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Effect of interdetector peak broadening and volume in size-exclusion chromatography with dual viscometric–concentration detection

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Abstract

For a polymer sample with a molecular mass distribution which obeys the log-normal function, the effect of intra- and extracolumn peak broadening, combined with the effect of the error in the interdetector volume determination, on uncorrected data of size-exclusion chromatography with the dual concentration–viscosity detection was theoretically examined. If the separation is not perfect and peaks recorded by the differential refractometric and viscometric detector are broadened to a different degree and/or an error in the interdetector volume occurs, the dependences of the detected molecular mass on elution volume are rotated and deformed. The error in the determination of uncorrected molecular mass averages for the whole polymer from the dual detection data is demonstrated and the effect of the Mark–Houwink–Kuhn–Sakurada exponent on uncorrected data was demonstrated. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Peak broadening combined with the uncertainty in attributing points on the concentration record to the points on the record of the molecular mass detector, e.g. viscometric [1–3] or light-scattering [4–12] detector, the condition of which is the determination of effective value of the interdetector volume [19,20], is a major obstacle in analyzing narrow molecular mass (M) distribution (MWD) samples by size-exclusion chromatography (SEC).

Both effects, the error, δ , in determination of the interdetector volume (detector lag) and peak broadening have already been studied [13–22]. The case, however, where peaks recorded by the two detectors are broadened to different extents, either as

a result of passing of eluent from one detector to the other in the serial connection or of different peak broadening due to differences in construction of the detectors in the parallel connection, has not yet been theoretically examined. The construction factors involve the volume necessary for the detection itself, e.g., the volume of the capillaries in the bridge connection for compensation of short-time flow-rate fluctuations in the viscometric detector [23,26]. In the one-capillary system, on the other hand, if short-time flow-rate fluctuations are dampened, the problem of the Lesec effect occurs – a hypothetical curvature of the recorded baseline due to change in viscosity of the eluent-containing polymer when passing the capillaries at the end of the separation system [24,25]. This effect cannot be included in our

considerations because its extent has not yet been determined experimentally.

Peak broadening of the viscometric and differential refractometer (DR) peak is quantified, in the simplest case, by two variances, called spreading factors, σ_α^2 and σ_0^2 , respectively, used for numerical correction of the peak broadening [26].

It is difficult to distinguish contributions of various parts of the separation system to the peak broadening. In the following, with some simplification, the case of evenly broadened signals of both detectors ($\sigma_\alpha^2 = \sigma_0^2$) will be referred to as intracolumn peak broadening (although it also involves some part of the extracolumn peak broadening, e.g., between the end of the column and the first detector) and the case of unevenly broadened signals ($\sigma_\alpha^2 \neq \sigma_0^2$) will be referred to as interdetector peak broadening (although the values of σ_α^2 and σ_0^2 express also the intracolumn peak broadening).

Parameters σ_α^2 , σ_0^2 and δ will be called “instrument parameters”. Our aim is to predict theoretically their influence on uncorrected experimental data.

2. Theoretical

In this paper, the effects of the interdetector volume combined with the interdetector- and column-peak broadening will be theoretically examined for a viscometric–concentration dual detection SEC analysis of a polymer with MWD which obeys log-normal function [27].

$$w(M) = \frac{1}{\beta\sqrt{\pi M}} \exp\left(-\frac{1}{\beta^2} \ln^2 \frac{M}{M_0}\right) \quad (1)$$

where $\beta = \sqrt{2 \ln(M_w/M_n)}$ and $M_0 = \sqrt{M_w M_n}$ where M_w and M_n are the weight- and number-average molecular mass, respectively. The uncorrected record (“chromatogram”) height, $F_k(V)$, of the detector sensitive to the k th power of M is expressed as [22]

$$F_k(V) = \int_{-\infty}^{\infty} W_k(V) G_k(V-y) dy \quad (2)$$

where $W_k(V) = W_0(V)M^k$ and $F_k(V) = F_0(V)M^k$ are, respectively, the corrected and uncorrected record heights and the kernel function $G_k(V-y)$ is called

here the “spreading” function of the record. The mechanism of peak broadening does not depend on the measured power of M but, as discussed in Section 1, it may depend on the construction of the particular detector. Hence, the subscript k with $G_k(V-y)$ only identifies to which record $G_k(V-y)$ refers. Eq. (2) as a special case of the Fredholm integral equation was first proposed for $k=0$ for the description of separation process in chromatography by Giddings and Eyring [31]. Eq. (2) can be solved analytically under two simplifying conditions: for MWD obeying the log-normal function and for the kernel function $G_0(V-y)$ approximated by the Gauss normal distribution. The solution for $k=0$ was first given by Tung [13,14]. The solution to Eq. (2) with the variance σ_k^2 of $G_k(V-y)$ is [22]

$$F_k(V) = \frac{\mu'_k}{\sqrt{\pi} \sqrt{2\sigma_k^2 + (\beta/B)^2}} \times \exp\left[-\frac{(V'_k - V)^2}{2\sigma_k^2 + (\beta/B)^2}\right] \quad (3)$$

where

$$\mu'_k = M_0^k \exp[k^2 \beta^2 / 4] \quad (4)$$

is the k th statistical moment of the distribution $w(M)$ about zero, defined [28]

$$\mu'_k = \int_0^{\infty} M^k w(M) dM \quad (5)$$

$$V'_k = V_k + \delta_k \quad (6)$$

where δ_k is the shift of the record due to the error in the determination of interdetector volume,

$$V_k = V_0 + k\beta^2 / 2B \quad (7)$$

and

$$V_0 = \frac{\ln M_0 - A}{B} \quad (8)$$

where parameters A and $B < 0$ of the equation (“calibration”)

$$\ln M = A + BV \quad (9)$$

are obtained, e.g., by calibration of the system with several narrow standard samples in a broad range of M , and their values are therefore not influenced by

the instrument parameters σ_k^2 and δ . For a given separation system, values of A and B will be assumed to be correct.

