

# An Analysis of the Accuracy of Determining Molar-Mass Averages of Polymers by GPC with an On-Line Light-Scattering Detector

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## Synopsis

The effect of errors of concentration and molar-mass detectors in GPC on the accuracy of determining molar-mass averages  $\bar{M}_n$  and  $\bar{M}_w$  was analyzed. Model calculations show that by means of GPC with an on-line low-angle laser light-scattering (LALLS) photometer only  $\bar{M}_w$  can be determined with acceptable accuracy.  $\bar{M}_n$  can be determined with acceptable accuracy only for polymers that have very small polydispersities.  $\bar{M}_n$  can be determined with greater accuracy from data of a concentration detector and chromatographic-column-calibration data. The most suitable procedure for the determination of  $\bar{M}_w$  seems to be a direct integration of the molar-mass detector output, even if the error due to neglecting the second virial coefficient term is significant. Compared with the inaccuracy of detectors, axial dispersion appears not to be the main source of errors in GPC with an on-line molar-mass detector.

## INTRODUCTION

In our preceding communication<sup>1</sup> we examined the accuracy of determination of the molar-mass distribution (MMD) by means of GPC with an on-line low-angle laser light-scattering photometer as a molar-mass detector. We derived a relation between the error in the molar-mass determination  $\sigma_M$  and errors caused by concentration and molar-mass detectors,  $\sigma_c$  and  $\sigma_R$ , respectively. The other effects on the accuracy of molar-mass determination, which include the axial dispersion inside and outside the chromatographic column, were intentionally omitted. A quantity  $C_r$ , which gives the relative part of the area under the MMD curve,  $w(\log M)$ , when the error  $(\sigma_M)_d$  is higher than a certain limit, was defined as the criterion of reliability of determination of a certain MMD.<sup>1</sup> By model calculations, we demonstrate the dependence of  $C_r$  on the MMD parameters of the analyzed polymer, that is, its average molar mass and the degree of polydispersity, and on the magnitude of injection at various working regimes of the molar-mass detector. [The subscript  $d$  at  $(\sigma_M)_d$  helps to distinguish it from  $(\sigma_M)_c$ , that is, from the error in the determination of  $M$  caused by using the concentration detector and a calibration curve].

In this paper, we use relations derived earlier; our model calculations are aimed at finding the effect of inaccuracy in the MMD determination on the most important moments: the number- and mass-average molar mass,  $\bar{M}_n$  and  $\bar{M}_w$ , respectively. These calculations are performed both for the determination of  $M_n^d$  and  $M_w^d$  using data from the molar-mass and concentration detectors

and for the determination of  $M_n^c$  and  $M_w^c$  from the output of the concentration detector and a calibration curve of the chromatographic column. For comparison, we also give results of model calculations used in the  $M_w^{\text{LALLS}}$  determination by the integration of the output of the LALLS photometer alone. For the sake of illustration, the results are compared with theoretically calculated errors due to axial dispersion in the column at various spreading factors  $h$ .<sup>2,3</sup>

### THEORETICAL

The model calculations were founded on principles and relations given in a previous paper.<sup>1</sup> Thus only basic assumptions are given below:

(a) The analyzed polymer has a logarithmic-normal (Wesslau's) molar-mass distribution<sup>4</sup> with parameters  $M_0$  and  $\beta^2$

$$w(\log_{10}M) = (1/\beta^2)\exp[-(1/\beta^2)\log_{10}^2(M/M_0)] \quad (1)$$

$$\bar{M}_n = M_0\exp(-2.3\beta^2/4)$$

$$\bar{M}_w = M_0\exp(2.3\beta^2/4)$$

$$\bar{M}_w/\bar{M}_n = \exp(2.3\beta^2/2)$$

(b) We disregard the axial dispersion in the column, extracolumn contributions, and any concentration effects.

(c) Calibration curve of the column is linear and is described by the function

$$\log_{10}M = K_1 + K_2V \quad (2)$$

with the constants<sup>5</sup>  $K_1 = 12.8$  and  $K_2 = -0.135 \text{ mL}^{-1}$ , where  $V$  is the elution volume of the polymer fraction having the molar mass  $M$ .

(d) The concentration  $c$  and light-scattering intensity values in terms of the excess Rayleigh ratio  $\Delta R_0$  are measured using the respective detectors with the variances  $\sigma_c^2$  and  $\sigma_R^2$ .

