Effect of local polydispersity in size exclusion chromatography with dual detection

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Abstract

The effect of local polydispersity combined with the error in the pre-determined value of interdetector volume was theoretically examined for a polymer sample with a molecular weight distribution which obeys the log-normal function. The effect results in rotation (change of the slope) of the uncorrected dependences of molecular weight, experimentally determined as local molecular weight average, vs. elution volume.

If the interdetector volume is determined correctly, the centre of the rotation due to the peak broadening of each uncorrected correlation lies in the correct correlation on the point corresponding to the n-, w- or z-average molecular weight. The experimental values of the n- and w-average of the whole polymer remain unchanged in the n- and w-detection even if the experimental correlations of molecular weight vs. elution volume are revolved. In the z-detection, on the other hand, the experimental polydispersity does not depend on the interdetector volume. © 1998 Elsevier Science B.V.

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1. Introduction

The recent improvements in experimental detection techniques (LALLS [1] MALLS [2–6], viscometric- [7,8] and n-detection [9,10]) in size exclusion chromatography (SEC) make precise determination of molecular-weight-distribution (MWD) possible. The characterization of broad MWD samples with acceptable precision, nowadays, poses no special problems. For narrow MWD samples, i.e., for samples with low polydispersity, defined as the weight- to number-average molecular weights ratio, $\bar{M}_w/\bar{M}_n$, the situation is different because the error in determination of the local (uncorrected) molecular weight due to peak broadening [11–16] as well as due to the error, δ, in the interdetector volume

[17–23] (interdetector lag) increases as the sample polydispersity goes down, $\bar{M}_w/\bar{M}_n \to 1$.

For those reasons, we decided to study the effect of local polydispersity on the detection in SEC with dual detection.

2. Theoretical

In the combination of DR as a detector of concentration and LS as a detector of molecular weight, the measured quantity is the mass concentration, c, of the polymer solute and the (excess) Rayleigh ratio $R(\theta)$ of light scattered to the direction of angle θ, respectively [24–27]. In order to find $\bar{M}_w$, it is

necessary to know $R(\theta)$ at low angles and concentrations ($\theta \to 0$, $c \to 0$). The condition of low c is usually fulfilled in SEC or a correction can easily be done. The limit of $R(\theta)$ for low angles of observation can be found in two ways: the direct measurement at low angles (low-angle laser light scattering, LALLS) or the extrapolation of the light intensities measured at several angles (multi-angle laser light scattering, MALLS) to the zero angle of observation is often used in SEC. By combining with the DR signal, the value of $\bar{M}_w$ for individual fractions is found and therefore its correct value is also obtained for the whole sample independently of the shape of the DR record [14,15]. This method will be called w-sensitive [13–20].

MALLS also offers another possibility of determining M only from the LS record [2–6]. According to the theory of light scattering, the value of $1/(c\bar{M}_w)$ can be found by extrapolating the $K^*/R(\theta)$ vs. $\sin^2 \theta/2$ (K^* is an optical constant) dependence to zero, angle θ and the z-average radius of gyration, $<s^2>_z$, can be found from the slope of this dependence. Provided that the exponent α of the equation [28]:

$$s^2 \propto M^{\alpha} \qquad (1)$$

is known, the (uncorrected) z-average molecular weight, $\bar{M}_z(V, \mathrm{uc})$, is obtained. This method, although it requires a complicated instrument, is very promising because the correlation $\ln M$ vs. V can be obtained by measurement in only one detector cell (MALLS) which largely eliminates the error in interdetector volume. This method is z-sensitive.

The n-sensitive methods [9,10] are based on the definition of the number-average molecular weight:

$$\bar{M}_n = \frac{\sum_i M_i n_i}{\sum_i n_i} \qquad (2)$$

where n_i is the number of molecules having molecular weight M_i and can be found, e.g., from the signal of an end-group-sensitive detector [9] or an on-line membrane osmometer [10]. The product $M_i n_i$ is proportional to the (weight) concentration and can be found, e.g., from the DR record. This will be discussed below for a polymer sample obeying the log-normal weight-MWD i.e., the function [29]:

$$w(M) = \frac{1}{\beta\sqrt{\pi}M} \exp\left(-\frac{1}{\beta^2} \ln^2 \frac{M}{M_0} \right) \qquad (3)$$