In the dual DR-viscometric detection, the intrinsic viscosity, $[\eta]$, is primarily determined from the dual record, e.g., as the ratio of specific viscosity calculated from the viscometric record divided by the polymer concentration, c , obtained from the DR data. It is assumed that c is low enough so that its effect, described by the Huggins constant, on the measurement can be neglected or that a due correction has been done [29,30]. Molecular mass is calculated by means of constants K and a of the Mark–Houwink–Kuhn–Sakurada (MHKS) equation [32]

$$[\eta] = KM^\alpha \quad (10)$$

It has been demonstrated [16,22] that the viscometric detector response (corresponding to zero concentration) can be expressed as $F_\alpha(V)$ defined by Eq. (3) for $k=\alpha$ and the DR response as $F_0(V)$. The results given below refer to either viscometric detection with MHKS exponent α or, for $\alpha=1$, to light scattering detection.

3. Results and discussion

3.1. Local molecular masses

The local uncorrected (uc) viscosity-average molecular mass is calculated from the dual detector record as

$$\bar{M}_\alpha(V,uc) = \left(\frac{F_\alpha(V)}{F_0(V)} \right)^{1/\alpha} \quad (11)$$

For $\alpha=1$, Eq. (11) describes the calculation of $\bar{M}_w(V,uc)$. Using substitutions

$$p = (2\sigma_0^2 + (\beta/B)^2)^{-1} \quad (12)$$

and

$$q = (2\sigma_\alpha^2 + (\beta/B)^2)^{-1} \quad (13)$$

the DR and viscosity chromatograms, respectively, can be expressed according to Eq. (3) (cf., the text following Eq. (10)) as

$$F_0(V) = \sqrt{\frac{p}{\pi}} \exp \left[-p(V_0 - V)^2 \right] \quad (14)$$

and

$$F_\alpha(V) = \mu'_\alpha \sqrt{\frac{q}{\pi}} \exp \left[-q(V'_\alpha - V)^2 \right] \quad (15)$$

where

$$V'_\alpha = V_0 + \alpha\beta^2/2B + \delta \quad (16)$$

where $\delta = \delta_\alpha$ refers to the viscometric record. (Because we are only interested in the relative shifts of the records, it is not necessary to consider the shift of both records; without the lack of generality, it is sufficient to consider only the shift of one record).

With chromatograms defined by Eqs. (14) and (15), the local molecular-weight average \bar{M}_α can be expressed according to Eq. (11) and taking logarithm (the details of calculation are given in Appendix A) as

$$\begin{aligned} \ln \bar{M}_\alpha(V,uc) &= \frac{1}{2\alpha} \ln \frac{q}{p} + \frac{p-q}{\alpha B^2} \\ &\quad \times \left(\ln \sqrt{\bar{M}_w \bar{M}_n} - A - BV \right)^2 \\ &\quad + \left[\frac{1+\alpha}{2} (1-\Sigma) - \frac{1+2\alpha}{2} \frac{\Delta}{2\alpha} \right] \ln \bar{M}_w \\ &\quad + \left[\frac{1-\alpha}{2} (1-\Sigma) - \frac{1-2\alpha}{2} \frac{\Delta}{2\alpha} \right] \ln \bar{M}_n \\ &\quad + \left(\Sigma + \frac{\Delta}{2\alpha} \right) (A + BV) - \frac{Z}{2\alpha} \end{aligned} \quad (17)$$

where

$$\Sigma = (\beta^2/B^2)q \quad (18)$$

$$\Delta = (4\delta/B)q \quad (19)$$

$$Z = 2\delta^2q \quad (20)$$

Eq. (17) describes deformations of the calibration (Eq. (9)), calculated from the experimental data obtained by the dual detection, due to the column peak broadening, interdetector peak broadening and error δ in the determination of the interdetector volume. For $\sigma_0^2 = \sigma_\alpha^2$ and $\alpha=1$, using identity valid for log-normal MWD

$$\bar{M}_z = \bar{M}_w (\bar{M}_w / \bar{M}_n) \quad (21)$$

where \bar{M}_z is the z -average molecular mass, Eq. (17) reduces into

$$\ln \overline{M}_w(V,uc) = (1 - \Sigma) \overline{M}_w - (\Delta/2) \ln \sqrt{\overline{M}_w \overline{M}_z} - Z/2 + (\Sigma + \Delta/2)(A + BV) \quad (22)$$

which is Eq. (20) of Ref. [22] valid for the weight-average detection. Although all three effects are described in single equation, it is more graphical to pick up individually the effects of σ_0^2 , σ_α^2 , δ and α on the analyses of samples differing in polydispersity defined as $\overline{M}_w/\overline{M}_n$. Two samples of molecular masses $\overline{M}_w = 1.1 \cdot 10^5$ and $\overline{M}_n = 1.0 \cdot 10^5$ (further referred to as sample I) and $\overline{M}_w = 1.4 \cdot 10^5$ and $\overline{M}_n = 1.0 \cdot 10^5$ (sample II) were chosen for the demonstration of the effects. The constants of the Eq. (9) were chosen $A=20$ and $B=-0.2$. The corrected and uncorrected chromatograms are depicted for comparison in Fig. 1.

