Determination of chemical composition of polymers by size-exclusion chromatography with coupled density and refractive index detection

III. Polyethylene oxide and polytetrahydrofuran

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ABSTRACT

It is shown that gel permeation chromatography with coupled density and refractive index detection is a useful tool in the analysis of copolymers of ethylene oxide and tetrahydrofuran with respect to their chemical composition as a function of molecular weight.

INTRODUCTION

In the analysis of copolymers or polymer blends it is very important to know the chemical composition along the molecular weight distribution, because non-uniform composition may affect product properties very strongly. Moreover, the chromatogram has to be corrected for chemical composition if the response factors of the detector for both monomer units are considerably different.

Basically, the chemical composition as a function of molecular weight can be obtained by a two-dimensional separation (cross-fractionation [1] or size-exclusion chromatography (SEC) coupled with liquid adsorption chromatography [2–4]) or by SEC with two detectors [5–9].

Because of its simplicity, the second approach is more convenient. However, it is limited by the detectors which can be applied: if one of the monomer units can be detected by a photometer, SEC with coupled refractive index (RI) and UV detection will be the method of choice. In this case, the selective UV detector yields the concentration of one component and the universal RI detector yields the overall concentration (after correction for different response factors). For all other copolymers, one would have to combine two universal detectors. Since the density detector (according to the mechanical oscillator principle) has proven to meet the

demand for an alternative universal detector [10–14], SEC with dual detection can be applied to non-UV-active copolymers.

The working principle of the density detector has been described previously, hence it shall be mentioned only briefly. Density measurement according to the mechanical oscillator method means measurement of the period of an oscillating U-shaped glass tube filled with the sample. Period measurement is performed by comparison with a time base (in the density detector an oven-controlled 10-MHz quartz oscillator). Hence the detector signal is inherently digital (the number of periods of the time base during a fixed number of the measuring cell) and integrated over each measuring interval.

EXPERIMENTAL

The density detection system (A. Paar, Graz, Austria) which was used for these investigations has been described in detail elsewhere [14]. It consisted of a thermo-statted box containing the columns and up to two independent measuring cells, which were connected to an intelligent interface. A differential refractometer (Sicon LCD 201) was coupled to one of the measuring cells and connected to the analog input of the interface. In order to maintain the same temperature in both detector cells, the RI detector was arranged in the thermostat circuit behind the column box.

All measurements were performed at a temperature of $25.00 \pm 0.01°C$. However, during each chromatogram, temperature was constant to approximately $1 \cdot 10^{-4}°C$, as can be deduced from the baseline value of the density detector, which was very stable after an equilibration period. As we have shown previously [14], it would even be satisfactory to reproduce temperature to $\pm 1°C$, as long as temperature changes are sufficiently slow. This was achieved by the special design of the column box and the density cell.

All separations were performed using chloroform [high-performance liquid chromatography (HPLC) grade, Merck LiChroSolv 2444] as the mobile phase at a flow-rate of 1.0 ml/min on three different column sets, which could be selected using two Rheodyne 7060 multiposition valves: A: 30×2 cm μStyragel, 100–500 Å (Waters); B: 30×2 cm μStyragel, 10^3–10^4 Å (Waters); C: 30×3 cm Microgel, 10^4–10^3–500 Å (Polymer Labs.). Two Gynkotek 300 C pumps were used in all experiments. Samples were injected using a manual injection valve (Gynkotek) and a Spark SP 125 FIX autosampler, both equipped with 50-μl sample loops. Sample sizes varied from 0.1 to 1 mg, corresponding to concentrations of 2.0–20 g/l, typically 4–8 g/l.

Polymer samples [polyethylene glycols (PEGs) from Merck, polytetrahydro-furan (PTHF) 1300 from Polymer Labs. (Batch No. 20423-1), tetrahydrofuran–ethylene oxide (THF–EO) copolymer from Aldrich] were used as received. Copolymer composition was also determined by ^{13}C nuclear magnetic resonance (NMR) spectroscopy (in chloroform) using a Gemini 200 spectrometer.

