Estimation of Number-Average Molecular Weights of Copolymers by Gel Permeation Chromatography−Light Scattering

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Received November 3, 1995; Revised Manuscript Received March 12, 1996⊗

ABSTRACT: The true number-average molecular weight, M_n, of copolymers is obtained by GPC coupled with a light-scattering detector even if the composition and therefore the refractive index increment varies with elution volume, provided slices taken are monodisperse with respect to molecular weight and composition. In contrast, only an apparent weight-average molecular weight, M_w^{app}, can be obtained by the conventional GPC−light scattering combination, even for a perfect chromatographic resolution. The errors in M_n associated with nonhomogeneous slices are estimated. Experimental data with mixtures of linear polystyrene and poly(methyl methacrylate) confirm these estimations and indicate that the error in M_n is less than 10% for the system under investigation.

Introduction

Gel permeation chromatography (GPC) has become a powerful method for the determination of the molecular weight distribution (MWD) of polymers. For homopolymers the column set can be calibrated with standards of narrow MWD or by using universal calibration[1] if the Mark−Houwink parameters for the polymer under investigation in the eluent are known. The lack of suitable standards for column calibration has been overcome by the use of molecular weight sensitive detectors, such as on-line viscosity or light-scattering detectors.[2−7]

For copolymers a multidetector approach[8] has been used as an approximate method which involves the use of at least one concentration detector for each component. From the ratios of the signals of the various detectors, the composition in each slice is calculated and the molecular weight in this slice is determined as the weighted average of the molecular weights obtained from the calibration curves for the homopolymers. This method, although simple, has serious disadvantages: it needs calibration of the detectors and of the column set for each homopolymer (or, for universal calibration, the Mark−Houwink constants must be known in the GPC eluent). Moreover, the hydrodynamic volume of the copolymer does not necessarily depend on composition in a linear way.

The use of a light-scattering detector for copolymers is complicated by the fact that for chemically nonhomogeneous copolymers the composition of the eluted molecules will vary as a function of elution volume, even if the slices are monodisperse. This leads to a change in the refractive index increment with elution volume and therefore introduces errors in the determination of the copolymer concentration, if a refractive index detector is used for the determination of the concentration. The same is true for the absorption coefficient in UV detection.

The most rigorous method to overcome these problems would be a two-dimensional separation according to both molecular weight and chemical composition.[9−13] Such systems have become commercially available.[14] The individual fractions would have to be analyzed in terms of composition using the multidetector approach. Knowing the concentrations of the individual components, the total copolymer concentration and the refractive index increments could be calculated for each GPC slice. Using these informations, correct molecular weight distributions could be obtained by on-line light scattering or viscometry. Obviously, this method, although probably the most correct one, involves a lot of labor.

Goldwasser[15] and Rudin[16] proposed a method for the determination of M_n of copolymers using exclusively an on-line viscosity detector together with a universal calibration curve, which overcomes the problem of compositional drift. The application of GPC−light scattering (GPC−LS) to copolymers has not yet reached much attention. It will be shown that under certain conditions this method provides the true number-average molecular weight of copolymers without the use of two-dimensional methods.

Theory

Monodisperse Slices. We first assume the GPC slices to be monodisperse in composition as well as in molecular weight. Since the concentrations in GPC−LS are low, the response of the light-scattering instrument which is proportional to the Raleigh ratio of the ith GPC slice of constant volume ΔV, extrapolated to the angle $\Theta = 0$ is given by

$$R_i = K_i c_i M_i = K' \nu_i^2 c_i M_i \qquad (1)$$

where c_i is the weight concentration in the respective slice and the optical constants K and K' are defined as

$$K_i = K' \nu_i^2 = \frac{2\pi n_0^2}{\lambda_0^4 N_A} \nu_i^2$$

where $\nu = dn/dc$ is the refractive index increment, λ_0 is the wavelength of the incident beam in vacuum, and n_0 is the refractive index of the solvent at λ_0.

⊗ Abstract published in *Advance ACS Abstracts,* May 15, 1996.