The effect of the (interdetector) peak broadening on the uncorrected M is demonstrated in Figs. 2–5 the effect of δ in Figs. 6–9 both effects for $\alpha=1$ (Figs. 2 and 3, 6 and 7) and $\alpha=0.5$ (Figs. 4 and 5, 8 and 9) for sample I (Figs. 2, 4, 6, 8) as well as for sample II (Figs. 3, 5, 7, 9). The values of the instrument parameters (σ_0^2 , σ_α^2 , δ) and (corrected and uncorrected) MWD averages (discussed in Section 3.2) are shown in Tables 4–7.

From Figs. 2–5 it can be seen that the (column)

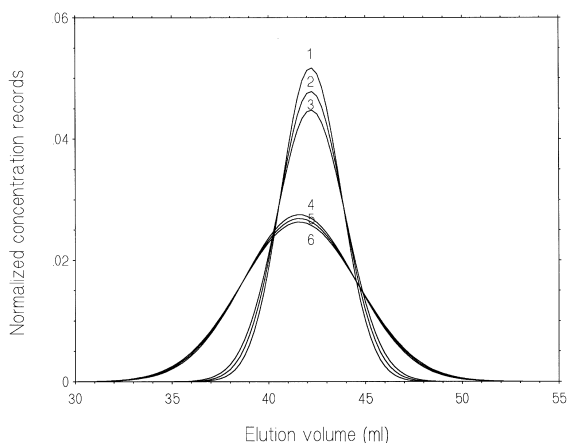


Fig. 1. Comparison of concentration records, $F_0(V)$ for two polymer samples. Sample I: $\overline{M}_w = 1.1 \cdot 10^5$, $\overline{M}_n = 1.0 \cdot 10^5$, sample II: $\overline{M}_w = 1.4 \cdot 10^5$, $\overline{M}_n = 1.0 \cdot 10^5$. Chromatograms of both samples are broadened according to Eq. (14) using spreading factors $\sigma_0^2 = 0, 0.4, 0.8$. Curves 1 (corrected), 2 and 3 for sample I and 4 (corrected), 5, 6, for sample II.

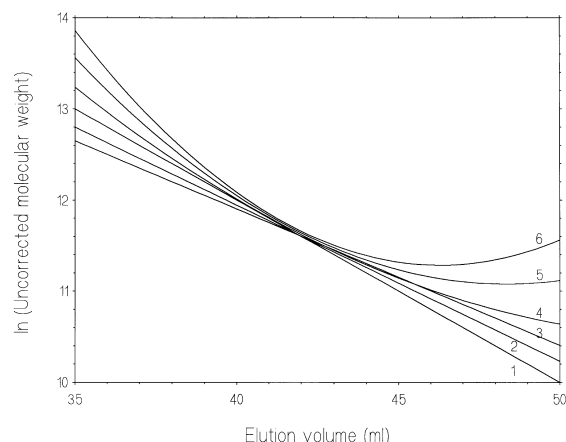


Fig. 2. Influence of spreading factors σ_0^2 and σ_α^2 (for $\delta=0$): the dependence of (natural logarithm of) uncorrected molecular mass $\ln \overline{M}_\alpha(uc)$ calculated according to Eq. (17) for sample I. The values of instrument parameters σ_0^2 and σ_α^2 , together with corrected and uncorrected molecular masses, are in Table 4. The MHKS exponent was $\alpha=1$.

peak broadening ($\sigma_\alpha = \sigma_0$) causes the dependences of $\ln \overline{M}_\alpha(V,uc)$ vs. V to rotate [16,22] while the interdetector broadening causes them to bend the $\ln \overline{M}_\alpha(V,uc)$ vs. V dependence upwards. (Only the case $\sigma_\alpha > \sigma_0$ was considered because larger peak spreading is expected in the viscometric record due to the volume of measuring capillaries. The case $\sigma_\alpha < \sigma_0$ has the opposite effect).

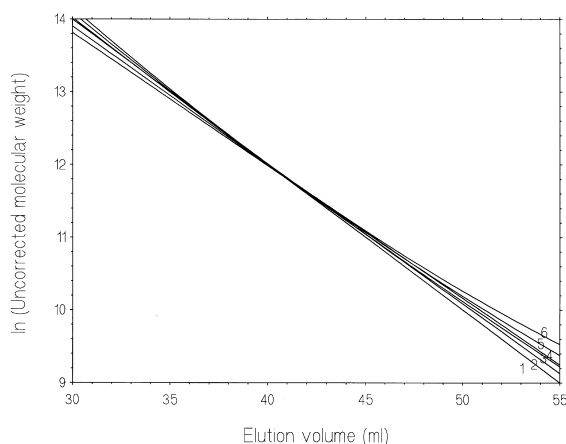


Fig. 3. The same dependences as in Fig. 2 calculated for sample II. The data are in Table 4.