Raw data were transferred to an MS-DOS computer and processed using the software CHROMA. Molecular weight tables were written to ASCII files from CHROMA and transferred to a spreadsheet (SYMPHONY and EXCEL).

Principle of dual detection with two universal detectors

If a mass m_i of a copolymer containing the weight fractions w_A and w_B ($= 1 - w_A$) of the monomer units A and B, respectively, passes the detector cells, it will cause a response x_D of the density detector and x_R of the RI detector:

$$x_D = m_i(f_{D,A}w_A + f_{D,B}w_B) \tag{1}$$

and

$$x_R = m_i(f_{R,A}w_A + f_{R,B}w_B) \tag{2}$$

where $f_{D,A}$, $f_{D,B}$, $f_{R,A}$, and $f_{R,B}$ are the corresponding response factors of the homopolymers of A and B, respectively.

Combination of eqns. 1 and 2 yields:

$$1/w_A = 1 - (f_{D,A}x_R/x_D - f_{R,A})/(f_{D,B}x_R/x_D - f_{R,B}) \tag{3}$$

from which the weight fractions of the monomer units can be calculated. The mass eluted within one measuring interval is given by:

$$m_i = x_D/[f_{D,B} + w_A(f_{D,A} - f_{D,B})] \tag{4}$$

from which the mass distribution is obtained.

$$w_i = m_i / \sum m_i \tag{5}$$

Once w_A and w_B are known, one may correct the chromatogram and the mass distributions using eqns. 4 and 5.

Multiplication of the weight fraction w_i by w_A and w_B, respectively, yields the separated distributions of the monomer units, as will be shown later:

$$w_i(A) = w_i w_A \tag{6}$$

$$w_i(B) = w_i w_B \tag{7}$$

RESULTS AND DISCUSSION

In previous communications [15,16], we have shown that mixtures of PEGs and polypropylene glycols as well as block copolymers of ethylene oxide and propylene oxide can be analyzed using SEC with coupled density and RI detection. We have now applied the new method to mixtures of PTHF and EO–THF copolymers.

As the first step, the validity of the SEC calibration for both homopolymers and the reproducibility of the results had to be checked by repeated injections of samples and calculation of average molecular weights using the calibrations obtained from narrow molecular weight standards of polyethylene oxide (PEO) and PTHF (both from Polymer Labs.). Table I shows the data thus obtained.

The molecular weight averages obtained using the calibrations with PEG and PTHF standards are in good agreement; for the following measurements only the PEG

TABLE I

MOLECULAR WEIGHT AVERAGES OF PEG 1500, PEG 2000 AND PTHF 1300 FROM SEC ON
DIFFERENT COLUMN SETS USING CALIBRATIONS WITH PEG AND PTHF STANDARDS

Sample	Column set	Standard	M_w	M_n	M_w/M_n
PEG 1500	B	PEG	1536 ± 5	1460 ± 5	1.052 ± 0.003
	C	PEG	1578 ± 19	1501 ± 24	1.052 ± 0.005
	C	PTHF	1551 ± 21	1454 ± 27	1.066 ± 0.008
PEG 2000	C	PEG	2061 ± 24	1975 ± 32	1.043 ± 0.002
	C	PTHF	2177 ± 13	2032 ± 14	1.072 ± 0.002
PTHF 1300	B	PEG	1272 ± 12	1010 ± 15	1.258 ± 0.012
	B	PTHF	1366 ± 12	1023 ± 12	1.352 ± 0.014
	C	PEG	1352 ± 14	1124 ± 14	1.192 ± 0.007
	C	PTHF	1332 ± 20	1082 ± 13	1.231 ± 0.006

calibration was used. The reproducibility of molecular weight averages is also
satisfactory, and so is the accuracy: the values found for PTHF 1300 (Batch
No. 20423-1 from Polymer Labs.) agree quite well with the data given by the
distributor: weight-average molecular weight, $M_w = 1296$; number-average molecular
weight, $M_n = 1163$; $M_w/M_n = 1.13$.

