two JASCO 880 PU pumps were used, which were equipped with Rheodyne 7125 injection valves with a 50- and a 500-μL loop, respectively.

Reversed-phase LC was performed with methanol-water 80:20 (w/w) on different analytical columns and a semi-preparative column filled with Spherisorb from PhaseSep (ODS-2 3 μm, 4.6 × 100 mm, ODS-2 5 μm, 4.6 × 250 mm, and ODS-2 5 μm, 10 × 250 mm). The flow rate was 0.5 mL/min in the analytical measurements and 2 mL/min in semi-preparative LAC. An Advantec 2120 fraction collector was used in the semi-preparative separations. Methanol and water were HPLC grade (Merck, LiChroSolv).

Poly(propylene glycols) were purchased from FLUKA or Aldrich and used without further purification.

MOLECULAR MASS DEPENDENCE OF RESPONSE FACTORS

The response factors of universal detectors are closely related to specific properties, such as refractive index increment or apparent specific volume [41–47]. Hence they will depend on molecular weight (due to different contributions of repeating unit and end groups). As has already been shown, [10, 16, 23, 31], this dependence can be compensated using

$$f_i = f_{i,\infty} + \frac{K}{M_i} \tag{1}$$

where f_i is the response factor of the oligomer with the molecular weight M_i, $f_{i,\infty}$ is the response factor of a polyether chain with infinite (or, at least sufficiently high) molecular weight, and K is a constant representing the influence of the end

groups. In a plot of f_i vs. $1/M_i$, K is the slope of the regression line. In a previous paper, [23] we have described three different approaches to determine $f_{i,\infty}$ and K.

PREFERENTIAL SOLVATION IN LC

In a solution of a polymer in a mixed solvent, the composition of the latter within the polymer coils will be different from outside because of different interactions of the polymer chains with the components of the solvent. This effect is called preferential solvation [48–52]. In the chromatographic column, the zone of "dialyzed solvent" [48] is separated from the solute molecules, and a "ghost" or vacant peak [48,49] appears. (Vacant peaks can, however, have other causes [49]). If a nonspecific detector, such as the RI detector, is used, its response will not only represent the concentration of the eluted polymer, but it will also contain a contribution of the preferential solvation. Hence, the response factor of the polymer will be rather an "apparent" one (the "true" response factors will be found, when the polymer solution is directly injected to the detector) [35].

The total amount of preferentially adsorbed solvent can be determined from the area of the vacant peak. As we have shown, [35] the interaction of the repeating unit and the end groups with the components of the solvent can be considerably different, hence the preferential solvation may—like the response factors—depend on molecular mass. If a polymer or oligomer is preferentially solvated, the area X of a peak eluting from a chromatographic column results from the mass m_p of polymer and the mass m_s of preferentially adsorbed solvent (with the corresponding response factors f_p and f_s):

$$X = m_p f_p + m_s f_s \tag{2}$$

To determine the unknown variables m_p and m_s, a second equation is required, which can be provided by a second universal detector (density and RI)[53].

It must be mentioned that the response factors in Equation (2) are the true ones, which are obtained by injecting the samples on the bypass. On the column, the zone of "dialyzed solvent" [48] would be separated from the sample peak, thus yielding the apparent response factors [35, 53].

With the response factor f_i of the oligomer with molecular mass M_i, one may write

$$X = m_p f_i + m_s f_s = m_i \left(f_\infty + \frac{K}{M_i} \right) + m_s f_s \tag{3}$$

The mass of preferentially adsorbed solvent is the given by

$$m_s = \frac{X - m_p f_i}{f_s} \tag{4}$$

As the same mass of preferentially adsorbed solvent must appear in both detectors, one may write

$$\frac{X_D - m_p f_{i,D}}{f_{s,D}} = \frac{X_R - m_p f_{i,R}}{f_{s,R}} \tag{5}$$

wherein the indices D and R denote the peak areas and response factors in density and RI detection. A simple rearrangement of Equation (5) yields

$$m_p = \frac{X_D f_{s,R} - X_R f_{s,D}}{f_{i,D} f_{s,R} - f_{i,R} f_{s,D}} \tag{6}$$

from which the amount of polymer is easily obtained.
The amount of preferentially adsorbed solvent can be determined using

$$m_s = \frac{X_D f_{i,R} - X_R f_{i,D}}{f_{i,R} f_{s,D} - f_{i,D} f_{s,R}} \tag{7}$$

Of course, the sum of all m_s thus obtained should equal the mass of solvent missing in the vacant peak, and the sum of all m_p should equal the sample size.