Thus, the true molecular weight, M_i, in the ith GPC slice is obtained from the equation

$$M_i = \frac{R_i}{K_i c_i} = \frac{R}{K' {\nu_i}^2 c_i} \tag{2}$$

The signal S_i of the refractive index detector, which is conventionally used as a concentration detector in GPC−LS experiments, is proportional to the product of refractive index increment and weight concentration, $c_i = m_i/\Delta V$

$$S_i = k_{\mathrm{RI}}\Delta n = k_{\mathrm{RI}} c_i \nu_i \qquad \text{or} \qquad c_i = \frac{S_i}{k_{\mathrm{RI}}\nu_i} \tag{3}$$

Here k_{RI} is the absolute response factor of the instrument and m_i is the polymer mass within the slice of constant volume ΔV.

Using the definition of the number-average molecular weight and eq 2 we obtain

$$M_{\mathrm{n}} = \frac{\sum c_i}{\sum \frac{c_i}{M_i}} = \frac{m_{\mathrm{inj}}/\Delta V}{\sum \frac{K_i {c_i}^2}{R_i}} = \frac{m_{\mathrm{inj}}/(K'\Delta V)}{\sum \frac{{\nu_i}^2 {c_i}^2}{R_i}} \tag{4}$$

where m_{inj} is the total polymer mass injected.

Combination with eq 3 renders

$$M_{\mathrm{n}} = \frac{{k_{\mathrm{RI}}}^2 m_{\mathrm{inj}}/(K'\Delta V)}{\sum ({S_i}^2/R_i)} \tag{5}$$

In this equation the right hand side consists of known constants in the numerator and measurable quantities in the denominator only. Thus, according to eq 5 the true number-average molecular weight of the copolymer can be obtained without explicit knowledge of the refractive index increment, when the absolute calibration constant of the refractive index detector has been determined. It should be stressed again that eq 5 is strictly valid for monodisperse slices only. The error introduced by nonhomogenous slices will be discussed later.

It should be noted that the cancellation of the refractive index increment is also beneficial for the determintion of M_{n} for homopolymers in cases where the refractive index increment is a function of the molecular weight. In fact the knowledge of the refractive index increment is not necessary at all.

For other moments of the molecular weight distribution the situation is different. For the weight-average molecular weight the same approach leads to

$$M_{\mathrm{w}} = \frac{\sum c_i M_i}{\sum c_i} = \frac{\sum (R_i/{\nu_i}^2)}{K' m_{\mathrm{inj}}/\Delta V} \tag{6}$$

Since the refractive index increments of the individual fractions, ν_i, enter into this equation, it is not possible to determine the true weight-average molecular weight of the copolymer by GPC−LS unless the refractive index increments of all fractions are determined. When using the average refractive index increment of the whole sample, $\bar{\nu} = \sum w_i \nu_i$, we can obtain an apparent weight-average molecular weight

$$M_{\mathrm{w}}^{\mathrm{app}} = \frac{\sum c_i^{\mathrm{app}} M_i^{\mathrm{app}}}{\sum c_i^{\mathrm{app}}} = \frac{\sum \frac{c_i^{\mathrm{app}} R_i}{K' \cdot \bar{\nu}^2 \cdot c_i^{\mathrm{app}}}}{\sum c_i^{\mathrm{app}}} = \frac{\sum R_i}{m_{\mathrm{inj}} K' \bar{\nu}^2 \Delta V} \tag{7}$$

where c_i^{app} is an apparent concentration calculated according to eq 3 using $\bar{\nu}$. The apparent molecular weight calculated according to eq 7 is identical to the one obtained by a conventional batch measurement[17] as is easily shown by introducing eq 2 into eq 7.

Effect of Polydispersity of Slices. Up to now, we have assumed the slices to be monodisperse. However, in reality the ith GPC slice will be polydisperse with respect to molecular weight and/or composition. This means that it will contain a mixture of molecules having different composition, w, with refractive index increment $\nu(w)$ and molecular weight $M_i(w)$.