In the second step the accuracy of the response factors was evaluated by
analyzing pure homopolymers of EO and THF using the new method.

In Figs. 1 and 2 the weight fractions w_A and w_B of EO and THF units in these
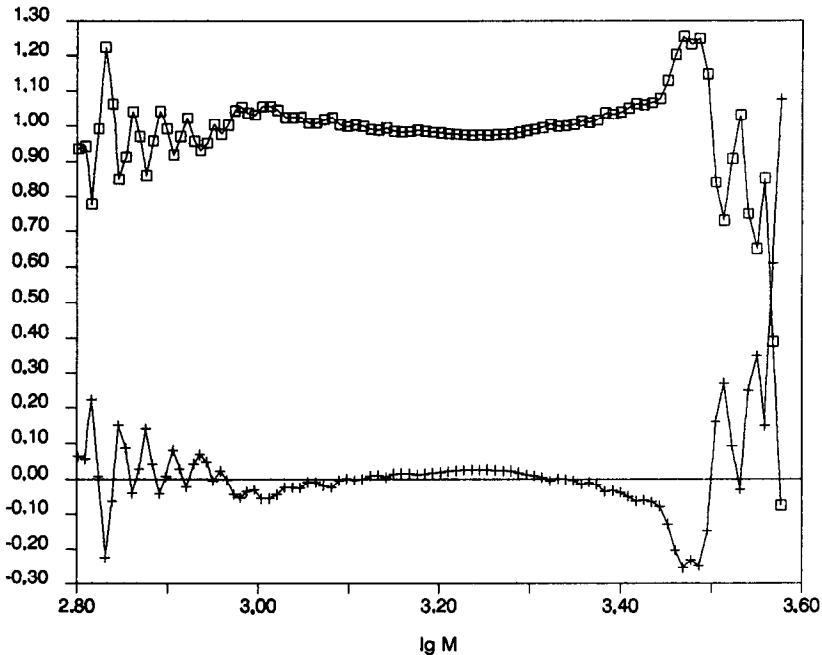

Fig. 1. Weight fractions of the monomer units in PEG 1500 as determined by SEC with density and RI
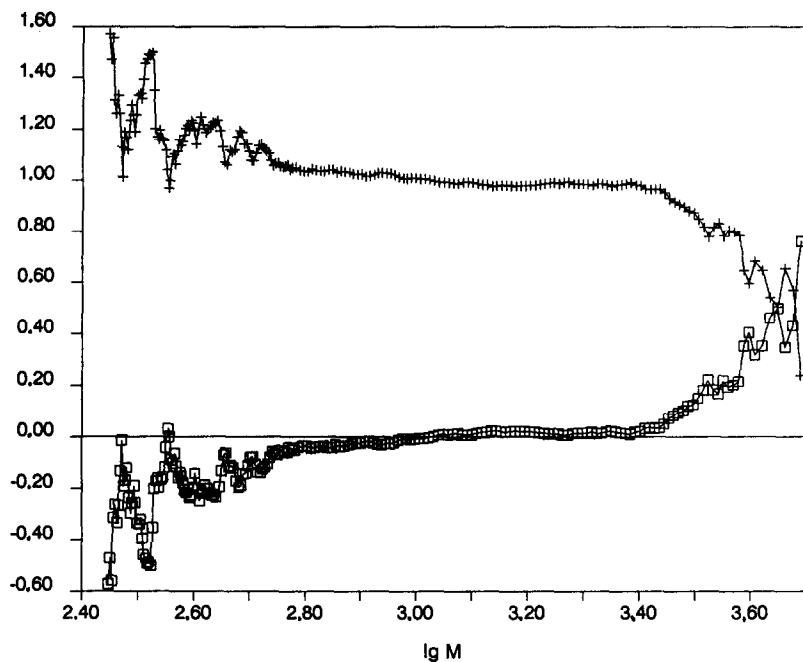detection. □ = w_i (EO); + = w_i (THF). lg = log.