where

$$\beta = \sqrt{2 \ln(\overline{\bar{M}_w/\bar{M}_n})} \qquad (4)$$

and

$$M_0 = \sqrt{\overline{\bar{M}_w/\bar{M}_n}} \qquad (5)$$

using the equation derived by Berger and Schultz [30]:

$$w(M) = -\frac{1}{MB} W(V) \qquad (6)$$

the theoretical chromatogram may be expressed as [11,12]:

$$W(V) = -\frac{B}{\beta\sqrt{\pi}} \exp\left(-\frac{B^2}{\beta^2} (V - V_0)^2 \right) \qquad (7)$$

where the parameters A and B (negative) of the equation ('calibration')

$$\ln M = A + BV \qquad (8)$$

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

$$V_0 = \frac{\ln M_0 - A}{B} \qquad (9)$$

For a given separation system, A and B will be assumed to be correct.

In the following, the theoretical development [17] for w-detection of a polymer of log-normal MWD will be shown to be valid also for the n- and z-detection.

3. Results and discussion

3.1. Experimental chromatograms

The imperfect resolution (peak broadening) causes individual polymer fractions to mix. To find the (uncorrected) record heights, $F_k(V)$, of the detector sensitive to a particular power, k, of M^k ('chromatograms'), it is necessary to integrate contributions

from all polymer fractions with molecular weight $M(y)$ characterized by the elution volume y (y is a dummy variable of elution volume). The chromatogram height is then:

$$F_k(V) = \int_{-\infty}^{\infty} \mathcal{W}_k(V, y)\, dy \tag{10}$$

where

$$\mathcal{W}_k(V, y) = M^k(y)W(y)G(V, y) \tag{11}$$

where

$$M(y) = \exp(A + By) \tag{12}$$

and $G(V, y)$ is the kernel function usually approximated by the Gaussian normal distribution with variance σ^2

$$G(V, y) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{(V - y)^2}{2\sigma^2}\right] \tag{13}$$

In this case, the 'uncorrected chromatogram heights' can be expressed (the details of calculation are given in Appendix A) as:

$$F_k(V) = \frac{\mu'_k}{\sqrt{\pi}\sqrt{2\sigma^2 + (\beta/B)^2}}$$
$$\times \exp\left[-\frac{(V'_k - V)^2}{2\sigma^2 + (\beta/B)^2}\right] \tag{14}$$

where

$$\mu'_k = M_0^k \exp[k^2\beta^2/4] \tag{15}$$

is the k-th statistical moment about zero, defined [31]:

$$\mu'_k = \int_0^{\infty} M^k w(M)\, dM \tag{16}$$

and

$$V'_k = V_k + \delta_k \tag{17}$$

where

$$V_k = V_0 + k\beta^2/2B \tag{18}$$

Here δ_k, which is the error in the determination of elution volume ('shift' of the record), was introduced. The lag between the detectors, which record $F_k(V)$ and $F_{k-1}(V)$, respectively, can be expressed as $\delta_k - \delta_{k-1}$. (This will be discussed in detail in the next

section). For $k = -1$, 0, 1 and 2, the record height of detectors sensitive, respectively, to M^{-1} (n-detector), M^0 (DR record), M (LS record), M^2 (z-detection) are obtained. According to Eqs. (14) and (18), all chromatograms are Gaussian with the same variance but shifted (if $\delta = 0$) mutually by the factor $k\beta^2/2B$ as shown in Fig. 1. (Experimental correlations also shown in this picture will be discussed in the following sections). Eq. (14) is a generalization of the equation proposed by Tung [11,12] for the DR record ($k = 0$ and $\delta = 0$).

3.2. Local molecular weights

The uncorrected local molecular weight in k-detection, which is experimentally obtained from the combination of $F_k(V)$ and $F_{k-1}(V)$ records, can be calculated as:

$$\overline{M}_k(V, \text{uc}) = \frac{F_k(V)}{F_{k-1}(V)} \tag{19}$$
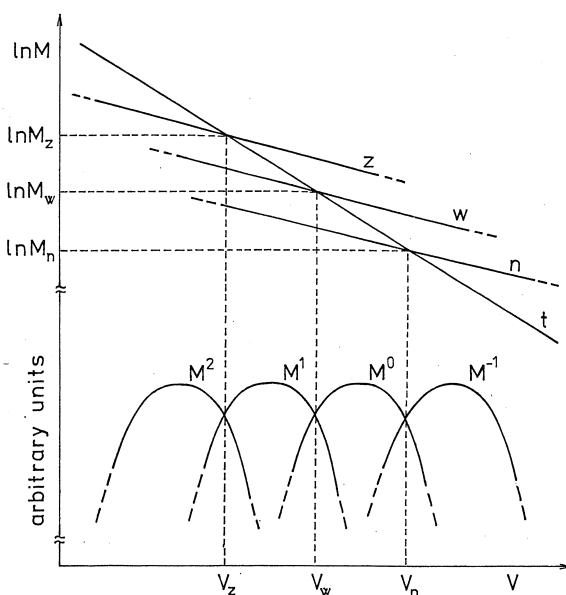
where $F_k(V)$ is defined by Eq. (14).

Fig. 1. Comparison of the experimental correlations ln $\bar{M}_z$, ln $\bar{M}_w$ and ln $\bar{M}_n$ vs. V, denoted respectively, z-, w- and n-, with the theoretical one, t, and with the records of detectors sensitive to M^{-1} (n-detection), M^0 (DR), M^1 (LS) and M^2 (z-detection, according to LS radius of gyration).

From the discussion following Eq. (18), it follows that the error in the interdetector volume can be expressed as a shift of one record. We chose the record with the higher power of M as 'shifted' by δ, i.e., $\delta_0 = \delta$ and $\delta_{-1} = 0$ in the combination of the n- and DR, $\delta_1 = \delta$ and $\delta_0 = 0$ in the combination of w-(LS) and DR.

As follows from the discussion of Eq. (1), the calculation of $\ln \bar{M}_z(V, \text{uc})$ from $F_2(V)$ and $F_1(V)$ is performed from the data of one detector and therefore δ plays no role in the calculation of $\ln \bar{M}_z(V, \text{uc})$. However, there can be some error due to δ between the MALLS and DR detector in z-detection in the calculation of MWD of the whole sample. The details are discussed in the last section, together with the definition of $\bar{M}_z$.

The local (uncorrected) molecular weight is given according to Eq. (19), (the details are given in Appendix B) by:

$$\ln \bar{M}_k(V) = (1 - \Sigma) \ln \bar{M}_k - (\Delta/2) \ln \sqrt{\bar{M}_k \bar{M}_{k+1}}$$
$$- Z/2 + (\Sigma + \Delta/2)(A + BV) \qquad (20)$$

where

$$\Sigma = \beta^2/(2\sigma^2 B^2 + \beta^2) \qquad (21)$$

$$\Delta = 4\delta B/(2\sigma^2 B^2 + \beta^2) \qquad (22)$$

and

$$Z = 2(\delta B)^2/(2\sigma^2 B^2 + \beta^2) \qquad (23)$$

From Eq. (20), we have respectively for the n-, w- [13,18,20], and z-detection:

$$\ln \bar{M}_n(V, \text{uc}) = (1 - \Sigma) \ln \bar{M}_n - (\Delta/2) \ln \sqrt{\bar{M}_n \bar{M}_w}$$
$$- Z/2 + (\Sigma + \Delta/2)(A + BV) \qquad (24)$$

$$\ln \bar{M}_w(V, \text{uc}) = (1 - \Sigma) \ln \bar{M}_w - (\Delta/2) \ln \sqrt{\bar{M}_w \bar{M}_z}$$
$$- Z/2 + (\Sigma + \Delta/2)(A + BV) \qquad (25)$$

$$\ln \bar{M}_z(V, \text{uc}) = (1 - \Sigma) \ln \bar{M}_z + \Sigma(A + BV) \qquad (26)$$

From Eq. (24) through Eq. (26), it is obvious that correlations in $\ln \bar{M}_k(V, \text{uc})$ are revolved in respect to the correct 'calibration' (Eq. (8)). For $\delta = 0$, the detection of a particular molecular weight average is correct. The coordinates, V_k, of the intersection point with calibration (given by Eq. (8)) are obtained by

subtracting Eq. (8) from Eq. (20) and setting this difference (of the right-hand-sides) to zero (the points which fulfill the condition $\ln M = \ln \bar{M}_k(V, \text{uc})$ are sought for). We readily have:

$$\ln \bar{M}_k = A + BV_k \qquad (27)$$

The correlations, Eq. (24) through Eq. (26) are together with 'chromatograms' depicted in Fig. 1. For $\sigma^2 \to \infty$ (extremely poor resolution) the correlations, Eq. (20), or Eq. (24) through Eq. (26) become parallel with the elution–volume axis but still $\ln M_k$ (of the whole sample) is correctly determined in the k-detection.