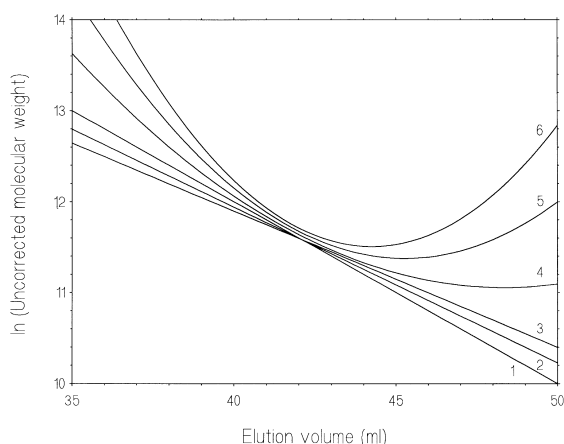


Fig. 4. The same dependences as in Fig. 2 calculated for sample I for the MHKS exponent $\alpha=0.5$. The data are in Table 5.

The error, δ , in interdetector volume causes the dependences $\ln \bar{M}_\alpha(V,uc)$ to rotate but the linearity of the dependences is maintained (Figs. 6–9). Only values of δ which give the (physically possible) negative slope of the uncorrected dependence of $\ln \bar{M}_\alpha(V,uc)$ were employed in the calculations.

As expected, the effect of δ as well as of σ_0^2 and σ_α^2 is more pronounced for sample I ($\bar{M}_w/\bar{M}_n=1.1$) compared to sample II ($\bar{M}_w/\bar{M}_n=1.4$). The effects are also less pronounced for $\alpha=0.5$ than for $\alpha=1$. This demonstrates the advantage of the light scattering detector over the viscometric one: if lower power

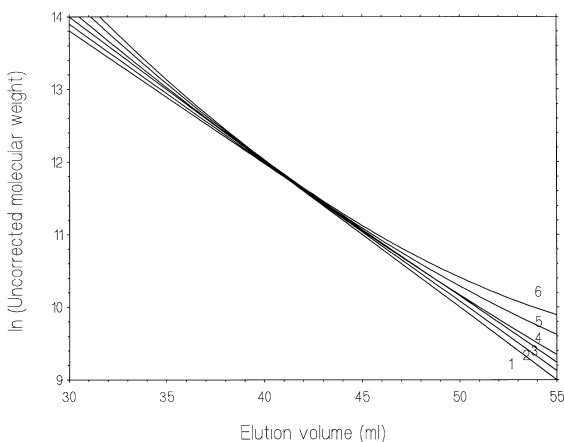


Fig. 5. The same dependences as in Fig. 4 calculated for sample II. The data are in Table 5.

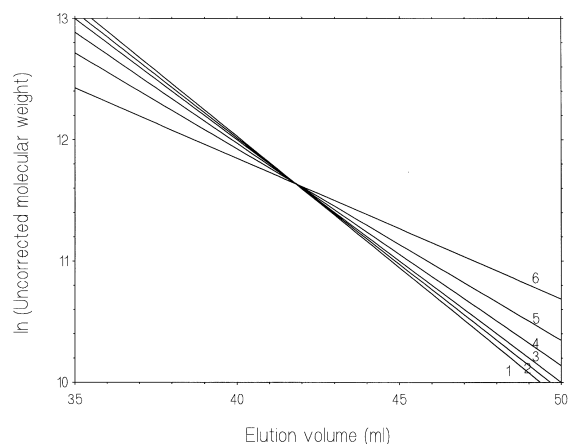


Fig. 6. The influence of the error δ in the interdetector volume: the dependence of (natural logarithm of) uncorrected molecular mass

of M is detected, the information is more prone to be lost due to the non-ideal separation and vice versa.

The values of uncorrected molecular masses contained in the Tables are discussed in Section 3.2.

3.2. Molecular mass averages of the whole polymer

The uncorrected number-, weight- and z -average molecular masses of the whole polymer are for $l=0$, 1 and 2, respectively, given by

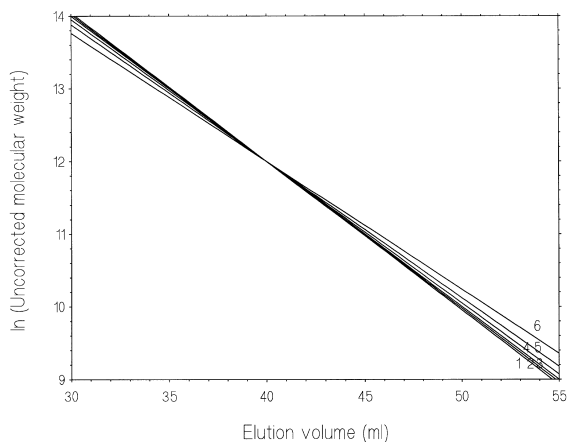


Fig. 7. The same dependences as in Fig. 6 calculated for sample II. The data are in Table 6.