RESULTS AND DISCUSSION

Poly(propylene glycols) can be separated on an ODS-2 column in methanol-water, as has been shown in a previous paper [36]. The appropriate composition of the mobile phase depends on the molecular mass of the sample: for low molecular samples 70:30 (w/w), for samples with a molecular mass between 600 and 1200 around 80:20, and for higher molecular masses 85:15 or 90:10 will give the best separation.

Since the critical point of adsorption for PEG was found to be about 80:20 on this column, [36] which allows a separation of EO-PO-block copolymers according to the length of the PO-block, we decided to focus on this composition for these investigations. (The analysis of block copolymers using two-dimensional LC with CC as the first and SEC as the second dimension will be described in another communication [54].)

Figure 1 shows a typical chromatogram of PPG 1000, which was obtained on a semi-preparative ODS-2 column (250 × 10 mm, 5μm) in methanol-water 80:20. The fractions thus obtained were analyzed by SEC. In Figure 2, a typical MMD of such an oligomer (from SEC) is shown. With dual detection, the peak was identified as pure PPG (as described in previous papers [21–23]). The molecular mass of this oligomer is 830, corresponding to the 13-mer.

The monodisperse oligomers obtained form semi-preparative LAC were used to establish a calibration for SEC, shown in Figure 3. With the new calibration, we

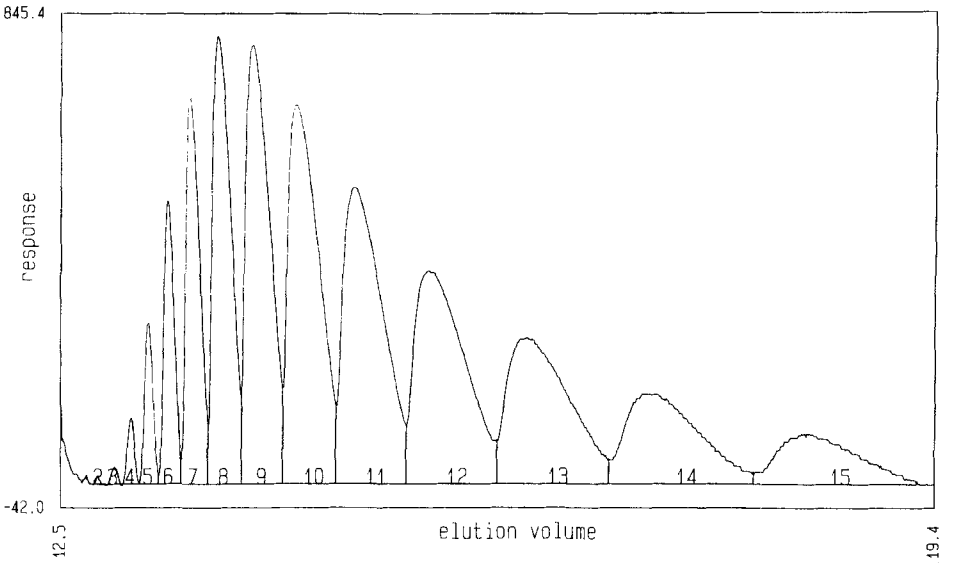

FIGURE 1 Semi-preparative LAC of PPG 1000 in methanol-water 80:20 (w/w) on an ODS-2 column (250 × 10 mm, 5 μm), as obtained with density detection (sample size: 21.02 mg).