For the errors in determining  $M$  (or  $\log M$ ), which is calculated using

$$M = (Kc/\Delta R_0 - 2A_2c)^{-1} \quad (3)$$

a relation has been derived under these assumptions,<sup>1</sup>

$$\left(\sigma_{\log M}^2\right)_d = \left(\frac{1}{2.3c}\right)^2 \left\{ \left[ \frac{(1 + 2A_2Mc)^2}{KM(1 + 2\alpha A_2Mc)} \right]^2 \sigma_R^2 + \sigma_c^2 \right\} \quad (4)$$

where  $K$  is the optical constant and  $A_2$  is the second virial coefficient, whose dependence on  $M$  is approximated by

$$A_2 = \alpha M^{-\alpha} \quad (5)$$

For the constants  $K$ ,  $\alpha$ , and  $\alpha$  in eq. (4), their numerical values for a

polystyrene solution in toluene at 25°C are<sup>1</sup>

$$K = 1.1 \times 10^{-7} \text{ mol cm}^2 \text{ g}^{-2}, \quad \alpha = 0.227,$$

and

$$\alpha = 8.4 \times 10^{-3} \text{ mol}^{0.773} \text{ cm}^3 \text{ g}^{-1.773}.$$

The variance of experimental values  $c$  and  $\Delta R_0$ ,  $\sigma_c^2$  and  $\sigma_R^2$ , respectively, was assumed to be half the noise from the respective detector. Depending on the magnitude of the signal, the LALLS photometer used as the molar-mass detector may operate either in the regime of constant absolute error,  $\sigma_R^2 = \sigma_R'^2$ , when  $\sigma_R'$  is the sensitivity limit of the detector ( $\sigma_R' = 3 \times 10^{-8} \text{ cm}^{-1}$ ),<sup>6</sup> or in the regime of constant relative error,  $\sigma_R^2 = \sigma_R''^2 > \sigma_R'^2$ , where  $\sigma_R''$  is proportional to the magnitude of the signal in the maximum ( $\sigma_R'' = 1.2 \times 10^{-2} (\Delta R_0)_{\text{max}}$ ). In an experimental arrangement suggested by Hamielec et al.,<sup>7</sup> measurements can be performed in the regime of constant absolute error also when  $\sigma_R'' > \sigma_R'$ , thus making full use of possibilities offered by the LALLS photometer.

For the transformation of the elution curve  $c(V)$  into the distribution function  $w(\log M)$ , we have

$$w(\log M) = -c(V)/K_2 m_0 \quad (6)$$

where  $m_0$  is the amount of the analyzed polymer. In the calculation of molar-mass averages

$$(M_n^d)^{-1} = \int_{M_1}^{M_2} M^{-1} w(\log M) d \log M / \int_{M_1}^{M_2} w(\log M) d \log M \quad (7)$$

$$M_w^d = \int_{M_1}^{M_2} M w(\log M) d \log M / \int_{M_1}^{M_2} w(\log M) d \log M \quad (8)$$

we integrated in the interval of molar masses ( $M_1, M_2$ ), where  $(\sigma_{\log M}^2)_d$  is smaller than  $4(\sigma_M^2)_{\text{LS}}$ , that is, four times smaller than the average scatter of molar masses obtained from light-scattering measurements.

For calculations of  $M_n^c$  and  $M_w^c$  by means of the calibration dependence (2) and the concentration detector output

$$(M_n^c)^{-1} = \int_{V_1}^{V_2} M^{-1} c(V) dV / \int_{V_1}^{V_2} c(V) dV \quad (9)$$

$$M_w^c = \int_{V_1}^{V_2} M c(V) dV / \int_{V_1}^{V_2} c(V) dV \quad (10)$$

we integrated a model output of the concentration detector in the interval of elution volumes ( $V_1, V_2$ ), when the magnitude of the signal  $c(V)$  is at least twice as high as the noise level, that is,  $c(V) \geq 4\sigma_c$ .

Similarly, the quantity

$$M_w^{\text{LALLS}} = \int_{V_1'}^{V_2'} \Delta R_0(V) dV / Km_0 \quad (11)$$

was obtained directly by integrating the output of the LALLS photometer in the interval of elution volumes ( $V_1'$ ,  $V_2'$ ), where  $\Delta R_0(V) \geq 4\sigma_R$ , that is, at least twice as high as the noise level of the detector. The error caused by neglecting the second virial coefficient term in eq. (3) is regarded as being much smaller than the inaccuracy arising from the axial dispersion of the detector.<sup>8-10</sup>