Fig. 2. Weight fractions of the monomer units in PTHF 1300 as determined by SEC with density and RI detection. Symbols as in Fig. 1.

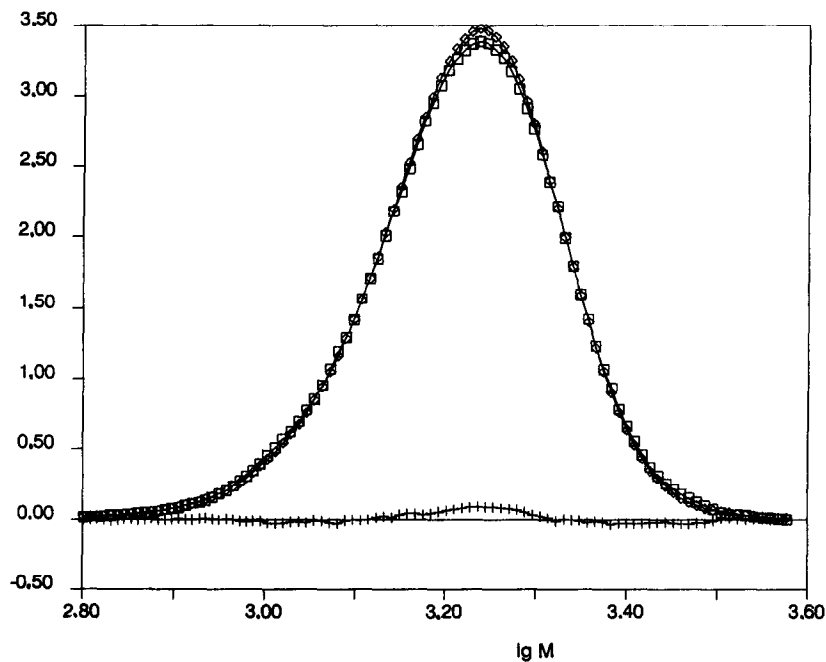Fig. 3. Molecular weight distribution of PEG 1500 and separated distributions of the monomer units. $\square$ = w_i (EO); + = w_i (THF); $\Diamond$ = w_i (total).
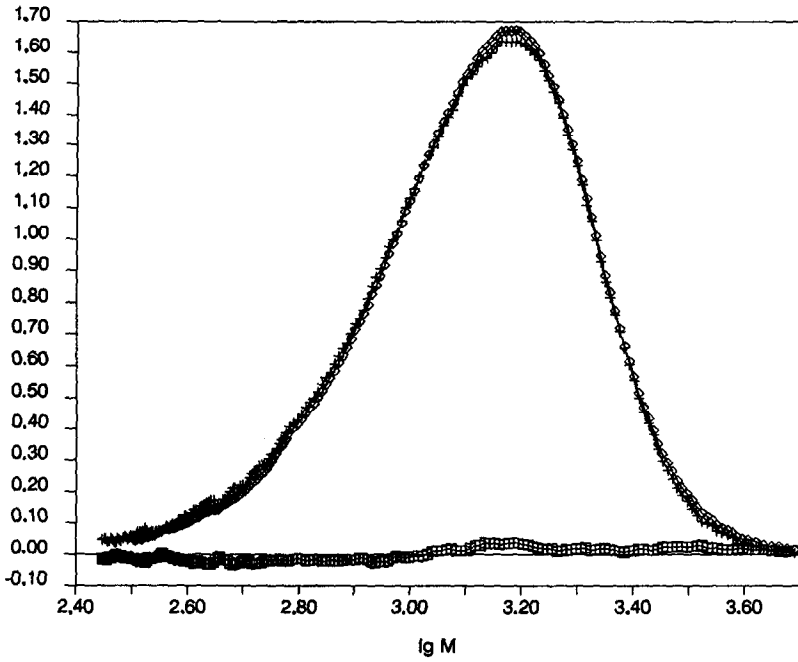
Fig. 4. Molecular weight distribution of PTHF 1300 and separated distributions of the monomer units. Symbols as in Fig. 3.
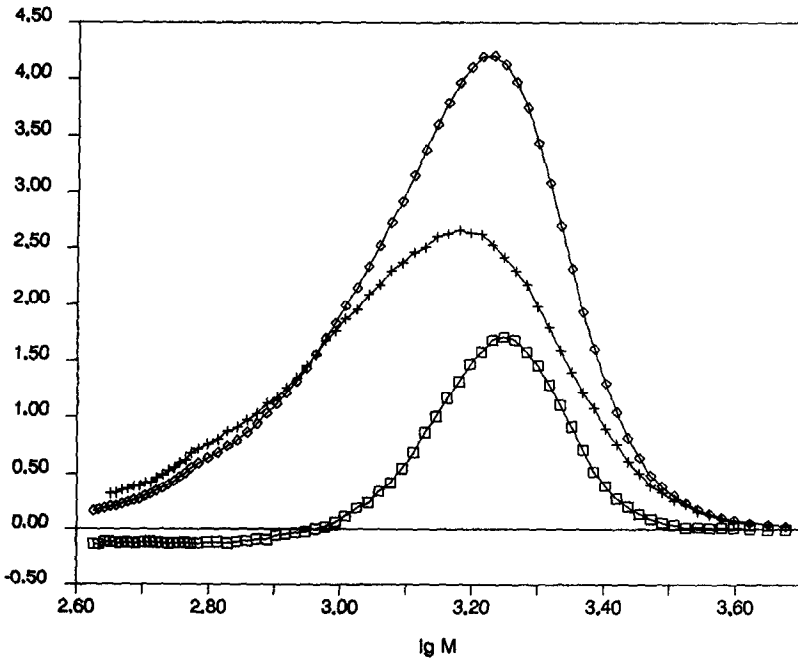