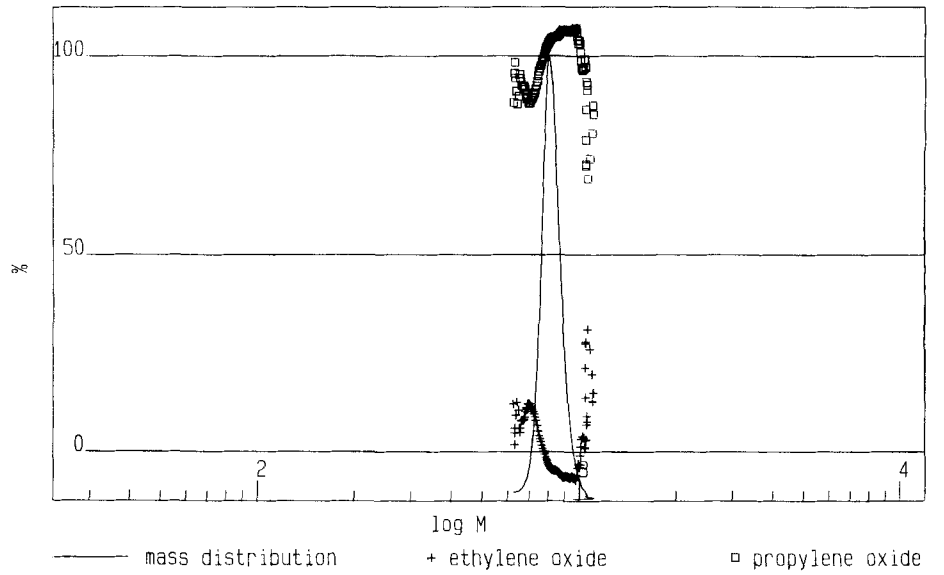

FIGURE 2 MMD of fraction 7 of PPG 725 (oligomer 13 with M = 830) from semi-preparative LAC in methanol-water 80:20 (w/w) on an ODS-2 column (250 × 10 mm, 5 μm), as obtained from SEC in $CHCl_3$, w_{PO} = 1.022, w_{EO} = −0.22 (from dual detection).

analyzed PPG 425, PPG 725, and PPG 1000 and calculated the molecular mass averages with and without compensation of molecular mass dependence or response factors, and with calculation of chemical composition [21–23]. For comparison, the oligomer peaks were separated by SEC of PPG 425 using a deconvolution procedure and the MMD was calculated from these peak areas using Equation (1). The results thus obtained are shown in Table I.

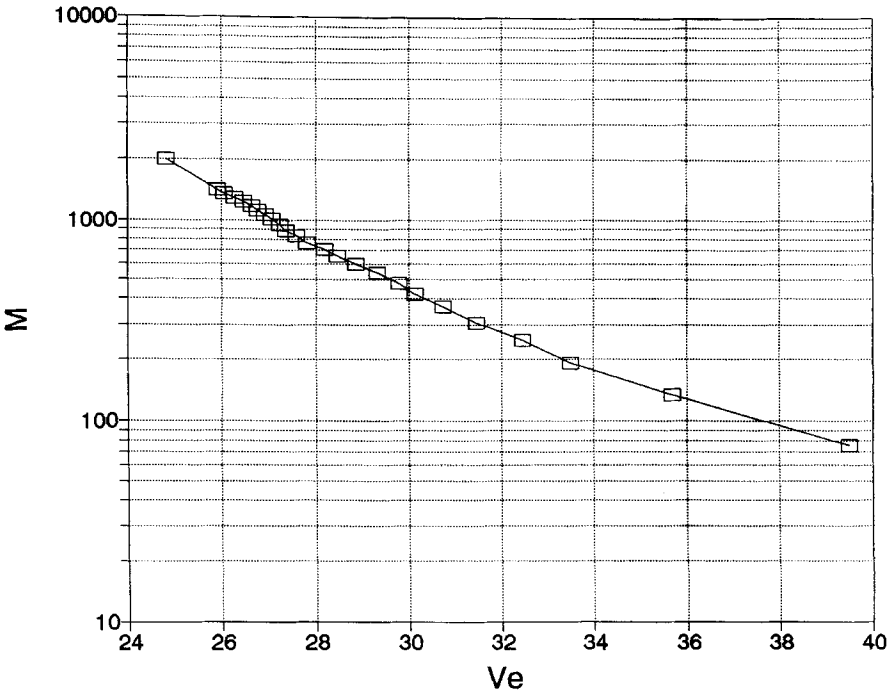

FIGURE 3 SEC-calibration, as obtained with monodisperse oligomers from semi-preparative LAC of PPG in methanol-water 80:20 (w/w) on an ODS-2 column (250 × 10 mm, 5 μm).