A comparison is made regarding the errors of determining  $M_w^d$ ,  $M_n^d$ ,  $M_w^c$ ,  $M_n^c$ , and  $M_w^{\text{LALLS}}$  for polymers having MMD with various parameters  $\bar{M}_0$  and  $\beta^2$  with the errors found for the same quantities, but caused by axial dispersion in the column at various spreading factors  $h$ . Assuming  $h$  to be constant, Hamielec and Ray<sup>2</sup> derived the following relationships for the determination of  $M_n^c(h)$  and  $M_w^c(h)$  from the spread chromatogram and calibration dependence (2):

$$M_n^c(h) / \bar{M}_n = \exp(-2.3^2 K_2^2 / 4h) \quad (12)$$

$$M_w^c(h) / \bar{M}_w = \exp(2.3^2 K_2^2 / 4h) \quad (13)$$

in which  $\bar{M}_n = M_n^c(\infty)$  and  $\bar{M}_w = M_w^c(\infty)$  corresponds to a chromatogram in which there is no band broadening ( $h \rightarrow \infty$ ). For GPC with an on-line molar-mass detector of the LALLS photometer type and for polymers having the logarithmic-normal distribution, Netopilík derived relations for an error due to spreading<sup>3</sup>

$$M_n^d(h) / \bar{M}_n = \exp[2.3\beta^2 / 2(1 + \beta^2 h / 2.3K_2^2)] \quad (14)$$

$$M_w^d(h) / \bar{M}_w = 1$$

## RESULTS AND DISCUSSION

The relative error of the investigated quantity  $M_x^i$  is denoted with  $\delta M_x^i$

$$\delta M_x^i = (M_x^i / \bar{M}_x) - 1$$

where  $M_x^i$  is  $M_n^i$  or  $M_w^i$ , and the index  $i$  denotes the method used to obtain this quantity ( $i = d, c, \text{LALLS}$ ). The symbol  $\bar{M}_x$  denotes the correct value of the respective quantity.

Preliminary calculations showed that the error of determining  $M_n^d$ ,  $\delta M_n^d$ , is positive and virtually independent of the magnitude of the injection mass  $m_0$  and the molar mass of the polymer  $M_0$ , if the molar-mass detector operates in the regime of constant relative error [Fig. 1(a), area B]. If the measurement is made in the constant absolute error regime [Fig. 1(a), areas A and C], the error is inversely proportional to  $m_0 M_0$ . The hatched area C corresponds to an experimental arrangement according to Hamielec et al.<sup>7</sup>

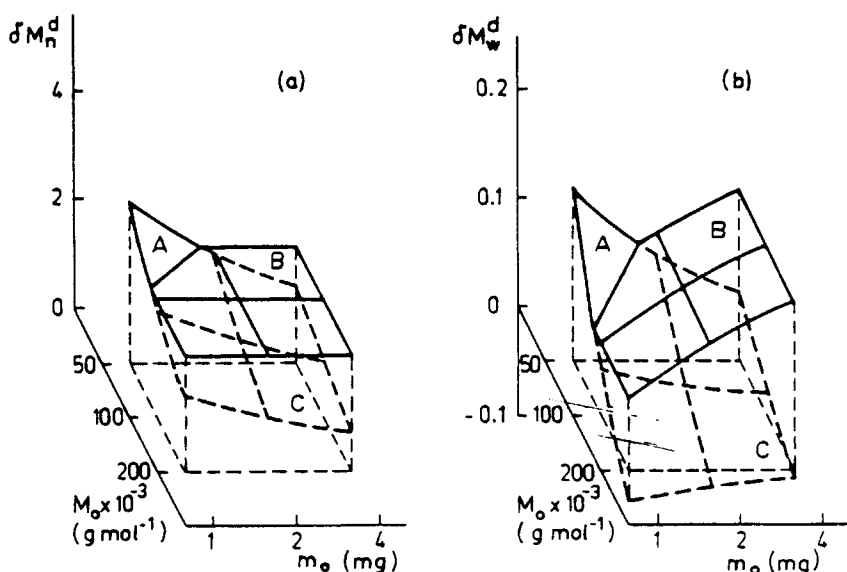


Fig. 1. Dependence of the error  $\delta M_n^d$  (a) and  $\delta M_w^d$  (b) on the molar-mass  $M_0$  and on the magnitude of injection  $m_0$  of a polymer sample having polydispersity characterized by  $M_w/M_n = 11$ : (area A) measurement in the regime of constant absolute error of the molar-mass detector; (area B) measurement in the regime of constant relative error of the molar-mass detector; (area C [hatched]) measurement according to Hamielec et al.<sup>7</sup>

The error of determining  $M_w^d$ ,  $\delta M_w^d$ , is also predominantly positive, but it is smaller by more than an order of magnitude, and its dependence on  $M_0$  and  $m_0$  is somewhat more complicated. In measurements with the molar-mass detector in the regime of constant absolute error [Fig. 1(b), area A],  $\delta M_w^d$  steeply decreases with increasing  $M_0$  and  $m_0$ ; the decrease with  $M_0$  is much steeper, in an experimental arrangement according to Hamielec<sup>7</sup> [Fig. 1(b), area C] even down to zero; the sign of  $\delta M_w^d$  changes to negative and then its absolute value increases again. At the same time,  $\delta M_w^d$  always decreases with increasing injected amount. These trends, which are somewhat surprising, are a consequence of the partial compensation of errors in integrals in the numerator and denominator of eq. (8).