Fig. 5. Molecular weight distribution of a mixture of PEG 2000 with PTHF 1300 and separated distributions of the monomer units. Symbols as in Fig. 3.
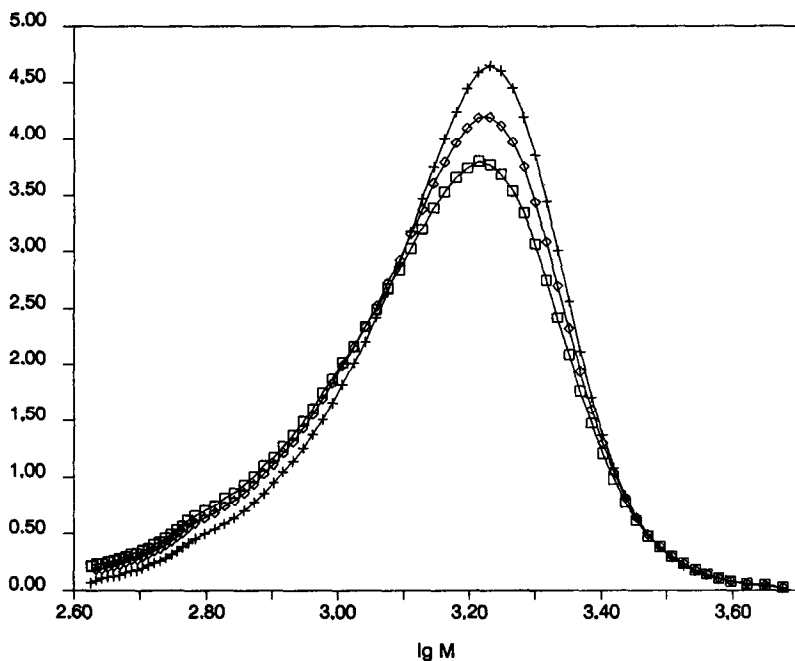
Fig. 6. Molecular weight distribution of a mixture of PEG 2000 with PTHF 1300 from each of the detectors and corrected distribution. $\square$ = w_i (density); + = w_i (RI); $\Diamond$ = w_i (corr.).

samples are plotted as a function of molecular weight, and Figs. 3 and 4 show the corrected mass distribution together with the separated distributions of the monomer units. In both cases, the weight fraction of the other monomer is found to be very close to zero over the entire range of the molecular weight distribution, which proves the accuracy of the response factors.