Before analyzing the same samples by LAC, we had to determine the true response factors of various PPGs for both detectors in this mobile phase by injecting the samples in which the column was by passed. The slope K and intercept $f_{i,\infty}$ in the plot of f_i vs. 1/M, is seen in Figure 4. The molecular mass dependence of response factors was found to be rather small. The deviations of column measurements at higher molecular masses originate from the integration error (because the sum of all peak areas is used here) than from preferential

TABLE I

Molecular mass averages of different PPG samples from SEC using four Phenogel 30-cm columns (2 × 100 + 2 × 500 Å) in chloroform, as obtained with coupled density and RI detection

Sample	M_w	M_n	M_w/M_n	w_{PO}	Method
PPG 425	443	416	1,064	—	density, no correction
	494	472	1,045	—	RI, no correction
	445	419	1,064	—	density, correction with K
	443	416	1,065	1,044	dual detection
	447	424	1,055	—	density, from separated peaks
PG 725	794	761	1,044	—	density, no correction
	800	774	1,042	—	RI, no correction
	795	761	1,044	—	density, correction with K
	788	755	1,044	—	RI, correction with K
	793	760	1,044	1,050	dual detection
PPG 1000	1042	996	1,046	—	density, no correction
	1034	990	1,045	1,009	dual detection

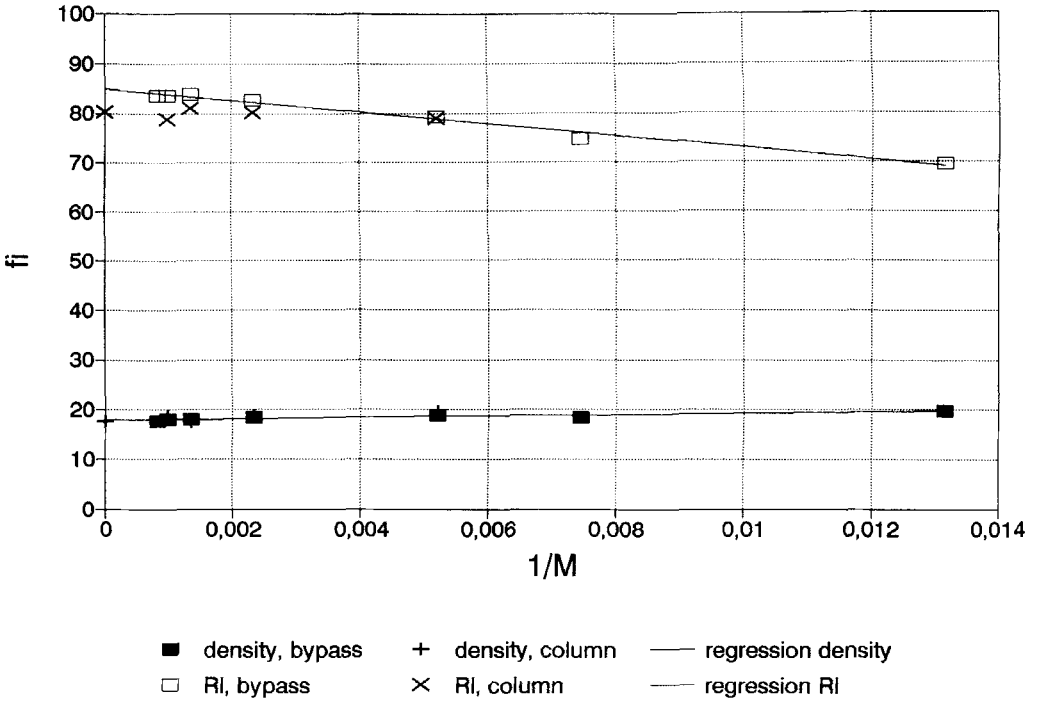

FIGURE 4 Response factors of PPGs in methanol-water 80:20 (w/w) using density and RI detection *vs.* $1/M$, as obtained from bypass and column measurements.