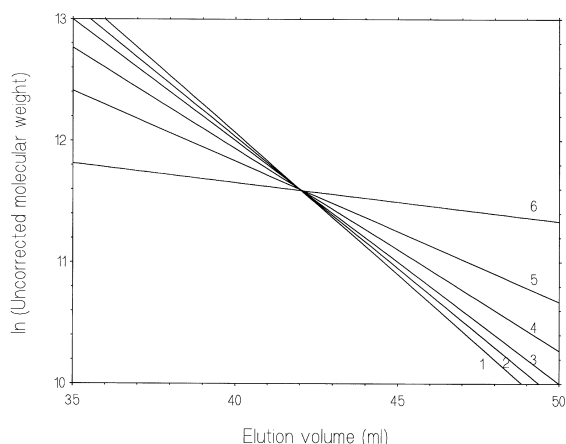


Fig. 8. The same dependences as in Fig. 7 calculated for sample I for the MHKS exponent $\alpha=0.5$. The data are in Table 7.

$$\bar{M}_l(\text{uc}) = \frac{\int_{-\infty}^{\infty} \bar{M}_\alpha^l(V, \text{uc}) F_0(V) dV}{\int_{-\infty}^{\infty} \bar{M}_\alpha^{l-1}(V, \text{uc}) F_0(V) dV} \quad (23)$$

Evaluating the integrals in the calculation of $\bar{M}_l(\text{uc})$ is possible if the condition

$$\sigma_\alpha^2 - \sigma_\alpha'^2 < \frac{\alpha}{B^2} \ln \bar{M}_w / \bar{M}_n \quad (24)$$

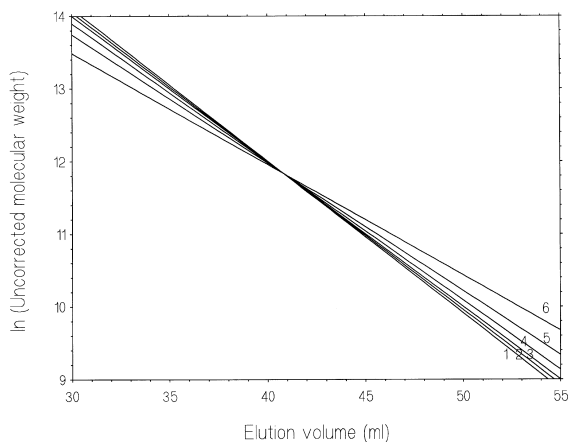


Fig. 9. The same dependences as in Fig. 8 calculated for sample II. The data are in Table 7.

is fulfilled. $\bar{M}_n(\text{uc})$ and $\bar{M}_w(\text{uc})$ can be calculated for all values of σ_0^2 and σ_α^2 . The details of the calculation are given in Appendix B). The result is

$$\bar{M}_1(\text{uc}) = \bar{M}_w^{\frac{\alpha+1}{2\alpha}} \bar{M}_n^{\frac{\alpha-1}{2\alpha}} \sqrt{D_l} \left(\frac{\bar{M}_w}{\bar{M}_n} \right)^{\left(\frac{\alpha^2 \beta^2}{B^2} + \frac{4\alpha\delta}{B} \right) E_1} \exp(2\delta^2 E_1) \quad (25)$$

where D_l and E_l are, together with the simplified formulae for particular values of l , α and q , for later discussion as well as for the reader's convenience, given in Tables 1 and 2. For the uncorrected polydispersity, we have

$$\frac{\bar{M}_w(\text{uc})}{\bar{M}_n(\text{uc})} = \sqrt{\frac{D_1}{D_0}} \left(\frac{\bar{M}_w}{\bar{M}_n} \right)^{\left(\frac{\alpha^2 \beta^2}{B^2} + \frac{4\alpha\delta}{B} \right) (E_1 - E_0)} \exp(2\delta^2 (E_1 - E_0)) \quad (26)$$

where D_1/D_0 and $E_1 - E_0$ are, for the reader's convenience, given in Table 3. From Table 1 it is seen that for $\sigma_\alpha^2 = \sigma_0^2$ D_l disappears from the equations ($D_l = 1$ for $p = q$, α arbitrary).

By comparison, it ensues that Eqs. (25) and (36) of Ref. [22] (for $l=1$, which corresponds to w -detection) are identical in the limit $\alpha=1$ and $q=p$ ($\sigma_\alpha = \sigma_0$, w -detection).

The uncorrected values of molecular masses together with correct values as well as instrument and

Table 1
Formulae for D_l in Eq. (25)

l	$\alpha \neq 1$	$\alpha = 1$
l	$\left(\frac{p}{q} \right)^{1/\alpha} \frac{\alpha + l(q-p)}{\alpha + (q-p)(l-1)}$	$\frac{p}{q} \frac{l(p-q)-1}{j(p-q)-p+q-1}$
0	$\left(\frac{p}{q} \right)^{1/\alpha} \frac{\alpha}{\alpha p + p - q}$	$\frac{p}{q(1+p-q)}$
1	$\left(\frac{p}{q} \right)^{1/\alpha} \frac{\alpha - p + q}{\alpha}$	$\frac{p(1+q-p)}{q}$
2	$\left(\frac{p}{q} \right)^{1/\alpha} \frac{\alpha + 2(q-p)}{\alpha - p + q}$	$\frac{p(2p-2q)-1}{q(p-q-1)}$

