Quantitation in liquid chromatography of polymers: size-exclusion chromatography with dual detection[1]

Bernd Trathnigg*, Sabine Feichtenhofer, Manfred Kollroser

Department of Polymer Chemistry, Institute of Organic Chemistry, Karl-Franzens-University Graz, Heinrichstrasse 28, A-8010 Graz, Austria

Abstract

The problem of quantitation in size-exclusion chromatography (SEC) of polymers and oligomers is discussed, and a strategy for finding an appropriate combination of detectors and mobile phases for a given type of copolymer is described. This approach comprises the determination of response factors of different detectors for each homopolymer, and a simulation of dual detector SEC. The reliability of results is evaluated by analysis of homopolymers, polymer mixtures and copolymers of methyl methacrylate, ethylene oxide and dimethyl siloxane. Monodisperse fatty alcohol ethoxylates are used as models for block copolymers. © 1997 Elsevier Science B.V.

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1. Introduction

In the analysis of polymers by size-exclsuion chromatography (SEC), three transformations from chromatographic raw data to molar mass distributions (MMD) are required: (1) elution time to elution volume, (2) elution volume to molar mass and (3) detector response to weight fraction. Each of these steps can be subject to different sources of error, depending on the nature of the samples.

Step 1 is performed rather easily by using an internal standard for compensation of flow-rate varia-

tions. In a systematic study, Johan and Kilz [1] demonstrated the effect of flow-rate changes and the use of the internal standard method.

Step 2 requires either a reliable calibration function, which can be obtained in different ways, or the use of molar mass sensitive detectors (such as viscosimeters or light scattering detectors) in addition to the concentration sensitive detectors. There are numerous articles and books describing the different approaches for this step, hence they will not be discussed here in detail.

Step 3 is especially important in the case of oligomers and copolymers, where severe errors may result from the assumption of constant response factors over an entire peak.

This paper deals with the particular problems

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*Corresponding author.
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related to the type of polymer to be analyzed, as well as the mobile phase and the detectors which can be applied.

1.1. Oligomers

The concentration detectors most frequently used in SEC of polymers are the UV absorbance and the refractive index (RI) detectors. Recently, two other detectors have been introduced, which are useful in the analysis of non-UV absorbing polymers: the evaporative light scattering detector (ELSD) [2–4] and the density detector (according to the mechanical oscillator principle).

The UV absorbance detector detects UV-absorbing groups in the polymer, which may be the repeating unit, the end groups, or both. The ELSD detects any non-volatile material, but its response depends on various parameters [5,6], and the nature of these dependencies is rather complex. RI and density detectors measure a property of the entire eluate, which is related to a specific property of the sample (the refractive index increment or the apparent specific volume, respectively).

It is a well known fact [7] that specific properties are related to molar mass:

$$x_i = x_\infty + \frac{K}{M_i} \tag{1}$$

where x_i is the property of a polymer with the molar mass M_i, x_∞ is the property of a polymer with infinite (or at least very high) molar mass, and K is a constant reflecting the influence of the end groups [8–10]. A similar relation describes the molar mass dependence of response factors for RI and density detection:

$$f_i = f_\infty + \frac{K}{M_i} \tag{2}$$

In the case of the ELSD no such simple relation exists, and the (more volatile) lower oligomers can be lost at higher evaporator temperatures, as we have shown in a recent paper [11].

In a plot of the response factors, f_i, of polymer homologous series (with defined end groups) as a function of $1/M_i$ straight lines will be obtained. Their intercept f_∞ can be considered as the response factor of a polymer with infinite molar mass, or the

response factor of the repeating unit, the slope K represents the influence of the end groups [12,13].

The magnitude of K determines the molar mass range above which response factors can be considered as constant, which is often the case only at molar masses of several thousands.

Once f_∞ and K have been determined, the correct response factors for each fraction with the molar mass M_i (which is obtained from the SEC calibration) can be obtained. In a previous paper [14], three methods were described for the determination of f_∞ and K.

Neglecting the molar mass dependence of response factors can lead to severe errors, as has been shown in another paper [15], in which the analysis of ethoxylated fatty alcohols (FAEs) by SEC in chloroform was described.