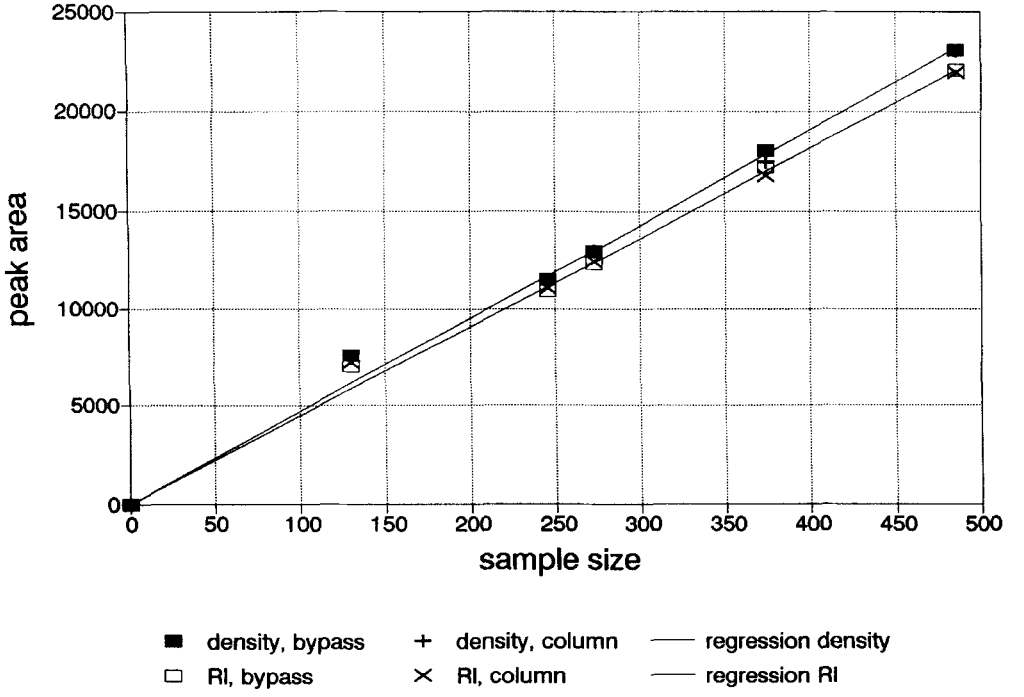

FIGURE 5 Peak areas of water in methanol-water 80:20 from bypass and column measurements.

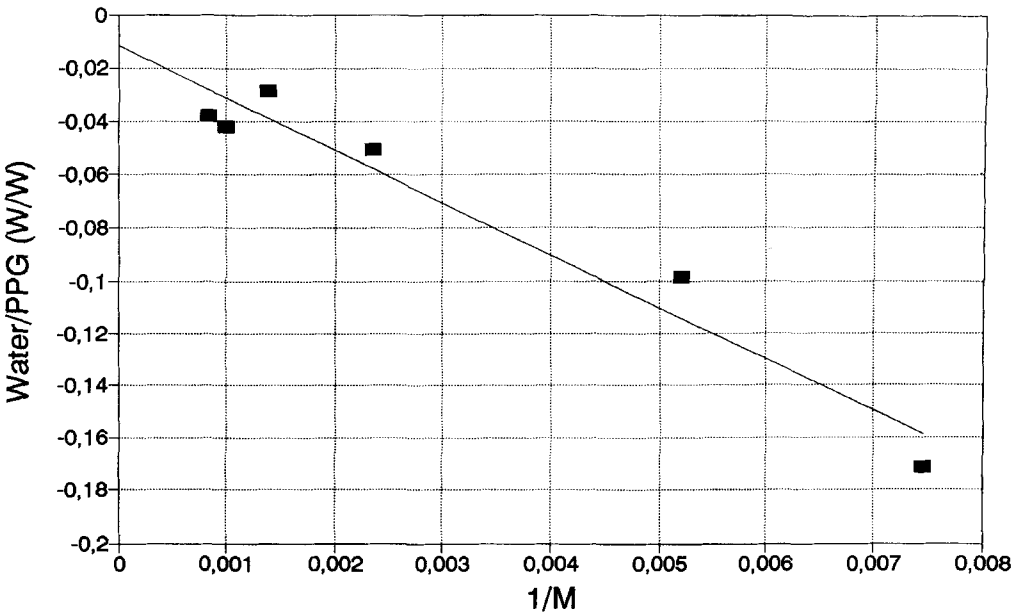

FIGURE 6 Relative water adsorption (w/w) (from solvent peak) of PPG in methanol-water 80:20 (w/w).

solvation. In the same way, we determined the response factors of water from a concentration series, as is shown in Figure 5. As expected, measurements with and without the column coincide in this case.