Regarding the dependence of the error of determining  $M_n^d$  and  $M_w^d$  on the molar-mass distribution width of the analyzed polymer,  $\delta M_n^d$  progressively increases with  $\beta^2$  in both working regimes of the molar-mass detector (Fig. 2). The rise in  $\delta M_n^d$  is much slower if  $m_0$  is chosen so that the maximum height of the concentration or molar-mass detector output is constant rather than injecting constant amounts of samples with various polydispersities.

The accuracy of determining  $M_w^d$  is better by more than an order of magnitude than with  $M_n^d$ , but its dependence on molecular parameters of the analyzed sample is somewhat ambiguous. In measurements with the molar-mass detector operating in the regime of constant relative error,  $\delta M_w^d$  is a predominantly increasing function of polydispersity of the sample [Fig. 2(b), area B]. When working in the regime of constant absolute error, errors of opposite sign are combined in the determination of  $M_w^d$ . With increasing

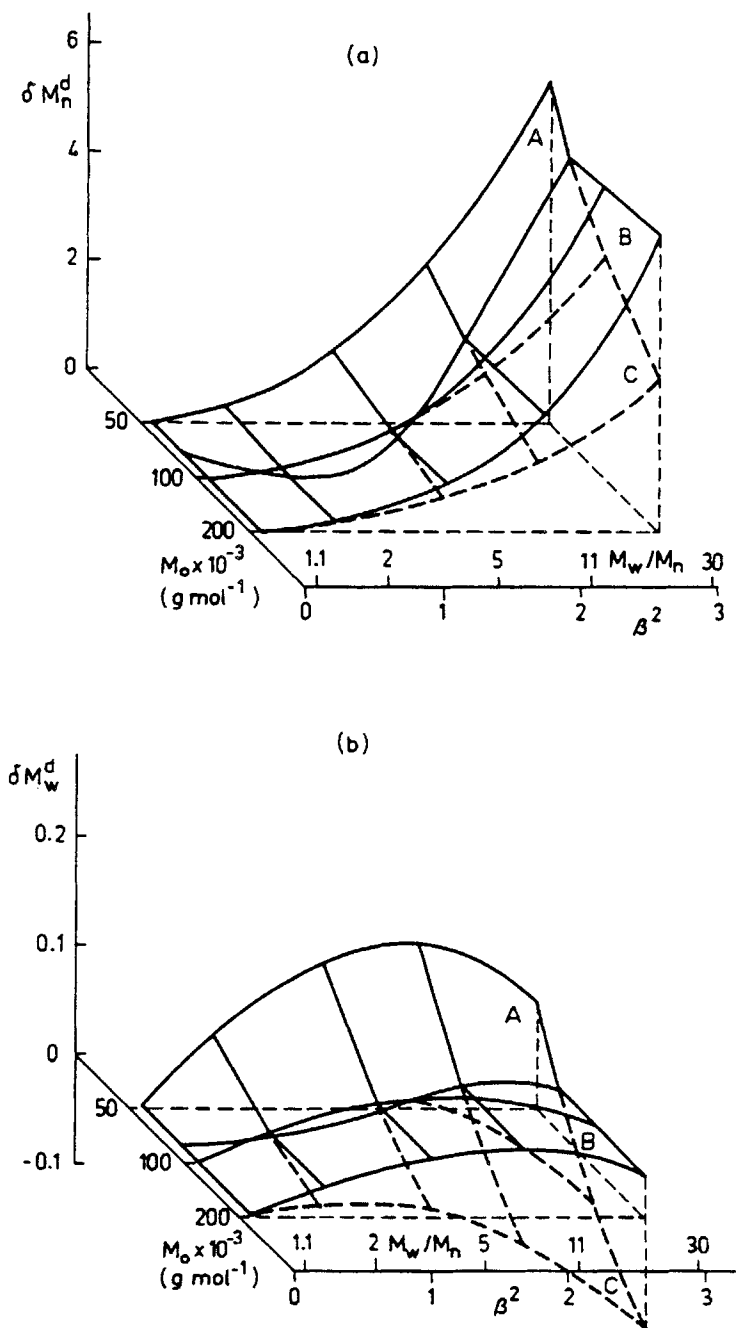


Fig. 2. Dependence of the error  $\delta M_n^d$  (a) and  $\delta M_w^d$  (b) on the parameters of the MMD of the polymer,  $M_0$  and  $\beta^2$  (or  $M_w/M_n$ ), at a constant injected amount  $m_0 = 1 \times 10^{-3}$  g. Areas denoted as in Figure 1.