1.2. Copolymers and polymer blends

In the analysis of copolymers or polymer blends, the chemical composition may vary considerably within a peak. In this case, the use of coupled concentration detectors is inevitable. If the response factors of the detectors for the components of the polymer is sufficiently different, the chemical composition of each slice of the polymer peak can be determined from the detector signals.

Basically, only very few concentration detectors may be applied: UV absorbance, RI and density detectors. Infrared (IR) detection suffers from problems with the absorption of the mobile phase, and the ELSD method is not suitable for this purpose because of its unclear response to copolymers [16]. Moreover, the response of this detector is not linear with concentration [17].

For UV absorbing polymers, a combination of UV absorbance and RI detection is typically used. If the components of the copolymer have different UV spectra, a diode-array detector (DAD) can also be applied. It must, however, be mentioned, that non-linear detector response may also occur with UV absorbance detection [18].

In the case of non-UV absorbing polymers, a combination of RI and density detection yields the desired information on chemical composition [19–21].

Dual detection can also be applied in the analysis

of FAEs, where the fatty alcohol is considered as one block, and the polyoxyethylene chain as the other [15].

The principle of dual detection is rather simple: when a mass m_i of a copolymer, which contains the weight fractions w_A and w_B ($= 1 - w_A$) of the monomers A and B, is eluted in the slice i (with the volume ΔV) of the peak, the areas $x_{i,j}$ of the slice obtained from both detectors depend on the mass m_i (or the concentration $c_i = m_i / \Delta V$) of polymer, its composition (w_A) and the corresponding response factors $f_{j,A}$ and $f_{j,B}$, wherein j denotes the individual detectors.

$$x_{i,j} = m_i(w_A f_{A,j} + w_B f_{B,j}) \qquad (3)$$

The weight fractions w_A and w_B of the monomers can be calculated using:

$$\frac{1}{w_A} = 1 - \frac{\left(\dfrac{x_1}{x_2} \cdot f_{2,A} - f_{1,A}\right)}{\left(\dfrac{x_1}{x_2} \cdot f_{2,B} - f_{1,B}\right)} \qquad (4)$$

and therefore the correct mass of polymer in the corresponding interval:

$$m_i = \frac{x_i}{w_A \cdot (f_{1,A} - f_{1,B}) + f_{1,B}} \qquad (5)$$

Obviously, the precision as well as the accuracy of the results obtained by this technique will depend on the individual response factors. Hence it is highly important to know, which detector combination and which mobile phase will yield the most reliable results for a given analytical problem. As trial and error is rather time consuming, one should choose a better approach for optimization.

In this paper, a less time consuming strategy is described and its performance evaluated for selected analytical tasks.

In dual detector SEC, the (selective) UV detector is the first instrument to be taken into account: its sensitivity is typically better than that of the (universal) RI or density detector. Hence there may be different situations which will determine the selection of detectors:

(a) One component can be detected in the UV, the other one does not absorb UV light. Obviously, this is the most fortunate case, because it allows selective

detection of one component, provided that the other detector detects both components. Typical examples are poly(methyl methacrylate-g-ethylene oxide) and poly(methyl methacrylate-g-dimethyl siloxane). While polymethacrylates can be detected by a UV detector at low wavelengths (235 nm), this is not the case for polysiloxanes and the polyethers.

(b) Both components can be detected in the UV: in the case of poly(methylmethacrylate-b-styrene) [22] the UV spectra of the components are significantly different, and the UV detector can be regarded as a selective detector, in the case of poly(methylmethacrylate-b-decylmethacrylate) [23] they are identical, and the UV absorbance detector has to be regarded as a universal one.

(c) None of the components can be detected in the UV: this is the case with poly(ethylene oxide-b-propylene oxide) [24] and FAEs [15]. In the analysis of such samples a combination of density and RI detection can be applied.

2. Experimental

2.1. Chemicals

The polymethylmethacrylates (PMMAs) and poly(ethylene glycol)s (PEGs) used as calibration standards were purchased from Polymer Labs. (Church Stretton, Shropshire, UK), other PEGs, PPGs (polypropyleneglycols), EO-oligomers, fatty alcohols and the corresponding ethoxylates (Brij) were from Fluka (Buchs, Switzerland).