In the third step a mixture of PEG 2000 and PTHF 1300 was analyzed. Fig. 5 shows the overall and the separated mass distributions of the monomer units, which clearly show the non-uniform composition of this sample. In this case, the use of each detector alone would lead to serious errors in the mass distributions and in the molecular weight averages, as is shown in Fig. 6 and Table II.

The fourth step was the application of the new method to a copolymer of EO and

TABLE II

MOLECULAR WEIGHT AVERAGES OF A MIXTURE OF PEG 2000 AND PTHF 1300 DETER-MINED BY SEC USING DENSITY AND RI DETECTION

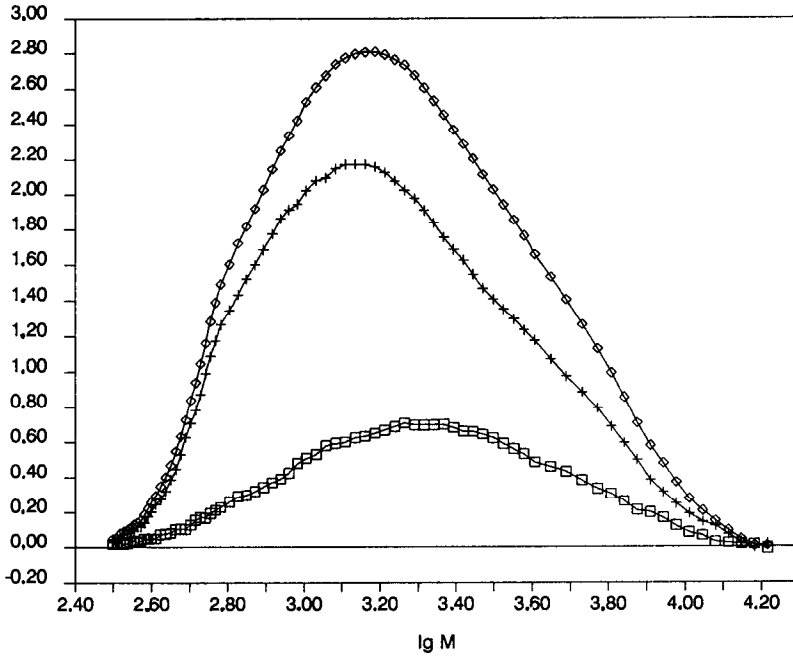| Detection	M_w	M_n
Density	1428	1102
RI	1556	1321
Corrected	1502	1243

Fig. 7. Molecular weight distribution of EO–THF copolymer and separated distributions of the monomer units. Symbols as in Fig. 3.
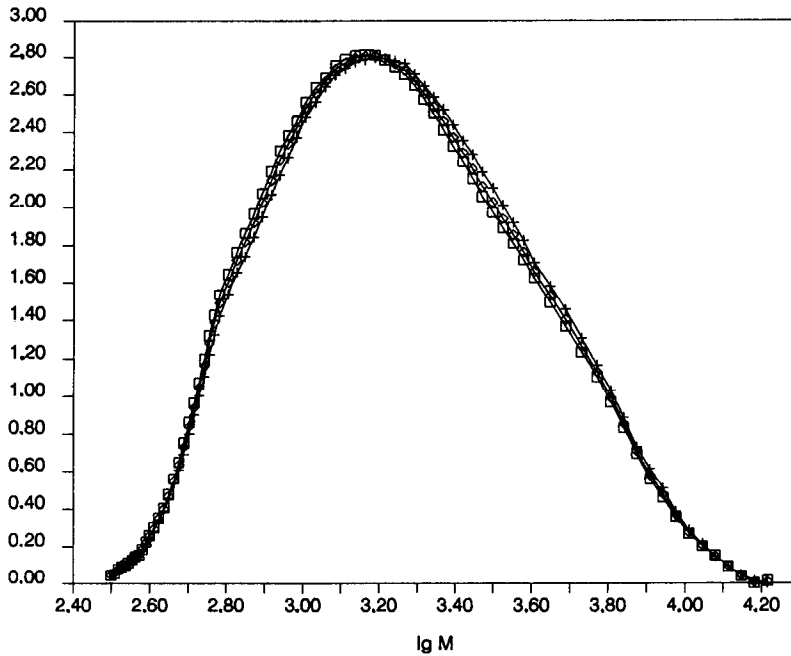