The weight concentration of copolymers having composition in the range $[w, w+\mathrm{d}w]$ in slice i can be expressed as

$$c_i(w, w+\mathrm{d}w) = \gamma_i(w) c_i \,\mathrm{d}w \tag{8}$$

where $\gamma_i(w)$ is the weight fraction of copolymers having composition w in slice i and c_i is the total polymer concentration in the respective slice. Then, the responses of the light-scattering instrument and the refractive index detector are given by

$$R_{\mathrm{i}} = K' c_i \int_0^1 \gamma_i(w) \nu^2(w) \mathrm{M}_i(w) \,\mathrm{d}w \tag{9}$$

$$S_i = k_{\mathrm{RI}} c_i \int_0^1 \gamma_i(w) \nu(w) \,\mathrm{d}w \tag{10}$$

We restrict ourselves to the case of a binary copolymer with $w = w_1$. For simplicity, we assume the refractive index increment and the molecular weight of the copolymer to be the weighted average of the refractive index increment and the molecular weight obtained from the homopolymer's calibration curves, respectively, i.e.

$$\nu(w) = \nu_1 w + \nu_2 (1 - w) \tag{11}$$

$$M_i(w) = M_{i,1} w + M_{i,2}(1 - w) \tag{12}$$

Doing so we obtain

$$R_i = K' c_i \int_0^1 \gamma_i(w) [\nu_1 w + \nu_2(1 - w)]^2 [M_{i,1} w + M_{i,2}(1 - w)] \,\mathrm{d}w \tag{13}$$

$$S_i = k_{\mathrm{RI}} c_i \int_0^1 \gamma_i(w) [\nu_1 w + \nu_2(1 - w)] \,\mathrm{d}w \tag{14}$$

Equations 5 and 4 become

$$M_{\mathrm{n}}^{\mathrm{app}} = \frac{m_{\mathrm{inj}}/\Delta V}{\sum_i \frac{c_i \{\int_0^1 \gamma_i(w)[\nu_1 w + \nu_2(1 - w)] \,\mathrm{d}w\}^2}{\int_0^1 \gamma_i(w)[\nu_1 w + \nu_2(1 - w)]^2 [M_{i,1} w + M_{i,2}(1 - w)] \,\mathrm{d}w}} \tag{15}$$

$$M_n = \frac{m_{inj}/\Delta V}{\sum_i \int_0^1 \frac{c_{i,w}\, dw}{M_i(w)}} = \frac{m_{inj}/\Delta V}{\sum_i c_i \int_{w=0}^1 \frac{\gamma_i(w)\, dw}{M_i(w)}} = \frac{m_{inj}/\Delta V}{\sum_i c_i \int_0^1 \frac{\gamma_i(w)\, dw}{M_{i,1} w + M_{i,2}(1-w)}} \qquad (16)$$

Equation 15 gives the apparent value of M_n as obtained by applying eq 5 to nonuniform slices, while eq 16 is the true value directly derived from the definition of M_n. By denoting $y = \nu_2/\nu_1$ and $x = M_{i,2}/M_{i,1}$, we finally obtain a quantity which allows for the estimation of the errors introduced by applying eq 5 to nonuniform slices:

$$\frac{M_n^{app}}{M_n} = \frac{\sum_i \left[\frac{c_i}{M_{i,1}} \int_0^1 \frac{\gamma(w)\, dw}{w(1-x)+x}\right]}{\sum_i \left[\frac{c_i}{M_{i,1}} \frac{\{\int_0^1 \gamma(w)[w(1-y)+y]\, dw\}^2}{\int_0^1 \gamma(w)[w(1-y)+y]^2 [w(1-x)+x]\, dw}\right]} \qquad (17)$$

The definition of x assumes that molecular weights of the two homopolymers differ in all slices by a constant factor. According to universal calibration,[1] this is the case if both homopolymers have similar Mark–Houwink parameters a.

Since the proposed method is useful for perfectly monodisperse slices, we are interested in the error introduced by heterogeneity. In order to introduce a large heterogeneity, we assume that we have no separation according to chemical composition at all. Under this assumption $\gamma_i(w) = \gamma(w)$ is independent of slice number i. Thus, we finally obtain

$$\frac{M_n^{app}}{M_n} = \frac{\int_0^1 \frac{\gamma(w)\, dw}{w(1-x)+x} \int_0^1 \gamma(w)[w(1-y)+y]^2 [w(1-x)+x]\, dw}{\{\int_0^1 \gamma(w)[w(1-y)+y]\, dw\}^2} \qquad (18)$$