Table 2
Formulae for E_l in Eq. (25)

l	$\alpha \neq 1, p \neq q$	$\alpha \neq 1, q = p$	$\alpha = 1, q \neq p$	$\alpha = 1, q = p$
l	$\frac{pq(\alpha^2 p + \alpha p(1-2l) + l(p-q)(1-l))}{2\alpha(\alpha p + (q-p)(l-1))(\alpha p + l(q-p))}$	$\frac{p(2l - \alpha - 1)}{2\alpha^2}$	$\frac{pq(l(p-q) - 2p)(1-l)}{2(l(p-q) - 2p + q)(l(p-q) - p)}$	p^{l-1}
0	$\frac{pq(\alpha + 1)}{2\alpha(q - \alpha p - p)}$	$-\frac{p(\alpha + 1)}{2\alpha^2}$	$\frac{pq}{q - 2p}$	$-p$
1	$\frac{pq(1 - \alpha)}{2\alpha(\alpha p - p + q)}$	$\frac{p(1 - \alpha)}{2\alpha^2}$	0	0
2	$\frac{pq(\alpha^2 p - 3\alpha p + 2(p - q))}{2\alpha(p - \alpha p - q)(\alpha p + 2(q - p))}$	$\frac{p(3 - \alpha)}{2\alpha^2}$	$\frac{pq}{2q - p}$	p

Table 3
Formulae for D_1/D_0 and $E_1 - E_0$ in Eq. (26)

	D_1/D_0	$E_1 - E_0$
$\alpha \neq 1, q \neq p$	$\frac{(\alpha - p + q)(\alpha + p - q)}{\alpha^2}$	$\frac{-pq^2}{(\alpha p - p + q)(\alpha p + p - q)}$
$\alpha = 1, q \neq p$	$(1 - p + q)(1 + p - q)$	$\frac{pq}{2p - q}$
$\alpha = 1, q = p$	1	p

MWD parameters are given in Tables 4–7 for analysis the results of which are depicted in Figs. 1–9.

From the Tables we can see that the uncorrected values deviate from the correct ones; for the nar-

rower MWDs and for $\alpha = 0.5$, the deviation is larger than for broad MWDs and $\alpha = 1$. This is in accord with the conclusions drawn from the analysis of the uncorrected local molecular masses given in Section 3.1.

Table 4
Influence of the variance of peak spreading functions σ_0^2 (concentration signal) and σ_α^2 (viscometric signal) on the uncorrected molecular masses $\bar{M}_i(\text{uc})$ calculated for $\alpha = 1$ according to Eq. (25) for two samples differing in polydispersity

Curve	σ_0^2	σ_α^2	Sample I			Sample II		
			$\bar{M}_n(\text{uc})$	$\bar{M}_w(\text{uc})$	$\frac{\bar{M}_w(\text{uc})}{\bar{M}_n(\text{uc})}$	$\bar{M}_n(\text{uc})$	$\bar{M}_w(\text{uc})$	$\frac{\bar{M}_w(\text{uc})}{\bar{M}_n(\text{uc})}$
1	0	0	100 000	110 000	1.100	100 000	140 000	1.40
2	0.4	0.4	101 379	110 000	1.085	101 539	140 000	1.37
3	0.8	0.8	102 424	110 000	1.073	102 965	140 000	1.35
4	0.2	0.3	102 952	111 704	1.085	102 092	140 763	1.37
5	0.2	0.4	105 080	113 382	1.079	103 378	141 523	1.36
6	0.2	0.5	107 135	115 036	1.073	104 641	142 278	1.35

For denotation curves, see Figs. 2 and 3. Correct values are calculated for $\sigma_\alpha = \sigma_0$, see curve 1.

Table 5

The same molecular mass averages as in Table 4 calculated for $\alpha=0.5$

Curve	σ_0^2	σ_α^2	Sample I			Sample II		
			$\overline{M}_n(\text{uc})$	$\overline{M}_w(\text{uc})$	$\frac{\overline{M}_w(\text{uc})}{\overline{M}_n(\text{uc})}$	$\overline{M}_n(\text{uc})$	$\overline{M}_w(\text{uc})$	$\frac{\overline{M}_w(\text{uc})}{\overline{M}_n(\text{uc})}$
1	0	0	100 000	110 000	1.1	100 000	140 000	1.400
2	0.4	0.4	101 032	109 623	1.085	101 152	139 466	1.37
3	0.8	0.8	101 813	109 343	1.073	102 215	139 981	1.35
4	0.2	0.3	104 416	113 322	1.085	102 535	141 391	1.37
5	0.2	0.4	108 201	116 857	1.079	104 452	143 062	1.36
6	0.2	0.5	111 931	120 403	1.075	106 340	144 740	1.35

For denotation curves, see Figs. 4 and 5. Correct values are calculated for $\sigma_\alpha = \sigma_0 = 0$, see curve 1.