With the response factors thus obtained, we calculated the overall amount of preferentially adsorbed water from the solvent peak. In Figure 6, the relative water adsorption (μg water/μg sample) is plotted versus 1/M for PPG. As can be seen, preferential solvation shows a molecular mass dependence for PPG (due to different polarity of end groups and repeating units). This is not the case for PEG, as will be shown in reference 54. PPG samples were then analyzed by LAC in methanol-water 80:20 and the corresponding chromatograms are shown in Figures 7–9. Peaks were identified from overlapping chromatograms by spiking with monodisperse oligomers. Using a spreadsheet, we calculated the mass of each oligomer using Equations (1) and (6) (with and without compensation of preferential solvation. The sum of the calculated masses was compared with the sample size, and the results agreed quite well. The agreement was, of course, better for PEGs, because these—at the critical point of adsorption—elute in a narrow peak, which causes a smaller integration error [54].

Molecular mass averages for PPGs were calculated from the masses of the oligomers with and without compensation for preferential solvation (Equations (1) and (6)). The results thus obtained are given in Table II. Obviously, these results agree very well with SEC data, only the polydispersity in SEC was slightly higher (as expected). Only in the case of PPG 1000, the molecular masses as well as the calculation sample masses were too low, which indicate that the areas of the highest oligomers were under estimated because of the broad peaks. This can, however, be avoided by using a mobile phase with a higher methanol content. The molecular mass distribution of PPG 725, as obtained from LAC without and with

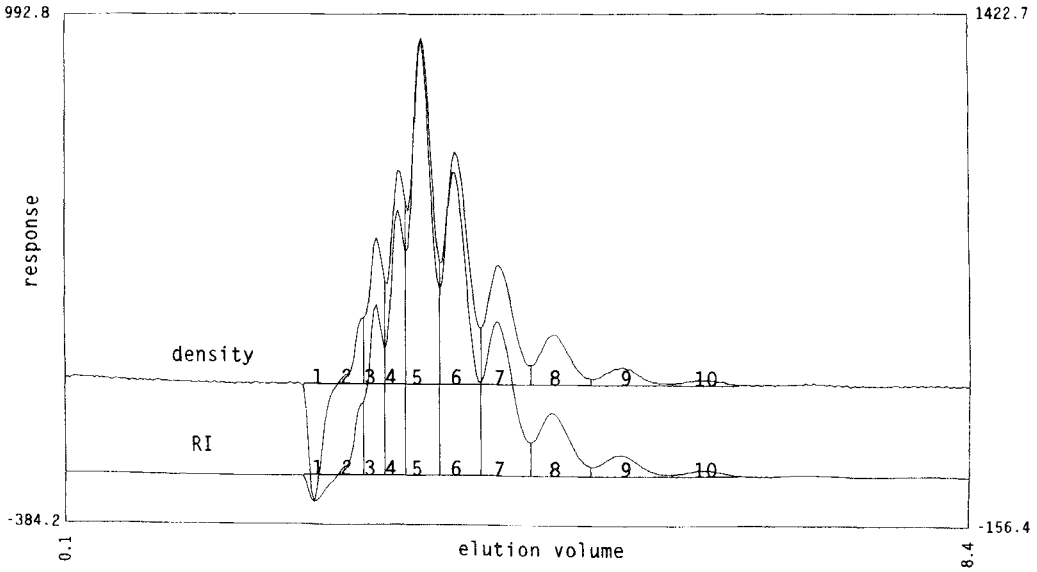

FIGURE 7 LAC of PPG 425 in methanol-water 80:20 (w/w) on an ODS-2 column (250 × 4.6 mm, 5 μm), as obtained with density and RI detection.