We now calculate the ratio M_n^{app}/M_n for three different limiting cases. The simplest case is obtained when we assume a mixture of two homopolymers having identical eluograms. For this case γ is nonzero only for $w = 0$ and $w = 1$ and eq 18 becomes

$$\frac{M_n^{app}}{M_n} = \frac{[\bar{w}x + (1-\bar{w})][\bar{w} + y^2 x(1-\bar{w})]}{x[\bar{w} + (1-\bar{w})y]^2} \qquad (19)$$

where $\bar{w} = \int_0^1 \gamma(w) w\, dw$ is the average composition of the copolymer. Next we assume the contrary case that all chemically different molecules have the same weight fraction, i.e. $\gamma = \text{const} = 1$. The overall composition becomes $\bar{w} = 0.5$. This distribution function leads to

$$\frac{M_n^{app}}{M_n} = \frac{4 \ln x}{(x-1)(1+y)^2}\left(\frac{1+x}{2} - \frac{(1-x)(1-y)^2}{4} - \frac{2x(1-y)^2}{3} - \frac{y(1-x)(1-y)}{3} - xy(1-y)\right) \qquad (20)$$

Finally, we use a triangular distribution function of the form

$$\gamma(w) = \frac{2}{w_{Max}} w \qquad w \le w_{Max}$$

$$\gamma(w) = \frac{2}{(1-w_{Max})}(1-w) \qquad w \ge w_{Max}$$

$$\bar{w} = {}^1/_3(1 + w_{Max}) \qquad {}^1/_3 \le \bar{w} \le {}^2/_3$$

For this type of distribution function, we obtain

$$\int_0^1 \frac{\gamma(w)\, dw}{w(1-x)+x} = \frac{2}{w_{Max}(1-x)^2}\left[w_{Max}(1-x) + x \ln\left(\frac{x}{w_{Max}(1-x)+x}\right)\right] + \frac{2}{(1-w_{Max})(1-x)^2}[(1-x)(w_{Max}-1) - \ln(w_{Max}(1-x)+x)] \qquad (21)$$

$$\int_0^1 \gamma(w)(w(1-y)+y)\, dw = \frac{2}{w_{Max}}\left(\frac{1-y}{3} {w_{Max}}^3 + \frac{y}{2} {w_{Max}}^2\right) + \frac{2}{1-w_{Max}}\left[\frac{1-y}{3}({w_{Max}}^3 - 1) + \frac{(1-2y)}{2}(1 - {w_{Max}}^2) + y(1-w_{Max})\right] \qquad (22)$$

$$\int_0^1 \gamma(w)[w(1-y)+y]^2[w(1-x)+x]\, dw = \frac{2}{w_{Max}}\left(\frac{(1-x)(1-y)^2}{5} {w_{Max}}^5 + \frac{[2y(1-y)(1-x) + x(1-y)^2]}{4} {w_{Max}}^4 + \frac{(1-x)y^2 + 2xy(1-y)}{3} {w_{Max}}^3 + \frac{xy^2}{2} {w_{Max}}^2\right) + \frac{2}{(1-w_{Max})}\left(\frac{(1-x)(1-y)^2}{20}(1 + 4{w_{Max}}^5 - 5{w_{Max}}^4) + \frac{(1-y)[2y(1-x) + x(1-y)]}{12}(1 + 3{w_{Max}}^4 - 4{w_{Max}}^3) + \frac{y[(1-x)y + 2x(1-y)]}{6}(1 + 2{w_{Max}}^3 - 3{w_{Max}}^2) + \frac{xy^2}{2}(1 + {w_{Max}}^2 - 2w_{Max})\right) \qquad (23)$$

Equations 19–23 together with 18 allow an estimate of the error introduced due to nonhomogeneity of the slices, based on the relative values of refractive index increments of the homopolymers, $y = \nu_2/\nu_1$, the overall composition, $\bar{w}$, which can be easily obtained from NMR data or simply from the area of the refractive index detector signal and the refractive index increments of the homopolymers, and a reasonable estimate of the difference of the calibration curves of the homopolymers, $x = M_{i,2}/M_{i,1}$.