Broad MMD polymers: PMMA was synthesized by solution polymerization (in diethlyene glycol diethyl ether) at 60°C with AIBN as initiator. The poly(dimethyl siloxane) (PDMS) macromonomer and the graft copolymers were supplied by Y. Tsukahara, Kyoto Institute of Technology, Department of Materials Science.

All measurements were performed on a modular SEC system comprising of a Gynkotek 300C pump equipped with a VICI injector (sample loop 100 µl), two column selection valves Rheodyne 7060, a density detection system DDS 70 (Chromtech, Graz, Austria) coupled with an ERC 7512 RI detector or a JASCO 875 UV absorbance detector.

Data acquisition and processing were performed

using CHROMA software which is part of the DDS 70.

The following columns were used: Phenogel M (5 μm), 600×7.6 mm, PL Microgel M (10 μm), 600× 7.6 mm I.D., a set of four columns Phenogel (5 μm), 2×500 and 2×100 Å, 300×7.6 mm I.D. each, and a set of two columns PL Microgel (10 μm), $10^3 + 10^4$ Å, 300×7.6 mm I.D. each.

All measurements were performed at a flow-rate of 1.00 ml/min and a column temperature of 25.0°C. Sample concentrations were 3.0–10.0 g/l.

The following mobile phases were used: chloroform (HPLC-grade, stabilized with 2-methyl-butene, Mallinckrodt) and tetrahydrofuran (THF) (UV-grade, Aldrich).

3. Results and discussion

3.1. Determination of response factors

Obviously, the first step in the development of a suitable method is the choice of an appropriate mobile phase, which allows a separation in the SEC mode, and two detectors, which are sufficiently sensitive for at least one of the components.

For these detectors, the response factors of the components (the homopolymers) have to be determined. In order to save time, this need not be done on the column set that will be used in the analysis. A short column (or even a bypass) will do as well, which also avoids reducing the lifetime of an expensive column due to frequent changes of the mobile phase. From the response factors thus obtained, one may estimate quite roughly, whether or not a certain combination could make sense.

As can be seen from Fig. 1, the analysis of PMMA and PEG (or PPG) in THF should be possible with a combination of UV absorbance (at 235 nm) and density or RI detection, while no reliable results can be expected in this mobile phase for PEG and PPG.

In Fig. 2, the response factors of density and RI detection for various polymers in chloroform are shown (UV absorbance detection cannot be used for these polymers because of the UV cut-off of this mobile phase). The most favorable combinations are in this case PMMA–PDMS, FAEs and PEG–PPG.

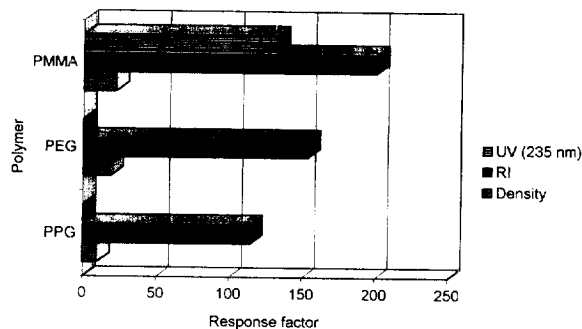However, such an estimation is not very accurate.

Fig. 1. Response factors of density, RI and UV absorption (at 235 nm) detection for different polymers in THF.

There exists, nevertheless, another approach, which allows better predictions of the reliability of dual detector SEC: once the response factors have been determined, a simulation of real chromatograms can be used to evaluate the suitability of the detectors and the mobile phase for the polymer to be analysed.

3.2. Simulation of dual detector SEC

With the above response factors one may calculate the areas, which would be obtained per mass unit of polymer (m_i in μg) with a given composition (w_A) in a slice of the peak (using Eq. (3)). Then the smaller area (which will be subject to baseline errors to higher extent) is varied by 1 digit, and from the new values the composition is again calculated for all values of w_i and w_A. The difference between the w_A value thus obtained and the original one is the parameter which can be used to estimate the error in
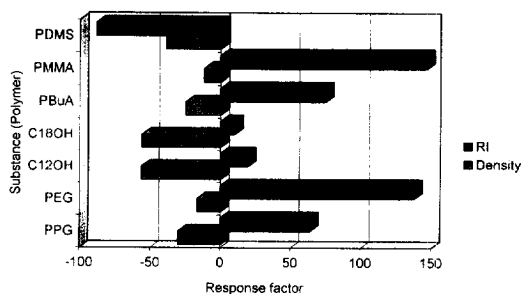

Fig. 2. Response factors of density and RI detection for different polymers and structural units in chloroform.

a real separation. In the ideal case, the error is smaller than 2% even for small values of m_i (1–2 µg) in a slice of the peak.