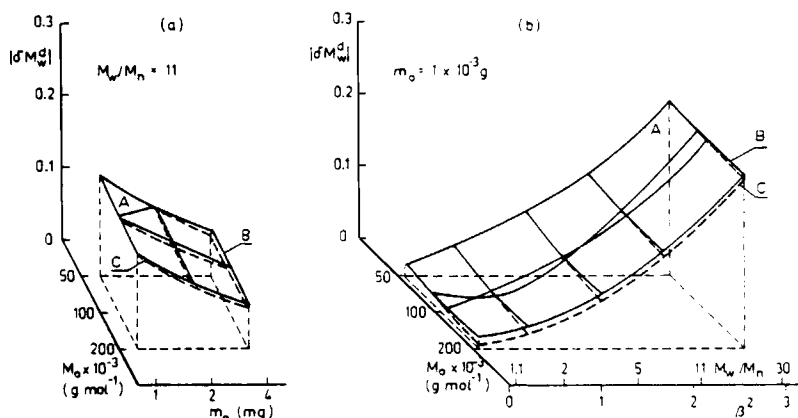


Fig. 3. Dependence of the absolute value of the error  $|\delta M_w^d|$  calculated using eq. (16) on the injected amount  $m_0$  (a) and on the MMD parameters of the polymer  $M_0$  and  $\beta^2$  (b). Areas denoted as in Figure 1.

polydispersity, the originally small negative error of the integral in the numerator of eq. (8) increases, in its absolute value, more quickly than the error of the integral in the denominator. This results in a maximum in the  $\delta M_w^d$  vs.  $\beta^2$  dependence, or in a change in the sign of the error with higher molar masses [Fig. 2(b), areas A and C]. [A partial compensation of the errors, of course, takes place also in the determination of  $M_n^d$  and with  $M_w^d$  in the regime of constant relative error, but in this case the error of the integral in the numerator of eqs. (7) and (8) always predominates.]

A somewhat more graphic situation arises, if the integral  $\int_{V_1}^{V_2} c(V) dV$  is used instead of  $\int_{M_1}^{M_2} w(\log M) d \log M$  in

$$(M_n^d)^{-1} = \int_{M_1}^{M_2} M^{-1} w(\log M) d \log M / \int_{V_1}^{V_2} c(V) dV \quad (15)$$

$$M_w^d = \int_{M_1}^{M_2} M w(\log M) d \log M / \int_{V_1}^{V_2} c(V) dV \quad (16)$$

The character of the dependence of  $\delta M_n^d$  on  $m_0$ ,  $M_0$ , and  $\beta^2$  remains unchanged, only the magnitude of the error is increased more.  $M_w^d$  is then systematically subjected to a negative error, the absolute value of which decreases with  $m_0$  and  $M_0$ , and increases with  $\beta^2$  [Figs. 3(a) and 3(b)]. The working regime of the molar-mass detector is not very important here.

The error of determining  $M_w^{\text{LALLS}}$  by a direct integration of the LALLS photometer output [eq. (11)],  $(\delta M_w^{\text{LALLS}})_0$ , is negative; in a measurement in the regime of constant absolute error, it is inversely proportional to  $m_0 M_0$  [Fig. 4(a), areas A and C] and the dependence of the absolute value  $|\delta M_w^{\text{LALLS}}|_0$  on polydispersity has a maximum [Fig. 4(b), areas A and C]. In the regime of constant relative error,  $|\delta M_w^{\text{LALLS}}|_0$  is independent of both  $m_0$ ,  $M_0$ , and  $\beta^2$  [Figs. 4(a), (b), areas B], and its magnitude under our model conditions is about 1.5%. This, however, is an inaccuracy due only to integration, and it

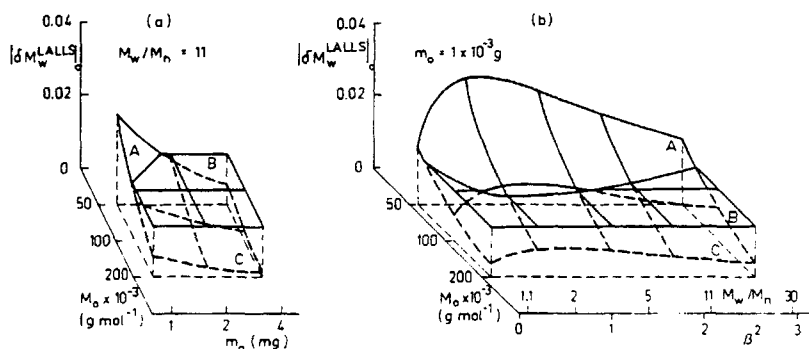


Fig. 4. Dependence of the absolute value of the error  $|\delta M_w^{\text{LALLS}}|_0$  in which the second virial coefficient term is negligible on the injected amount  $m_0$  (a) and on the MMD parameters of the polymer (b). Areas denoted as in Figure 1.