For $\delta \neq 0$, in each detection we suppose that one of the chromatograms is shifted, and consequently the centre of the rotation moves. Eq. (27) is not fulfilled in this case. There is, in general, no point in which (any average of) molecular weight is determined correctly. The MWD averages of the whole polymer, however, can be computed. This will be demonstrated in the last section.

3.3. Local polydispersity

Here, the local polydispersity for the polymer having log-normal MWD will be computed directly. The results will be then compared with uncorrected correlations of the molecular weight vs. V.

It has been shown in Appendix A that the function $\mathscr{W}(V, y) = W(y)G(V, y)$, defined by Eq. (11), can be (for $k = 0$) expressed as:

$$\mathscr{W}(V, y) = \frac{-B}{\sqrt{2}\beta\sigma\pi} \exp\left[- \frac{(V_0 - V)^2}{2\sigma^2 + (\beta/B)^2} \right]$$
$$\times \exp\left[-\left(\frac{B^2}{\beta^2} + \frac{1}{2\sigma^2}\right) \right.$$
$$\left. \times \left(y - \frac{2\sigma^2 V_0 + V(\beta/B)^2}{2\sigma^2 + (\beta/B)^2} \right)^2 \right] \qquad (28)$$

In Eq. (28), the elution volume is denoted by two variables, y and V. The former (common for both functions in the product $W(y)G(V, y)$ stands for the theoretical values with M characterized by elution volume y (cf. Eq. (8)), the latter is a real value at which the measurement is performed. Physically, the function $\mathscr{W}(V, y)$ describes a theoretical chromatogram (concentration detector record) obtained on an

ideal separation system (i.e., not broadened) of a polymer fraction which had been previously collected in an infinitesimal fraction of eluent at elution volume *V*, on a non-ideal separation system (i.e., where the chromatograms are broadened in dependence on the factor of σ^2), in both cases on otherwise identical separation systems with the 'calibration' given by Eq. (8).

The first two factors in Eq. (28) are constant (at constant *V*), from the third (the second exponential), it is obvious that the 'chromatogram' given by Eq. (28) is Gaussian which means that the molecular weight distribution of polymer is log-normal. The factor $B^2/\beta^2 + 1/2\sigma^2$ in Eq. (28) corresponds to the factor B^2/β^2 of Eq. (7). Let

$$\beta' = \sqrt{2 \ln \overline{M}_w(V, \text{uc})/\overline{M}_n(V, \text{uc})} \qquad (29)$$

be the parameter describing the local polydispersity. By substitution β' into Eq. (7) and comparing with Eq. (28) we have the equation:

$$\frac{B^2}{\beta'^2} = \frac{B^2}{\beta^2} + \frac{1}{2\sigma^2} \qquad (30)$$

from which, using Eq. (4), we readily have:

$$\overline{M}_w(V, \text{uc})/\overline{M}_n(V, \text{uc}) = (\overline{M}_w/\overline{M}_n)^{1-\Sigma} \qquad (31)$$

From Eq. (31) and the identity $\bar{M}_z/\bar{M}_w = \bar{M}_w/\bar{M}_n$ (valid for the log-normal MWD) we have for the z-average:

$$\overline{M}_z(V, \text{uc})/\overline{M}_w(V, \text{uc}) = (\overline{M}_z/\overline{M}_w)^{1-\Sigma} \qquad (32)$$

According to Eq. (31) and Eq. (32), the local polydispersity in a particular analysis with constant σ^2 (this is a plausible assumption for a narrow-distribution sample) is constant throughout the whole region of *V*.

Let us compare the results (Eq. (31)) and (Eq. (32)) with what is obtained on the basis of Eq. (24) through Eq. (26). For $\Delta = 0$ (i.e., for $\delta = 0$), according to this equation, the n-, w- and z-detections are true and the shift between the experimental correlations ln $\bar{M}_w(V)$, ln $\bar{M}_n(V)$ and ln $\bar{M}_z(V)$ is $(1 - \Sigma)$ ln $\bar{M}_w/\bar{M}_n$. From this, Eq. (31) and Eq. (32) are directly obtained.