This approach was applied to different systems, some of which have already been described in previous papers, such as FAE [15] and PEG–PPG [24] and new ones such as PMMA–Poly-(butylacrylate), PMMA–PEG and PMMA–PDMS.

Fig. 3 shows the results of such a simulation for polymer mixtures or copolymers with equal content of the components ($w_A = 0.5$). As can be seen, the error caused by baseline uncertainties is reasonably low for most of the curves except for PEG–PPG in THF and PMMA–PEG in chloroform (both with density and RI detection), which could, however, be expected from the response factors shown in Figs. 1 and 2.

In many cases it is important to calculate the errors for compositions between 0 and 100%, as can be seen from Figs. 4–6.

In the analysis of FAE in chloroform with density and RI detection good results can be expected for all compositions (Fig. 4).

A special situation is found for PMMA–PDMS in chloroform with density and RI detection, where the RI detector is very sensitive for both PMMA and PDMS, but with opposite sign. In this case the error

Fig. 4. Simulation of errors in the analysis of FAE by SEC with density and RI detection in chloroform.

due to baseline uncertainties changes its sign (Fig. 5).

PMMA and PEG could also be expected to be an easy case, where PMMA can be detected in the UV, while the PEG would be invisible in the UV. Density and RI, on the other hand, detect both components.

The main problem in the analysis of PMMA–PEG is, however, the choice of the mobile phase, which must be a good solvent for both components to allow a separation in the SEC mode, and it must be sufficiently transparent at the absorption maximum of PMMA. In practice, only THF fulfilled both preconditions (even though not easily: normal
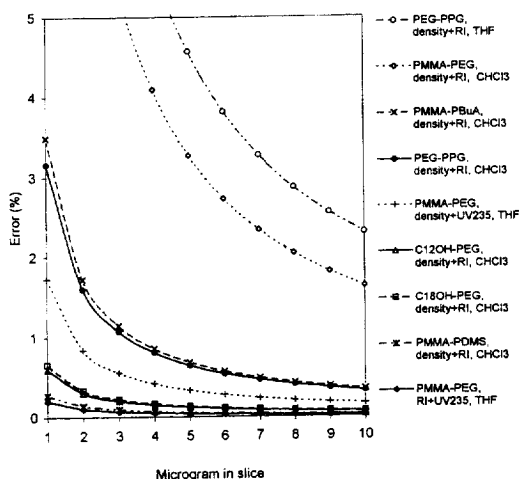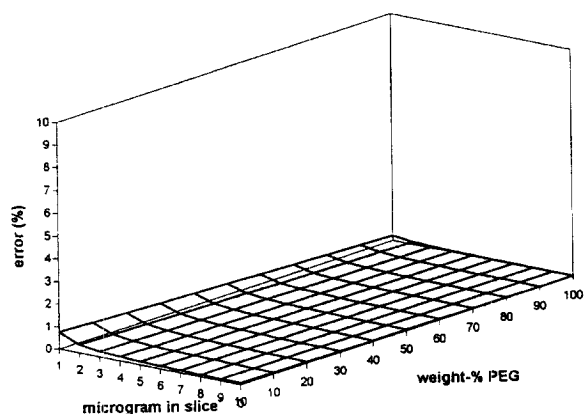

Fig. 3. Simulation of dual detector SEC of different polymers. Errors caused by a baseline uncertainty of 1 digit at the less sensitive detector as a function of sample amount (chemical composition: $w_A = 0.5$) in a slice of the peak.
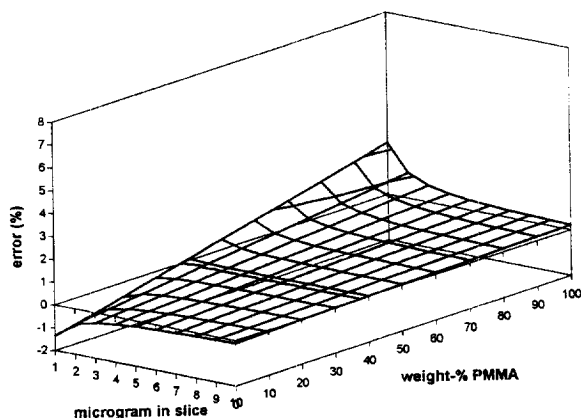