does not include the error caused by neglecting the second virial coefficient term in eq. (3). The calculations were performed assuming  $A_2 = 0$  (therefore, we write the subscript 0 at  $|\delta M_w^{\text{LALLS}}|_0$ ). This error is far from being always negligible, as one can see by comparing with model calculations using constants of eq. (5) for a solution of polystyrene in toluene at 25°C.<sup>1</sup> The absolute value of the error in  $M_w^{\text{LALLS}}$  caused by neglecting the second virial coefficient terms,  $|\delta M_w^{\text{LALLS}}|_{A_2}$ , increases with both  $M_0$  and  $m_0$  [Fig. 5(a)]. At low polydispersity ( $M_w/M_n < 2$ ), the absolute value of the error also increases, while at higher  $M_w/M_n$  it is virtually independent of  $m_0$  [Fig. 5(b)]. As to their magnitude,  $(\delta M_w^{\text{LALLS}})_0$  and  $(\delta M_w^{\text{LALLS}})_{A_2}$  are comparable and have the same sign.

In the determination of  $M_n^c$  and  $M_w^c$  from the concentration detector output and a known calibration dependence, the errors  $\delta M_n^c$  and  $\delta M_w^c$  are

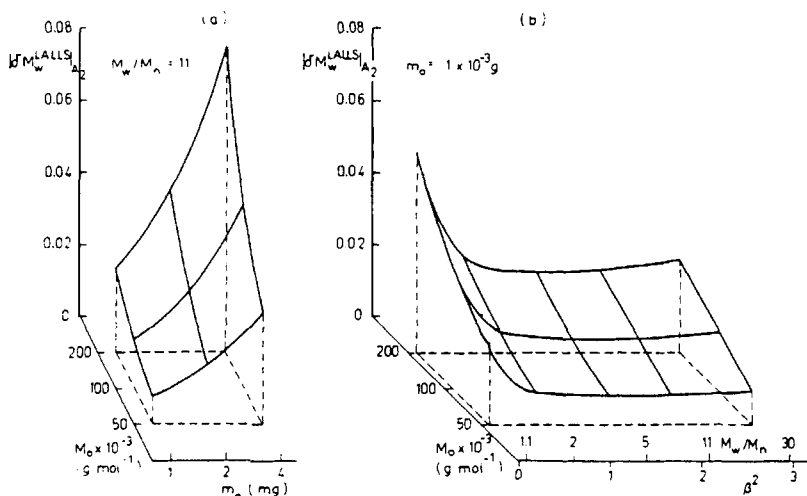


Fig. 5. Dependence of the absolute value of the error  $|\delta M_w^{\text{LALLS}}|_{A_2}$  caused by neglecting the second virial coefficient term on the injected amount  $m_0$  (a) and on the parameters of the polymer (b);  $A_2 = 8.4 \times 10^{-3} \times M^{-0.227} \text{ mol cm}^3 \text{ g}^{-2}$ .