From the above discussion, it follows that the shifts between the experimental correlations (calculated from the broadened records), ln $\bar{M}_k(V, \text{uc})$ vs. *V*, in the n-, w- and z-detections, are the direct consequence of local polydispersity. For $\sigma^2 \to 0$ (and $\delta \to 0$), $\Sigma \to 0$ and consequently according to Eq. (31) $(\bar{M}_w/\bar{M}_n) \to 1$, and Eq. (20) turns into correlation (Eq. (8)).

On the other hand, for $\sigma^2 \to \infty$ (no separation), from Eq. (21), it follows $\Sigma \to 0$; consequently from Eq. (31) it follows that $\bar{M}_w(V, \text{uc})/\bar{M}_n(V, \text{uc}) \to \bar{M}_w/\bar{M}_n$ and from Eq. (20), it follows that ln $\bar{M}_k(V, \text{uc}) \to \ln \bar{M}_k$. This means that with decreasing resolution power the local polydispersity approaches the sample polydispersity and the 'experimental' molecular weight in the n-, w- and z-detection approach, the number-, weight- and z-average molecular weight respectively. This is in accord with the sketch in Fig. 1. More information about the physical meaning of the points on elution volume axis corresponding to various MWD-averages can be found in Ref. [20].

Examples of the dependences of $\bar{M}_w(V, \text{uc})/\bar{M}_n(V, \text{uc})$ on $\bar{M}_w/\bar{M}_n$ (for several values of σ^2) and on σ^2 (for several values of $\bar{M}_w/\bar{M}_n$) are depicted in Figs. 2 and 3, respectively, for a common value of $B = 0.46$ ($B = 0.2$ if $\log_{10} M$ is used).
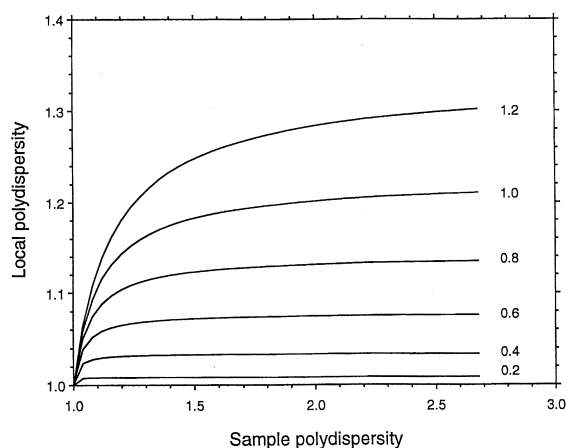

Fig. 2. Local polydispersity [$\bar{M}_w(V, \text{uc})/\bar{M}_n(V, \text{uc})$] as a function of the peak spreading variance, σ^2, for the sample polydispersity denoted with the curves.
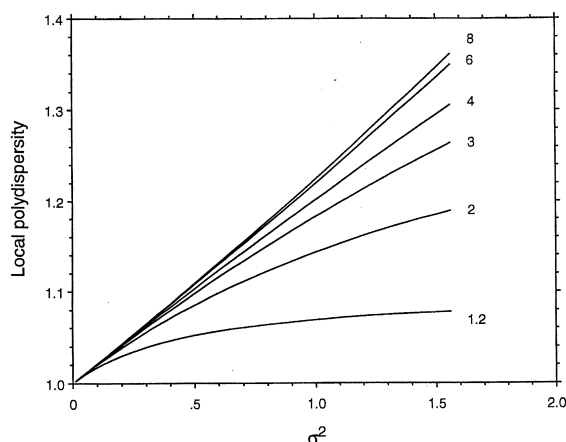
Fig. 3. Local polydispersity $[\bar{M}_w(V, \text{uc})/\bar{M}_n(V, \text{uc})]$ as a function of the sample polydispersity for values of peak spreading variance, σ^2, denoted with curves.

3.4. Uncorrected molecular weight averages of the whole polymer

The (uncorrected) n-, w- and z- averages of the whole polymer are for $l = 0$, 1 and 2, respectively, defined [32]:

$$\bar{M}_l(\text{uc}) = \frac{\int_0^\infty M^l f(M)\, dM}{\int_0^\infty M^{l-1} f(M)\, dV} \tag{33}$$

where $f(M)$ is the (uncorrected) MWD.