Fig. 5. Simulation of errors in the analysis of poly(methylmethacrylate) and poly(dimethylsiloxane) in chloroform, density and RI detection.
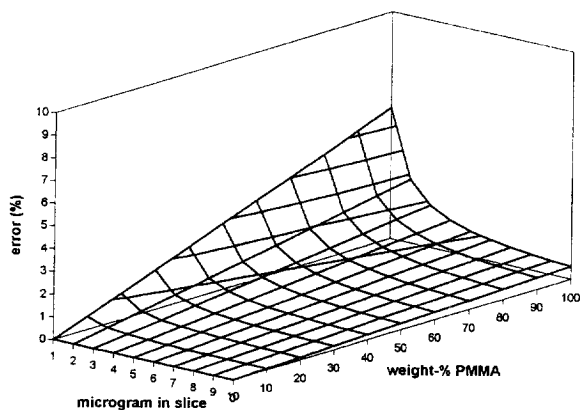
Fig. 6. Simulation of errors in the analysis of poly(methyl methacrylate) and poly(ethylene glycol) in chloroform, density and UV detection (at 235 nm).
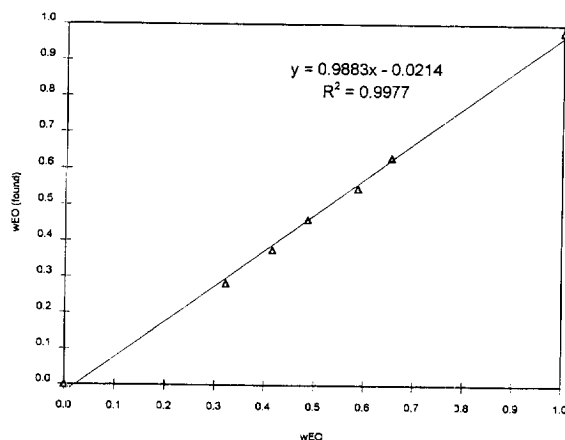

Fig. 7. Weight fractions of ethylene oxide in (monodisperse) fatty alcohol ethoxylate oligomers, as determined by SEC in chloroform with density and RI detection, versus the real composition.

HPLC-grade THF is not suitable, only UV-grade THF is sufficiently transparent at 235 nm).

As the sensitivity of the RI detector for PMMA and PEG is higher than that of the density detector, the combination of RI and UV will be the method of choice. The combination of density and UV detection works quite well at a high PEG content, while the errors increase dramatically with increasing PMMA content (Fig. 6).

3.3. Analysis of chemically homogeneous polymers and oligomers

With an appropriate combination of detectors and mobile phase, one will find overall compositions of 0 and 100%, respectively, for the homopolymers, which does not necessarily mean that the results obtained for samples with a composition between these extremes are also accurate. There are, however, no homogeneous or at least sufficiently defined copolymers available, which could be used to prove the validity of Eq. (4).

Hence we have chosen monodisperse FAE oligomers [$C_{12}O(EO)_nH$] as a model for two-block copolymers. These samples were analyzed in chloroform with a combination of density and RI detection [15,25]. As can be seen from Fig. 7, the composition found by this technique was accurate over the entire

range from 0 to 100% EO, only at the monoethoxylate the error was somewhat larger, because this oligomer has a very small response in the RI.

As such homogeneous samples are not available for other polymers, the only way to evaluate the reliability of such a technique is the analysis of the homopolymers and their mixtures.

There are, however, two other sources of error, which affect narrow peaks (such as monodisperse oligomers) much stronger than broad MMD polymers. In dual detection SEC, the chemical composition along the peak is obtained from the ratio of the detector signals (x_1/x_2), which will be influenced by peak dispersion between the detectors as well as by an incorrect interdetector volume. In data processing, the shift between the detector traces has to be compensated, hence the volume of the capillaries between the detector cells has to be determined with very high accuracy. An insufficiently compensated delay will lead to an excessively low value of x_1/x_2 at the beginning of the peak and an excessively high one at the end. This will result in a variation of chemical composition along the peak.