Table 6

Influence of the error δ in the interdetector volume on the uncorrected molecular mass averages $\overline{M}_i(\text{uc})$ calculated according to Eq. (25) for $\alpha=1$

Curve	δ	Sample I			Sample II		
		$\overline{M}_n(\text{uc})$	$\overline{M}_w(\text{uc})$	$\frac{\overline{M}_w(\text{uc})}{\overline{M}_n(\text{uc})}$	$\overline{M}_n(\text{uc})$	$\overline{M}_w(\text{uc})$	$\frac{\overline{M}_w(\text{uc})}{\overline{M}_n(\text{uc})}$
1	-0.04	101 749	110 000	1.081	101 651	140 000	1.37
2	-0.02	100 837	110 000	1.090	100 812	140 000	1.38
3	0	100 000	110 000	1.100	100 000	140 000	1.40
4	0.04	104 416	110 000	1.116	98 450	140 000	1.42
5	0.1	108 201	110 000	1.135	96 307	140 000	1.45
6	0.2	111 931	110 000	1.152	93 193	140 000	1.50

For denotation curves, see Figs. 6 and 7. Correct values are calculated for $\delta=0$, see curve 3.

4. Conclusions

The correlation between corrected and uncorrected dependences of the molecular mass vs. elution volume as well as MWD averages for the whole

polymer calculated from the combination of signals of the viscometric and concentration detectors, were theoretically examined. The formulae describing the combined effect of the column peak broadening, interdetector peak broadening and error in the inter-

Table 7

The same molecular mass averages as in Table 6 calculated for $\alpha=0.5$

Curve	δ	Sample I			Sample II		
		$\overline{M}_n(\text{uc})$	$\overline{M}_w(\text{uc})$	$\frac{\overline{M}_w(\text{uc})}{\overline{M}_n(\text{uc})}$	$\overline{M}_n(\text{uc})$	$\overline{M}_w(\text{uc})$	$\frac{\overline{M}_w(\text{uc})}{\overline{M}_n(\text{uc})}$
1	-0.04	101 411	109 487	1.079	101 265	139 414	1.37
2	-0.02	100 652	119 761	1.090	100 616	139 713	1.38
3	0	100 000	110 000	1.100	100 000	140 000	1.40
4	0.04	99 006	110 366	1.114	98 863	140 534	1.42
5	0.1	98 274	110 640	1.125	97 391	141 239	1.45
6	0.2	99 040	110 353	1.114	95 529	142 150	1.48

For denotation curves, see Figs. 8 and 9. Correct values are calculated for $\delta=0$, see curve 3.

detector volume were given. The relation between corrected and uncorrected data for two samples differing in polydispersity, both for two values of MHKS exponent, α , were presented. The error both in interdetector volume and column peak broadening cause change of slope of the dependence $\overline{M}_\eta(V,uc)$ whereas the interdetector peak broadening causes the change of shape of the dependences; if the peak broadening of the viscometric peak is larger, the correlations are bent upwards and vice versa.

If there is no interdetector peak broadening ($\sigma_\alpha^2 = \sigma_0^2$), the molecular mass average of the whole polymer \overline{M}_α corresponding to the method of detection) is correctly determined [6,7] and the other averages are aggravated by errors. On the contrary, if the interdetector peak broadening is present ($\sigma_\alpha^2 \neq \sigma_0^2$), an error in determining all averages of the whole polymer, including \overline{M}_α , is expected. For this reason, extraordinary attention has to be paid, when evaluating experimental data, to whether both peaks are broadened to the same degree or a numerical correction has to be done.

Compared to the serial connection of the detectors, the expected difference in peak broadening of the two signals is lower in the parallel one because the eluent flows directly from the columns into both detectors. From this it follows that the parallel connection [26] is the preferred one.

Effects of the instrument parameters on the dependences $\ln \overline{M}_\eta(V,uc)$ as well as on the uncorrected MWD averages of the whole polymer are more pronounced for less polydisperse samples and higher MHKS exponent ($\alpha=1$) than for more polydisperse ones and lower values of α ($\alpha=0.5$).

The commercial software [26] allows one to compensate for the error caused by the peak broadening provided that values of instrument parameters are correctly determined. It is, however, not an easy task to find reliable values of them, because they may compensate one for another [21]. Thus the values of α_α^2 and σ_0^2 found, e.g., by a numerical procedure for one sample, under the condition that corrected values of \overline{M}_w and \overline{M}_n equal to the declared ones, which may work well for one sample, may fail for another one, especially if it is less polydisperse. The aim of this paper is also to show the possible errors due to an erroneous choice of the instrument parameters. An experimental study of the reliability

of instrument parameters, involving several samples of various polydispersity, also very narrow ones [11], would be highly profitable.

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Appendix A

Derivation of Eq. (17)

Introducing $F_\alpha(V)$ and $F_0(V)$ into Eq. (11) we have

$$M(V) = E_1 \left(\frac{q}{p} \right)^{\frac{1}{2\alpha}} \exp E_2 \quad (\text{A1})$$

where

$$E_1 = M_0 \exp \frac{\alpha\beta^2}{4} = \overline{M}_w^{1+\alpha} \overline{M}_n^{1-\alpha} \quad (\text{A2})$$

and

$$\begin{aligned} E_2 &= \frac{p}{\alpha} (V_0 - V)^2 - \frac{q}{\alpha} (V'_\alpha - V)^2 \\ &= Q - q \left[\left(\frac{\alpha\beta^2}{2B} + \delta \right) \left(2(V_0 - V) + \frac{\alpha\beta^2}{2B} + \delta \right) \right] \\ &= Q - q \left[\left(\frac{\alpha\beta^2}{B^2} + \frac{2\delta}{B} \right) (\ln \sqrt{\overline{M}_w \overline{M}_n} - A - BV \right. \\ &\quad \left. + \frac{\alpha}{2} \ln \frac{\overline{M}_w}{\overline{M}_n} + \frac{B}{2} \delta \right) \right] \quad (\text{A3}) \end{aligned}$$

where

$$\begin{aligned} Q &= \frac{(p-q)}{\alpha} (V_0 - V)^2 \\ &= \frac{p-q}{\alpha B^2} (\ln \overline{M}_w \overline{M}_n - A - BV)^2 \quad (\text{A4}) \end{aligned}$$

Introducing E_1 and E_2 into Eq. (A1) and taking logarithm gives Eq. (17).