The definition of the $\bar{M}_z$ needs a comment. The value obtained on the basis of Eq. (1) is defined [33]:

$$\bar{M}_{z,\alpha}(\text{uc}) = \left(\frac{\int_0^\infty M^\alpha M f(M)\, dM}{\int_0^\infty M f(M)\, dM} \right)^{\frac{1}{\alpha}} \tag{34}$$

where the subscript α in its definition is used in order to distinguish it from the z-average defined by Eq. (33) (for $l = 2$).

Definition (Eq. (33)) is more suitable for calculation than Eq. (34). We shall now estimate a potential error due to the use of Eq. (33) instead of Eq. (34). By use of Eqs. (15) and (16), it is easy to find the ratio between the two averages as:

$$\bar{M}_{z,\alpha}/\bar{M}_z = (\bar{M}_w/\bar{M}_n)^{\frac{\alpha-1}{2}} \tag{35}$$

For $\alpha = 1$, which is the case of a random-flight chain [28], both definitions (Eqs. (33) and (34)) are identical. For slightly higher values, $\alpha \sim 1.2$ expected for polymers in good solvents, the error due to the use of definition (Eq. (33)) instead of Eq. (34) is, according to Eq. (35), below observable limit. Hence, the definition of $\bar{M}_z$ by Eq. (33) is acceptable.

Evaluating the integrals in Eq. (33) (the details of calculation are given in Appendix C) we have for n- and w- uncorrected averages ($l = 0$ and 1, respectively) in the n- and w-detections ($k = 0$ and *1*, respectively).

$$\bar{M}_l(k, \text{uc}) = \bar{M}_k(\bar{M}_w/\bar{M}_n)^{(l-k)(\Sigma+\Delta)} \exp(l-k)Z \tag{36}$$

and for the z-detection ($k = 2$) we have:

$$\bar{M}_l(2, \text{uc}) = \bar{M}_z(\bar{M}_w/\bar{M}_n)^{(l-2)\Sigma - \Delta/2} \tag{37}$$

From Eqs. (36) and (37), it is seen that, as stated by Hamielec [14,15], the n- and w-detection preserve 'its' average

$$\bar{M}_k(k, \text{uc}) = \bar{M}_k \tag{38}$$

It is remarkable that this equation holds for $k = 1$ and 2 also for $\delta \neq 0$ (i.e. when no local average of M is correctly determined).

From Eq. (36), it is seen that the uncorrected molecular weight as well as polydispersity change with σ^2 and δ, whereas in the z-detection, the uncorrected polydispersity does not change with δ. This needs a comment. In Eq. (36), the factors Δ and Z are multiplied by $(l-k)$, but in Eq. (37), there is only the term $\Delta/2$ in the exponent of $\bar{M}_w/\bar{M}_n$ and the exponential term is missing. Physical interpretation of this fact is as follows: Eq. (36) refers to the case where the difference in δ makes the dependence ln $\bar{M}_k(V, \text{uc})$ to rotate (change its slope) which results in the change in $\bar{M}_w(k, \text{uc})/\bar{M}_n(k, \text{uc})$. Eq. (37), however, refers to the case where the change in δ has no influence on the slope of the 'calibration' ln $\bar{M}_k(V, \text{uc})$ (which is determined entirely from the LS data as $F_2(V)/F_1(V)$ and it is only a relative shift of the 'calibration' with respect to the chromatogram $F_0(V)$. The shift affects all experimental averages in the same way.

As can be seen from Eqs. (36) and (37), the

expected effect of σ^2 (i.e. Σ) is the same in all ways of detection.

4. Conclusions

The local polydispersity $\bar{M}_w(V, \text{uc})/\bar{M}_n(V, \text{uc})$ due to peak broadening for a polymer sample with a MWD which obeys the log-normal function, was calculated. For a linear calibration dependence and a constant variance σ^2 of the spreading function $G(V, y)$, $\bar{M}_w(V, \text{uc})/\bar{M}_n(V, \text{uc})$ is constant over the whole range of V.