Peak dispersion between the detectors, on the other hand, leads to an excessively low ratio (x_1/x_2) on both sides of the peak. Especially at the very ends of narrow peaks, where both x_1 and x_2 approach

zero, this will cause considerable errors in the composition.

In the first case, the composition shows a slope, but a linear shape, while a U-shaped curve will be found in the second case. It must, however, be mentioned, that similar deviations from the expected shape (horizontal, straight line) may also have other reasons, such as molar mass dependence of response factors (see Eq. (2)), or simply an unstable baseline.

Bielsa and Meira [26] have studied the influence on instrumental broadening in copolymer analysis with dual-detection SEC, and demonstrated the effect of different corrections. In order to minimize peak dispersion between the detectors, several authors have used a 1:1 split of the solvent stream. The main problem of this parallel arrangement of detectors is, however, that the split ratio must be constant over the entire chromatogram, which can be neither easily achieved nor measured with sufficient precision.

By minimizing all sources of peak dispersion between the detectors, one may also achieve this goal in serial arrangement of detectors.

Fig. 8 shows the MMD and chemical composition of a PDMS macromonomer, which was determined by SEC in chloroform with density and RI detection. As can be seen, the chemical composition thus obtained is close to 0 and 100% for the components (PMMA and PDMS) and constant over the entire

peak, which indicates, that peak dispersion between the detectors is negligible, and the interdetector volume is correct.

3.4. Analysis of copolymers and polymer mixtures

As an example of a real copolymer, we have analyzed a graft copolymer, which has been synthesized by Tsukahara and Trathnigg [27] by copolymerization of MMA and the PDMS macromonomer from Fig. 9. At the lower molar mass end of the MMD, the content of PDMS is considerably higher, which indicates the presence of residual macromonomer. The composition thus obtained agreed quite well with the stoichiometric one. In a following paper, a full characterization of such copolymers by complementary chromatographic techniques shall be described.

As sufficiently defined copolymers are not easily available, the accuracy of chemical compositions was also evaluated by the analysis of mixtures of the homopolymers. As a model for PMMA–g-PEG we chose mixtures of a PMMA with a broad MMD (which had been prepared by radical polymerization in solution) and PEG 6000. These mixtures were analyzed by SEC in THF with a set of two columns packed with PL Microgel 10^3 and 10^4 Å with density and UV detection (at 235 nm). We would like to
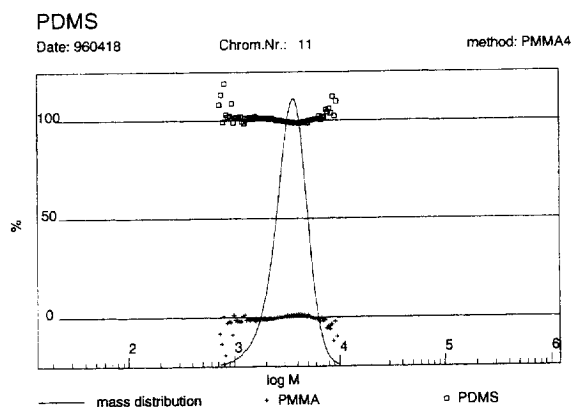

Fig. 8. MMD and chemical composition of a macromonomer (mono-methacryloyl-dimethylsiloxane), as obtained from SEC on PL Microgel M in chloroform with density and RI detection.
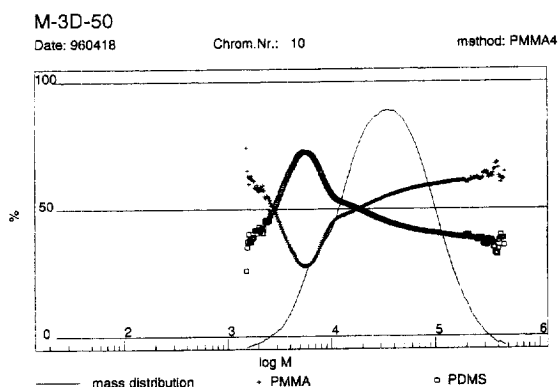

Fig. 9. MMD and chemical composition of a graft copolymer prepared from methyl methacrylate and a macromonomer (mono-methacryloyldimethylsiloxane), as obtained from SEC on PL Microgel M in chloroform with density and RI detection.