Figures 1–3 show the expected deviations from the true M_n values for $\bar{w} = 0.5$ according to the three models

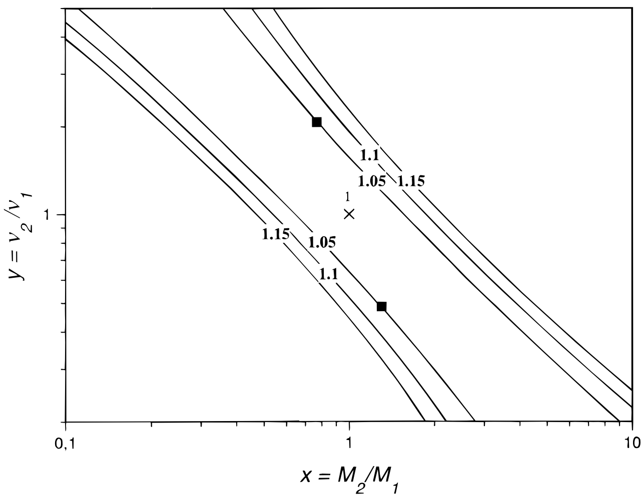

Figure 1. Error estimate M_n^{app}/M_n as a function of $x = M_{i,2}/M_{i,1}$ and $y = \nu_2/\nu_1$ for a mixture of two homopolymers according to eq 19 for $\bar{w} = 0.5$. The squares represent the symmetric x, y pairs for polystyrene/poly(methyl methacrylate) mixtures.

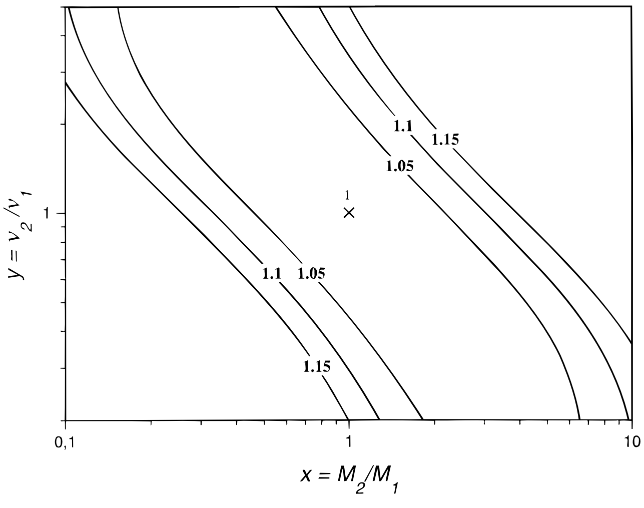

Figure 2. Error estimate M_n^{app}/M_n for copolymers with $\gamma(w)$ = constant according to eq 20 for $\bar{w} = 0.5$.

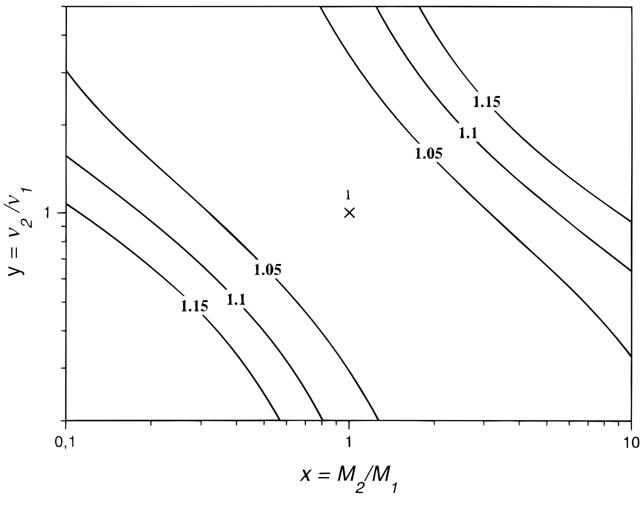

Figure 3. Error estimate M_n^{app}/M_n for a triangular distribution according to eqs 21–23 for $\bar{w} = 0.5$.

given above, as function of the parameters $x = M_{i,2}/M_{i,1}$ and $y = \nu_2/\nu_1$. It becomes clear that the error is largest for the model which assumes a mixture of two homopolymers (beside small areas in the upper right corner in which model 2 gives higher errors). Although the figures were given for $\bar{w} = 0.5$, the same trend is observed for other average compositions. Thus it seems useful to use eq 19 for the estimation of the expected maximum error. For negative values of $y = \nu_2/\nu_1$ the deviations become unacceptable.