Appendix B

Derivation of Eq. (25)

The integrals in Eq. (23)

$$I_{i,\alpha} = \int_{-\infty}^{\infty} \overline{M}_{\alpha}^i(V,uc) F_0(V) dV \quad (B1)$$

with $i=1$ and $l-1$, can be, according to the definition of local molecular mass (Eq. (11)), expressed as

$$I_{i,\alpha} = \int_{-\infty}^{\infty} \left(\frac{F_{\alpha}(V)}{F_0(V)} \right)^i F_0(V) dV \quad (B2)$$

Introducing $F_{\alpha}(V)$ and $F_0(V)$ from Eqs. (14) and (15), respectively, and rearranging the exponential terms by using the identity

$$\begin{aligned} & p \left(\frac{i}{\alpha} - 1 \right) (V - V_0)^2 - q \frac{i}{\alpha} (V - V'_{\alpha})^2 \\ &= \left((p - q) \frac{i}{\alpha} - p \right) \left(V - \frac{p \left(\frac{i}{\alpha} - 1 \right) V_0 - q \frac{i}{\alpha} V'_{\alpha}}{p \left(\frac{i}{\alpha} - 1 \right) - q \frac{i}{\alpha}} \right)^2 \\ &\quad - \frac{\frac{i}{\alpha} \left(\frac{i}{\alpha} - 1 \right) pq (V'_{\alpha} - V_0)^2}{p \left(\frac{i}{\alpha} - 1 \right) - \frac{i}{\alpha} q} \end{aligned} \quad (B3)$$

the integration can be performed (the Poisson integral) for

$$\left((p - q) \frac{i}{\alpha} - p \right) < 0 \quad (B4)$$

from which condition (Eq. (24)) directly ensues. The result of integration is

$$\begin{aligned} I_{i,\alpha} &= \frac{\mu'_{\alpha} \frac{i}{\alpha} q^{\frac{i}{\alpha}}}{p^{\frac{i}{\alpha} - \frac{1}{2}} \left(\frac{i}{\alpha} (q - p) + 1 \right)^{\frac{1}{2}}} \\ &\quad \times \exp \left(- \frac{\frac{i}{\alpha} \left(\frac{i}{\alpha} - 1 \right) pq (V'_{\alpha} - V_0)^2}{p \left(\frac{i}{\alpha} - 1 \right) - \frac{i}{\alpha} q} \right) \end{aligned} \quad (B5)$$

where

$$(\mu'_{\alpha})^{\frac{i}{\alpha}} = \overline{M}_{\alpha}^{\frac{\alpha+1}{2\alpha} i} \overline{M}_{\alpha}^{\frac{\alpha-1}{2\alpha} i} \quad (B6)$$

The term $(V'_{\alpha} - V_0)$ is expressed using Eq. (16) as

$$V'_{\alpha} - V_0 = \frac{\alpha \beta^2}{2B} + \delta \quad (B7)$$

by which the exponential term in Eq. (B5) can be expressed using the identity

$$\begin{aligned} & \exp \left[2E_l \left(\frac{\alpha \beta^2}{2B} + \delta \right)^2 \right] = \\ & \left(\frac{\overline{M}_w}{\overline{M}_n} \right)^{2E_l \left(\frac{1}{2} \frac{\alpha^2 \beta^2}{B^2} + \frac{2\alpha \delta}{B} \right)} \exp(2E_l \delta^2) \end{aligned} \quad (B8)$$

where the factor of 1/2 has been included in E_l (given in Table 2 to show the correspondence of the formulae with those derived in Ref. [22]). Introducing integrals into Eq. (23) and using the identities

$$D_l = \frac{f_l}{f_{l-1}} = \left(\frac{p}{q} \right)^{\frac{1}{\alpha}} \frac{\alpha + l(q - p)}{\alpha + (l - 1)(q - p)} \quad (B9)$$

where

$$f_j = \frac{q^{\frac{j}{\alpha}} p^{1 - \frac{j}{\alpha}}}{\left(\frac{j}{\alpha} (q - p) + p \right)} \quad (B10)$$

in the calculation of D_l , and

$$\begin{aligned} E_l &= g_l - g_{l-1} \\ &= \frac{pq(\alpha^2 p + \alpha p(1 - 2l) + l(p - q)(1 - l))}{\alpha(\alpha p + (q - p)(l - 1))(\alpha p + l(q - p))} \end{aligned} \quad (B11)$$

where

$$g_j = \frac{\frac{j}{\alpha} \left(\frac{j}{\alpha} - 1 \right) pq}{p \left(\frac{j}{\alpha} - 1 \right) - \frac{j}{\alpha} q} \quad (B12)$$

in the calculation of E_l , Eq. (25) directly ensues.

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