Fig. 8. Molecular weight distribution of EO–THF copolymer from each of the detectors and corrected distribution. Symbols as in Fig. 6.

TABLE III

OVERALL CHEMICAL COMPOSITION OF AN EO–THF COPOLYMER, AS DETERMINED BY ^{13}C NMR SPECTROSCOPY AND SEC WITH DENSITY AND RI DETECTION

	NMR (%)	GPC (%)
EO	23.4	23.5
THF	76.6	76.5

THF, the overall composition of which was also determined by ^{13}C NMR spectroscopy. Figs. 7 and 8 show the molecular weight distribution of this sample in the same representations as in Figs. 5 and 6. Overall this was found to be in very good agreement with the NMR data, as can be seen from Table III. However, the composition is not uniform. Obviously, the EO content increases with molecular weight, which can be seen from Fig. 9.

CONCLUSIONS

SEC with a combination of a density and a RI detector promises to be a very useful tool in the analysis of copolymers of any type with respect to their chemical composition along the molecular weight distribution. Further investigations shall show the scope and limitations of the new method.
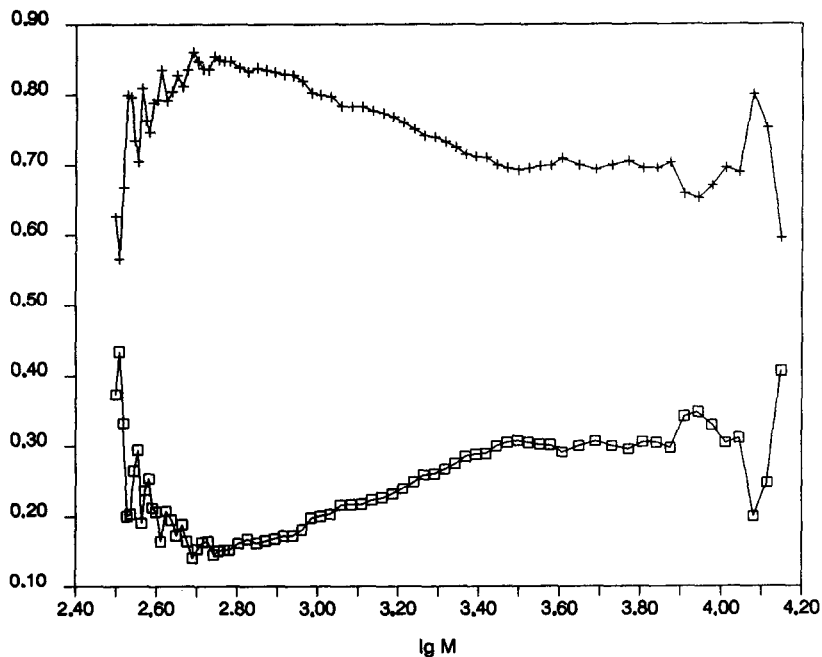

Fig. 9. Weight fractions of the monomer units in EO–THF copolymer as determined by SEC with density and RI detection. Symbols as in Fig. 1.

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