Experimental Section

Mixtures of poly(methyl methacrylate) (PMMA) and polystyrene (PS) standards (Polymer Laboratories) with narrow molecular weight distribution where used to test the usefulness of the method.

Measurements were performed at room temperature in THF using three 5 μm styragel columns (10^3, 10^5, and 10^6 Å, PSS-SDV gel) each of 30 cm length at a flow rate of 1 mL/min. Light scattering measurements were performed using a Wyatt Technology DAWN-F DSP instrument equipped with an He–Ne laser ($\lambda_0 = 633$ nm). A Bischoff model 8110 ($\lambda_0 = 950$ nm) refractive index detector was used for the concentration detection. Typically, the injected concentrations were ca. 2g/L. The injection volume was 100 μL. Data sampling and evaluation of the raw data were performed by ASTRA 3.04 software at intervals of 1 s. Since it is known that the light-scattering instrument loses its sensitivity at the low molecular weight side of the chromatogram while the error of the RI detector relative to the light-scattering detector increases at the high molecular weight side of the chromatogram, the semilogarithmic plots of molecular weight versus elution volume were linearly extrapolated using EASY 7.02 software. In order to obtain consistency between the molecular weight values of the homopolymers and the mixtures, the molecular weight averages of the standards were determined with our GPC–LS equipment, and these values were used for the calculations of the molecular weights of the mixtures. The agreement between the weight-average molecular weights given by the vendor and the ones determined by us was within 10%.

Duplicate measurements were performed in all cases. In the first series the molecular weights of PS and PMMA was sufficiently different to assume near baseline resolution in order to meet the requirement of monodisperse slices. In the second series the mixtures were prepared in such a way that the different polymers were not completely separated in order to investigate the effect of compositional heterogeneity in the slices.

The molecular weight averages of the polymer mixtures were calculated using the following relations:

$$M_n^{mix} = \frac{1}{w_S/M_{n,S} + w_M/M_{n,M}} \tag{24}$$

$$M_w^{mix} = w_S M_{w,S} + w_M M_{w,M} \tag{25}$$

$$M_w^{app,mix} = \frac{{\nu_M}^2}{\bar{\nu}^2} w_M M_{w,M} + \frac{{\nu_S}^2}{\bar{\nu}^2} w_S M_{w,S} \tag{26}$$

where w_M, w_S, $\nu_M = 0.089$ mL/g, and $\nu_S = 0.184$ mL/g denote the weight fractions and refractive index increments of PMMA and PS, respectively.

Results and Discussion

In order to test the usefulness of the method and to check the estimated errors, mixtures of poly(methyl methacrylate) (PMMA) and polystyrene (PS) with narrow molecular weight distribution were prepared. These mixtures represent the limiting case of a "copolymer with infinite chemical heterogeneity". In contrast to real copolymers, the molecular weight averages of the mixtures can be easily calculated from composition and molecular weights of the individual homopolymers according to eqs 24–26. The experimental number- and weight-average molecular weights of the mixtures were determined by GPC–LS and compared to the calculated ones. Table 1 shows the results for the mixtures in which PMMA and PS have sufficiently different molecular weights to be well separated. Thus, the polydis-

Table 1. Comparison of Molecular Weight Averages Obtained by GPC−LS with the Calculated Molecular Weights for Well-Separated Mixtures of PS and PMMA (See Text for Codes)

code	$10^{-5}M_w^{mix}$ eq 25	$10^{-5}M_w^{app,mix}$ eq 26	$10^{-5}M_w^{GPC-LS}$	$10^{-5}M_n^{mix}$ eq 24	$10^{-5}M_n^{GPC-LS}$
mS11	3.96	5.34	5.49	2.80	2.64
Ms11	3.47	2.67	2.59	2.41	2.46
mS21	3.56	5.01	5.09	2.45	2.29
Ms21	4.11	3.32	3.07	2.88	2.89
mS12	4.32	5.40	5.71	3.20	3.05
Ms12	2.89	2.26	2.24	2.11	2.17