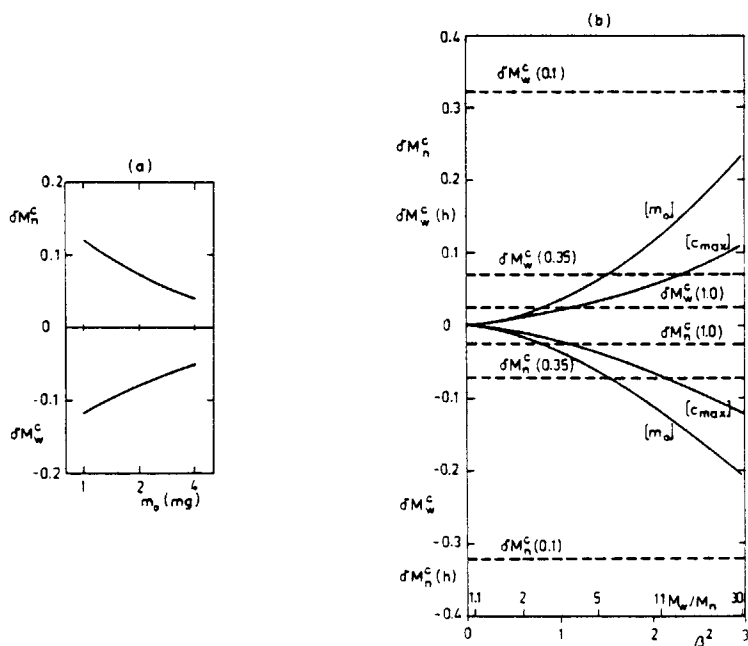


Fig. 6. Dependence of the errors  $\delta M_n^c$  and  $\delta M_w^c$  on the magnitude of the injected amount  $m_0$  (a) and on polydispersity  $\beta^2$  (or on  $M_w/M_n$ ) (b) at a constant  $m_0 = 1 \times 10^{-3}$  g (curve  $[m_0]$ ) and at a constant maximum height of the concentration detector output,  $c_{max} = 2 \times 10^{-4}$  g cm $^{-3}$  (curve  $[c_{max}]$ ). Dependence of  $\delta M_n^c(h)$  and  $\delta M_w^c(h)$  [eqs. (12) and (13)] for the spreading factor values  $h = 0.1, 0.35$ , and 1.0.

virtually independent of the molar mass of the polymer and decrease with the amount of injection [Fig. 6(a)]. With increasing polydispersity, the errors in both  $M_n^c$  and  $M_w^c$  increase as expected. Keeping the height of the concentration detector output constant by varying  $m_0$ , we find that the rate of increase in both errors is distinctly slower than at constant  $m_0$  [Fig. 6(b)].

At this point, it should be recalled that, in the calculation of  $M_n^d$  and  $M_w^d$ , MMD was integrated using eqs. (7) and (8) in the range  $(M_1, M_2)$ , when  $(\sigma_{\log M}^2)_d$  is smaller than  $4(\sigma_M^2)_{LS}$ , while in the calculation of  $M_n^c$ ,  $M_w^c$ , and  $M_w^{LALLS}$  the integration took place in the range of  $M$  when the signal-to-noise ratio was larger than 2, that is, when  $c(V) > 4\sigma_c$ , or  $\Delta R_0(V) > 4\sigma_R$ . Since the calculation conditions of  $\delta M_n^d$  and  $\delta M_w^d$  on the one hand, and those of  $\delta M_n^c$ ,  $\delta M_w^c$ , and  $\delta M_w^{LALLS}$  on the other, are not completely identical, the results cannot be exactly compared with respect to the magnitude. In spite of this, it can be said with certainty that the  $M_n^c$  values (if the calibration is tolerably reliable) are subjected to a distinctly smaller error than  $M_n^d$ . However, the errors in  $M_w^d$  and  $M_w^c$  are comparable with each other; which value is more exact is dependent on the magnitude of injection and MMD parameters ( $M_0$  and  $\beta^2$ ). The differences, however, are not large.

$\bar{M}_w$  can be determined much more exactly by a direct integration of the molar-mass detector output alone, when the absolute value of the error  $|\delta M_w^{LALLS}|$ , including  $|\delta M_w^{LALLS}|_0$  [Fig. 4(b)] and  $|\delta M_w^{LALLS}|_{A_2}$  [Fig. 5(b)], is merely 2–4%. The low polydispersity range ( $\bar{M}_w/\bar{M}_n < 2$ ) is an exception,

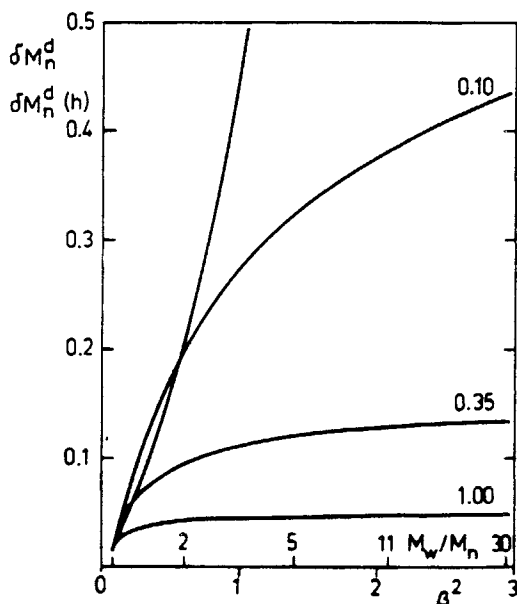


Fig. 7. Comparison of the dependence of  $\delta M_n^d(h)$  on polydispersity  $\beta^2$  (or  $M_w/M_n$ ) [eq. (14)] for the spreading factor  $h = 0.1, 0.35,$  and  $1.0$  with  $\delta M_n^d$  (undenoted curve) in the regime of constant relative error of the  $M$ -detector.

where  $|\delta M_w^{\text{LALLS}}|$  is somewhat higher. The error of determining  $M_w^{\text{LALLS}}$  may be reduced further if eq. (11) is normalized by means of the integral  $\int V_1^{V_2} c(V) dV$  [cf. eqs. (9) and (10)] instead of  $m_0$ , which brings about a partial compensation of the errors.  $\delta M_w^{\text{LALLS}}$  can then assume both positive and negative values.