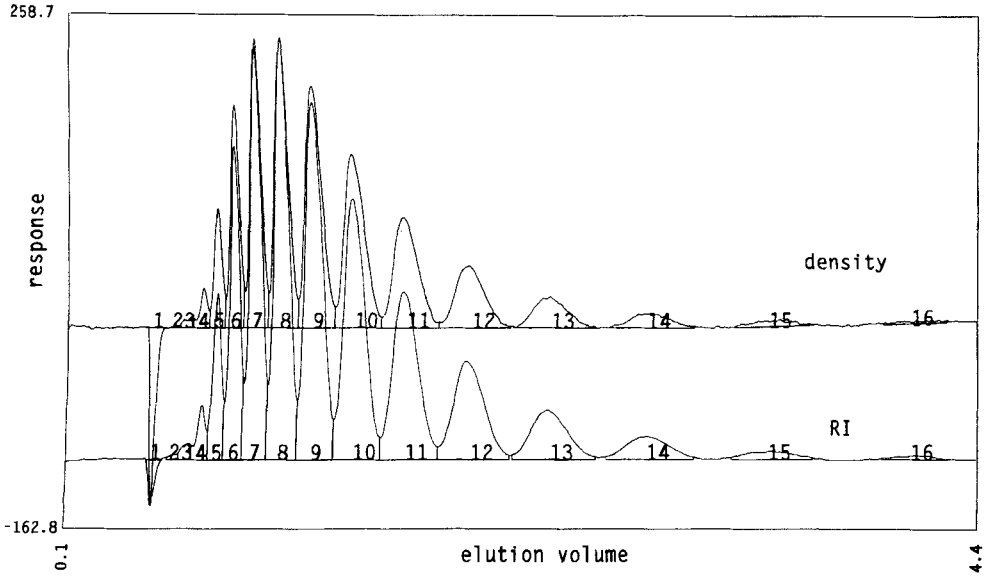

FIGURE 8 LAC of PPG 72.5 in methanol-water 80:20 (w/w) on an ODS-2 (250 × 4.6 mm, 5 μm), as obtained with density and RI detection.

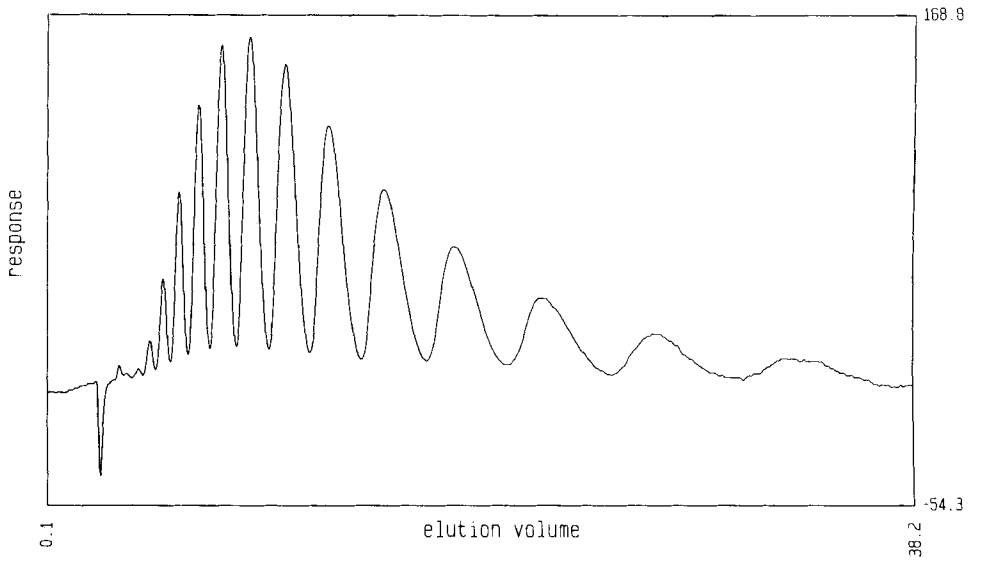

FIGURE 9 LAC of PPG 1000 in methanol-water 80:20 (w/w) on an ODS-2 (250 × 4.6 mm, 5 μm), as obtained with RI detection.