Table 2. Comparison of Molecular Weights Obtained by GPC−LS with the Calculated Molecular Weights for Nonseparated Mixtures of PS and PMMA (See Text for Codes)

code	$10^{-5}M_w^{mix}$ eq 25	$10^{-5}M_w^{app,mix}$ eq 26	$10^{-5}M_w^{GPC-LS}$	$10^{-5}M_n^{mix}$ eq 24	$10^{-5}M_n^{GPC-LS}$
MS11	5.12	5.85	6.12	4.41	4.60
ms11	2.29	2.15	2.16	1.83	2.09
MS21	5.11	5.90	6.14	4.32	4.52
ms21	2.46	2.33	2.29	1.89	1.83
MS12	5.14	5.64	5.79	4.55	4.73

persity of the slices with respect to composition can be neglected. The codes for the mixtures are as follows: capital letters S or M indicate the higher molecular weight PS (M_w = 516 500; M_n = 482 000) and PMMA (M_w = 508 700; M_n = 410 000) samples while the lower molecular weight PS (M_w = 170 000, M_n = 166 000) and PMMA (M_w = 298 000; M_n = 204 000) samples are designed as s and m, respectively. The numbers following the characters denote the relative amounts of the samples. The code Ms21 therefore has to be interpreted as a mixture consisting of two parts of the high molecular weight PMMA and one part of the low molecular weight PS.

Table 1 shows that the M_w values determined experimentally are close to the expected apparent molecular weights calculated using the average refractive index increments, the composition and molecular weight data of the components. These apparent molecular weights strongly deviate from the true weight-average molecular weights. In contrast to this observation, the calculated number-average molecular weights and those obtained by GPC−LS differ by less that ±10%, showing the correctness of eq 5 and indicating that the polydispersity of the slices due to axial dispersion can be neglected.

In order to test the effect of heterogeneity within the GPC slices, we performed measurements on mixtures in which the chromatograms of the components strongly overlap. Table 2 shows the results obtained.

Similar to the case of well separated samples, the weight-average molecular weights obtained by GPC−LS are close to the apparent molecular weights expected, but different from the true weight-average molecular weights, while the number-average molecular weights (except for one experiment) match the calculated values within less than 10%. This seems to indicate that, at least in our mixtures, the method is also not very sensitive toward the chemical heterogeneity in the GPC slices. The experimental deviations M_n^{app}/M_n are compared in Table 3 with those expected from eq 19 where we used $x = M_{PMMA}/M_{PS} = 1.3$ as a rough estimate which was obtained from the respective Mark−Houwink parameters.[18,19] As becomes obvious from Table 3, the expected errors and the errors found are in fair agreement. The larger experimental error of sample ms11 should be interpreted as uncertainty of the measurement rather than as a failure of the method.

Table 3. Comparison of Calculated Error Estimates, M_n^{app}/M_n, According to Eq 19 and Experimental Error (See Text for Codes)

code	M_n^{app}/M_n eq 19	M_n^{GPC-LS}/M_n^{mix} exp
MS11	1.05	1.05
ms11	1.05	1.14
MS21	1.04	1.05
ms21	1.04	0.97
MS12	1.06	1.04

Although it is shown that the requirement of monodisperse slices is of minor importance in our investigation, it should be kept in consideration. Copolymers which sufficiently meet the requirement will probably be copolymers synthesized by "living" polymerization, since these polymers only show chemical heterogeneity of second order (i.e. compositional changes along the polymer chain).

It should be stressed again at this point that the determination of molecular weights of copolymers by light scattering is a problem due to the two-dimensional distribution function of the polymer. Even if we would be able to determine the composition and therefore the refractive index increments of the individual slices, the determination of the molecular weights would not be correct, unless the slices are truly monodisperse. Therefore the use of a two-dimensional chromatographic system, not the implementation of further detectors, will be the method of choice to overcome this problem.

As shown by Goldwasser[15] and Rudin,[16] GPC−viscometry yields true M_n values for copolymers, even if the slices are heterogeneous. Their method relies on the validity of universal calibration for the copolymer under investigation whereas this requirement is not necessary for GPC−LS, i.e. separation according to size exclusion is not even required. In contrast, GPC−LS (in principle) requires monodisperse slices. Thus, both methods depend on different requirements and can be used to cross-check the results when using GPC equipped with both light-scattering and viscometric detection.

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MA9516495