Table 1
PEG content of mixtures of PMMA and PEG 6000, as obtained by SEC in THF on two columns packed with PL Microgel 10^3 and 10^4 Å, 300×7.6 mm I.D. each

	Real	Found
PEG 6000	100.0	99.9
2:1	70.7	71.5
1:1	49.7	49.4
1:2	35.4	35.3
PMMA	–	0.3

Detection: density and UV absorbance at 235 nm.

point out, that this is a rather unfavorable case, because this method performs best at low PMMA concentrations, as can be seen from Fig. 6. Nevertheless, the chemical compositions thus obtained agree quite well with the real ones, as can be seen from Table 1.

Fig. 10 shows the MMD and chemical composition for a 2:1 mixture of a PMMA with PEG 6000. Multiplication of the mass distribution with the weight fractions of the monomer units yields two distributions, which seem to be those of the homopolymers (Fig. 11). This is, however, not the case: as the SEC calibration functions of PMMA and PEG are considerably different, different molar masses of the homopolymers elute at the same volume. The molar mass averages for this sample differ very strongly, depending on the calibration function used for their calculation, as can be seen from Table 2.

PEG6000:PMMA1 1:1   3.25:3.28
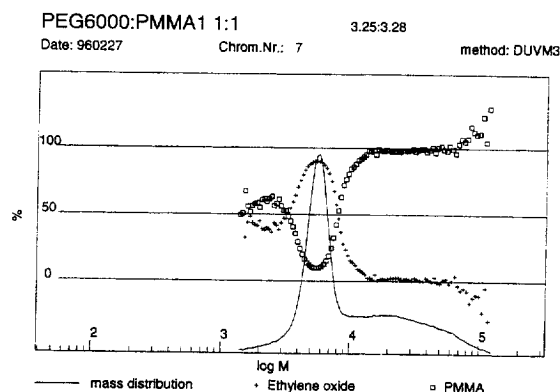Date: 960227   Chrom.Nr.: 7   method: DUVM3

Fig. 10. MMD and chemical composition of a mixture of poly(methylmethacrylate) and PEG 6000 (2:1, w/w), as obtained in THF on two columns packed with PL Microgel 10^3 and 10^4 Å, 300×7.6 mm I.D. each. Detection: density and UV at 235 nm.

PEG6000:PMMA1 1:1   3.25:3.28
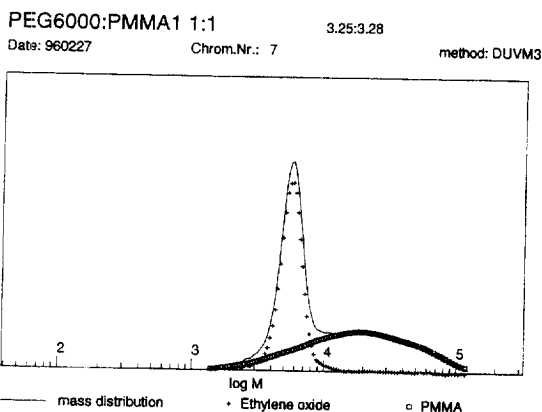Date: 960227   Chrom.Nr.: 7   method: DUVM3

Fig. 11. Separated distributions (product of MMD and chemical composition) of a mixture of poly(methyl methacrylate) and PEG 6000 (2:1, w/w), as obtained in THF on a set of two columns packed with PL Microgel 10^3 and 10^4 Å, 300×7.6 mm I.D. each. Detection: density and UV at 235 nm. Calibration: PEG.

In the case of copolymers, the molar mass M_C of the copolymer can obtained by interpolation between the calibration lines of the homopolymers [28]:

$$\ln M_C = \ln M_B + w_A \cdot (\ln M_A - \ln M_B) \qquad (6)$$

where M_A and M_B are the molar masses of the homopolymers, which would elute in this slice of the peak (at the corresponding elution volume V_e) [29]. One must, however, keep in mind that there is still a chemical polydispersity in each slice, which means that M_C is just the average molar mass, since w_A is also an average composition.