TABLE II

Molecular mass averages and sample masses of different PPG samples from LAC on ODS-2 column (250 × 4.6 mm, 5 μ) in methanol-water 80:20 (w/w), as obtained with coupled density and RI detection with correction of response factors using Equation (1)

Sample (μg)	M_w	M_n	M_w/M_n	m_P (μg)	Method
PPG 425	450	430	1.045	783.0	density, Eq. 1
761.0	454	435	1.042	730.6	RI, Eq. 1
	455	437	1.041	716.9	dual detection, Eq. 6
PPG 725	775	751	1.033	726.3	density, Eq. 1
742.5	779	753	1.034	715.4	RI, Eq. 1
	780	754	1.034	712.5	dual detection, Eq. 6
PPG 1000	1001	974	1.028	835.0	density, Eq. 1
802.5	1001	973	1.030	760.5	RI Eq. 1
	1001	972	1.030	741.5	dual detection, Eq. 6

response factos and preferential solvation correction [Equations (1) and (6)], is shown in Figure 10. As can be seen, the agreement of the different approaches was excellent.

CONCLUSIONS

LAC is an alternative to SEC in the analysis of polyethers with molecular masses below 2000. Moreover it provides an excellent method for improving the reliability of SEC data. In combination with SEC, LAC can be used to establish a three-dimensional map of EO-PO- and EO-THF-block copolymers, as will be shown in further communications.

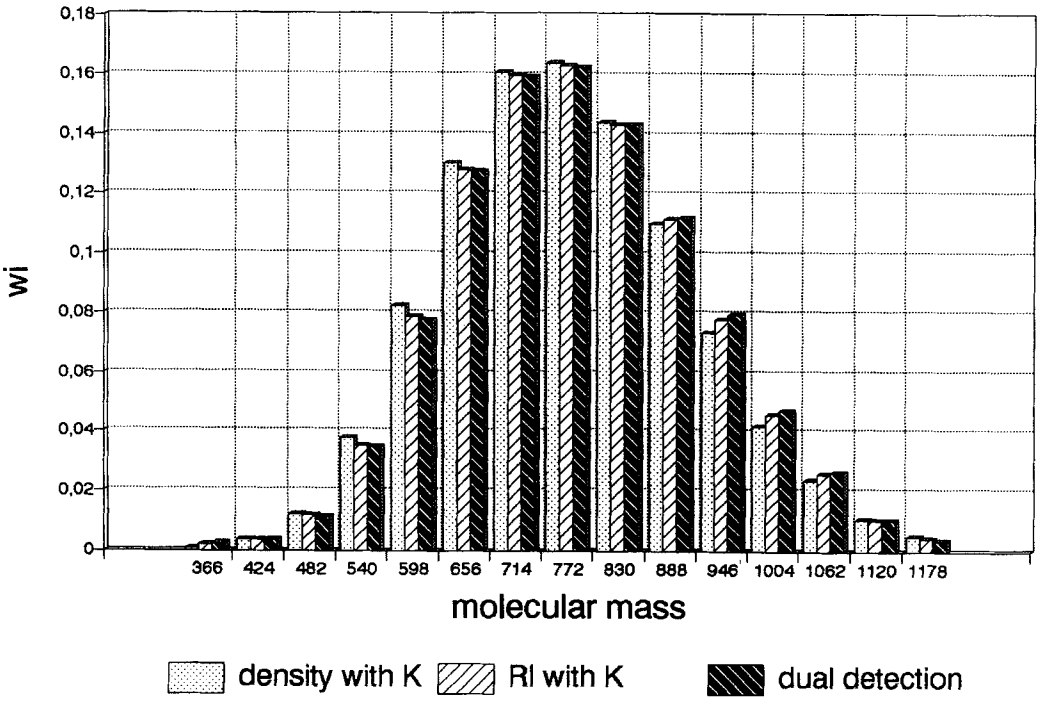

FIGURE 10 MMD of PPG 725, as obtained from LAC in methanol-water 80:20 (w/w) on an ODS-2 (250 × 4.6 mm, 5 μm), from density and RI detection, with and without compensation (K) for preferential solvation.

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