Let  $\delta M_n^d(h)$ ,  $\delta M_n^c(h)$ , and  $\delta M_w^c(h)$  denote errors of the respective quantities due to the axial dispersion (alone) in the column at a given spreading factor  $h$ . Using relations (12)–(14), we calculated the magnitude of these errors for three different values:  $h = 0.1, 0.35,$  and  $1.0$  [Figs. 6(b) and 7]. The value  $h = 0.35$  has been taken from a paper by Netopilík,<sup>5</sup> along with the respective value of the calibration constant  $K_2 = -0.135$ .

It should be noticed that, while  $\delta M_n^d(h)$  is always (with the exception of samples having a low polydispersity) much smaller than  $\delta M_n^d$  and both have the same sign, the errors  $\delta M_n^c(h)$  and  $\delta M_w^c(h)$  have opposite signs than  $\delta M_n^c$  and  $\delta M_w^c$ , so that they partly compensate each other. Which error predominates depends on the magnitude of  $h$ .

## CONCLUSIONS

Because of limited sensitivity of molar-mass and concentration detectors, only  $\bar{M}_w$  can be determined with acceptable accuracy by means of GPC with an on-line LALLS photometer;  $\bar{M}_n$  can be determined accurately only if the polydispersity of the analyzed polymer is small. A somewhat more exact determination of  $\bar{M}_n$  is possible using data of the concentration detector and calibration of the chromatographic column. Model calculations show that axial dispersion in the column certainly is not the main source of errors in

GPC used in the determination of  $\bar{M}_w$  and  $\bar{M}_n$ . Comparatively reliable data on  $\bar{M}_w$  can be obtained by a direct integration of the LALLS photometer output, although it is not true that the error caused by ignoring the second virial coefficient term would be negligible.

Although, in some cases, the accuracy of determining  $\bar{M}_n$  and  $\bar{M}_w$  may be increased by increasing the amount of the injected sample, this is at variance with the effort to suppress the concentration effect to a minimum, and an optimal injected amount should therefore always be sought.

#### APPENDIX: NOMENCLATURE

$a$	Constant in eq. (5)
$A_2$	Second virial coefficient
$c$	Mass concentration of a polymer in solution
$C_r$	Criterion of reliability of the determination of molar-mass distributions, that is, the relative part of the area under a molar-mass-distribution curve for which the error $(\sigma_M)_d$ is higher than a certain limit
$h$	Column spreading factor
$K$	Optical constant in eq. (3)
$K_1, K_2$	Constants of the linear calibration dependence (2)
$m_0$	Mass of the polymer analyzed
$M$	Molar mass
$M_0$	Parameter of the logarithmic-normal molar-mass distribution function (1)
$\bar{M}_n$	Number-average molar mass
$\bar{M}_w$	Mass-average molar mass
$M_x^i$	( $x = n, w$ ) Molar-mass average calculated: from the output of the concentration detector and the calibration curve ( $i = c$ ), from the output of the molar-mass and concentration detectors ( $i = d$ ), and directly from the output of the LALLS photometer ( $i = \text{LALLS}$ )
$\Delta R_0$	Excess Rayleigh ratio at zero scattering angle
$V$	Elution volume
$w(\log M)$	Differential molar-mass distribution function
$\alpha$	Exponent in eq. (5)
$\beta^2$	Parameter of the logarithmic-normal molar-mass distribution function (1)
$\delta M_x^i$	( $i = c, d, \text{LALLS}$ ; $x = n, w$ ) Relative error of molar-mass average $M_x^i$
$ \delta M_w^{\text{LALLS}} _0$	Absolute value of the relative error of the molar-mass $M_w^{\text{LALLS}}$ in which the second virial coefficient term is negligible
$ \delta M_w^{\text{LALLS}} _{A_2}$	Absolute value of the relative error of the molar-mass $M_w^{\text{LALLS}}$ caused by neglecting the second virial coefficient term
$\sigma_c$	Standard error of a concentration detector
$\sigma_M$	Standard error in molar-mass determination
$\sigma_R$	Standard error of a molar-mass detector
$(\sigma_M^2)_{\text{LS}}$	Variance of the molar mass obtained by an independent light-scattering measurement

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Received December 15, 1986

Accepted March 13, 1987