Obviously, this approach cannot be applied to mixtures of polymers. As Ogawa [30] has already shown by a simulation technique, the molar masses of polymers eluting at the elution volume V_e are given by the corresponding constants K and α in the Mark–Houwink equation. (The universal calibration

Table 2
Molar mass averages of a PMMA sample, as obtained by SEC in THF on two columns packed with PL Microgel 10^3 and 10^4 Å, 300×7.6 mm I.D. each

Calibration	M_w	M_n	M_w/M_n
PEG	24 866	11 315	2.198
PMMA	40 926	20 918	1.956

Detection: density and UV absorbance at 235 nm, two different calibration functions.

[31] is not capable of eliminating these errors, which originate from the simultaneous elution of two polymer fractions with the same hydrodynamic volume, but different composition and molar mass).

In SEC of a polymer blend, molar masses of the homopolymers eluting in the same interval can be calculated using the following equation:

$$\ln M = \frac{A \cdot V_e}{1 + a} + \frac{B - \ln K}{1 + a} \qquad (7)$$

where A and B are slope and intercept of the universal calibration.

A separate determination of the individual MMDs in polymer mixtures can be achieved with a combination of two concentration detectors and a molar mass sensitive detector, such as a low angle laser light scattering (LALLS) detector, as has been demonstrated by Lee et al. [32]. One has, however, to take into account the architecture of a copolymer (random, block, graft), as Revillon [33] has shown by SEC with RI, UV and viscosity detection: intrinsic viscosity varies largely with molar mass according to the type of polymer, its composition and the nature of its components.

If a sample has been identified as a mixture of homopolymers, the SEC calibration functions of which are known, one may as well use the following approach: once the total mass of polymer (m_i) and its composition (w_A) have been determined by dual detection for each interval within a peak, one may calculate the individual masses m_A and m_B as well as the corresponding molar masses M_A and M_B of the homopolymers which would elute in this interval.

This becomes clear from another example, which is shown in Fig. 12. When a mixture of two calibration standards with a very similar MMD was analyzed, two separated peaks were obtained. For one of them (PEG 6000) the MMD could be determined with reasonable accuracy, while the other one (PMMA 5270; Fig. 12) was shifted towards much lower molar mass, if PEG was used as the first calibration and vice versa. Using the procedure described above, the separated MMDs of both PMMA 5270 and PEG 6000 appear in the correct range.

Finally, there is the question about the meaning of a single molar mass distribution for polymer mixtures. A full characterization of such samples [with
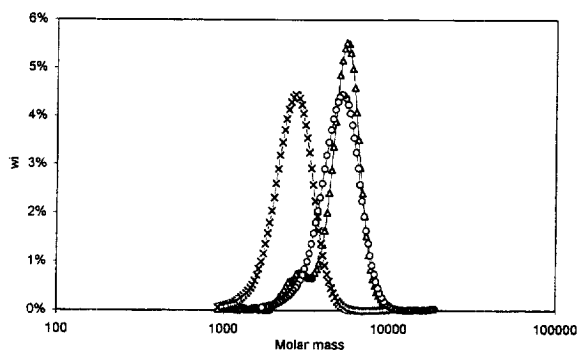

Fig. 12. Separated distributions (product of MMD and chemical composition) of a mixture of PMMA 5270 and PEG 6000 (1:1, w/w), as obtained with SEC calibration with PEG alone and with individual calibrations for both homopolymers. Chromatographic conditions as in Figs. 10 and 11.

respect to MMD and chemical composition distribution (CCD)] generally requires a two-dimensional separation. Nevertheless, the determination of the chemical composition of polymer mixtures is a simple test for the response factors.

4. Conclusions

In SEC of copolymers and polymer mixtures, quantitative accuracy can only be achieved using multiple detection. The selection of appropriate detectors and mobile phases can be made much easier by using a simulation procedure, which allows the estimation of the reliability and ruggedness of the method. Multiple detection can provide information on the chemical composition along a polymer peak, which can be used to detect traces of oligomers or starting materials (macromonomers) in a copolymer or a blend, but no information on chemical heterogeneity. A full characterization of complex polymers will often require a two-dimensional separation, and a combination of concentration detectors.

Acknowledgments

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