With increasing peak broadening, $\bar{M}_w(V, \text{uc})/\bar{M}_n(V, \text{uc})$ approaches the polydispersity of the non-fractioned sample, $\bar{M}_w/\bar{M}_n$.

In the case of perfect resolution and detection, the correlations of $\ln \bar{M}(V, \text{uc})$ vs. V determined by all detector combinations are identical with the true one, i.e., independent of the way of determination of M. If the resolution is poor the local polydispersity $\bar{M}_w(V, \text{uc})/\bar{M}_n(V, \text{uc})$ results; consequently the correlations of $\ln \bar{M}$ vs. V rotate about the points $(V_n, \ln \bar{M}_n)$, $(V_w, \ln \bar{M}_w)$ and $(V_z, \ln \bar{M}_z)$ for the detector combinations detecting, respectively, $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_z$. Only these averages are determined correctly; the other averages (e.g., $\bar{M}_n$ in the w- or z-detection with $\delta = 0$) as well as polydispersity are determined with errors.

If the value of interdetector volume has not been correctly determined, the rotation of $\ln \bar{M}(V, \text{uc})$ vs. V is also the consequence in the w- and n-detection and only $\bar{M}_w$ and $\bar{M}_n$, respectively, are determined correctly. In the z-detection, the correlation $\ln \bar{M}_z(V, \text{uc})$ vs. V is constructed from the MALLS record. The error in the interdetector volume does not affect the polydispersity determination and its precision depends on the peak broadening only.

If the resolution is very poor ($\sigma^2 \rightarrow \infty$), in the n-, w- and z-detection the values $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_z$ are detected in a broad range of V independent of the error, δ, in the interdetector volume.

Acknowledgements

Appendix A

Derivation of Eq. (14)

The product $\mathcal{W}_k(V, y)$ defined by Eq. (11) can be expressed as follows. First the quantity:

$$Q_k(y) = W(y)M^k(y) \tag{A.1}$$

is calculated as:

$$Q_k(y) = -\frac{B}{\beta\sqrt{\pi}} \exp E_1 \tag{A.2}$$

where the exponent:

$$E_1 = -\frac{B^2}{\beta^2}(y - V_0)^2 + k(A + By) \tag{A.3}$$

can be, using Eq. (9), expressed as:

$$E_1 = -\frac{B^2}{\beta^2}\left(y - V_0 - \frac{k\beta^2}{2B}\right)^2 + \ln M_0^k + \frac{k^2\beta^2}{4} \tag{A.4}$$

and Q_k is calculated using Eq. (18) as:

$$Q_k = -\frac{BM_0^k}{\beta\sqrt{\pi}} \exp \frac{k^2\beta^2}{4} \exp\left(-\frac{B^2}{\beta^2}(y - V_k)^2\right) \tag{A.5}$$

The quantity $\mathcal{W}_k(V, y)$ is calculated employing the definition (Eq. (11)), $\mathcal{W}_k(V, y) = Q_k G(V, y)$, as:

$$\mathcal{W}_k(V, y) = -\frac{B\mu_k'}{\beta\sigma\pi\sqrt{2}} \exp E_2 \tag{A.6}$$

where the exponent:

$$E_2 = -\frac{B^2}{\beta^2}(y - V_k)^2 - \frac{1}{2\sigma^2}(V - y)^2 \tag{A.7}$$

can be expressed as:

$$E_2 = -\left(\frac{B^2}{\beta^2} + \frac{1}{2\sigma^2}\right)\left(y - \frac{2\sigma^2 V_k + V(\beta/B)^2}{2\sigma^2 + (\beta/B)^2}\right)^2$$
$$- \frac{(V_k - V)^2}{2\sigma^2 + (\beta/B)^2} \tag{A.8}$$

Integration of $\mathcal{W}_k(V, y)$ expressed as Eq. (A.6) with E_2 given by Eq. (A.8) according to Eq. (10) is easy to perform (the Poisson integral). The result is Eq. (14), where, according to Eq. (17), the possible error, δ_k, in the interdetector volume has been introduced.

Appendix B

Derivation of Eq. (20)

The uncorrected molecular weight is according to the definition (Eq. (19)) calculated as:

$$\overline{M}_k(V, \text{uc}) = M_0 \exp \frac{(2k-1)\beta^2}{4} \exp E_3 \tag{B.1}$$

which may be written using Eqs. (4) and (5) and taking the logarithm:

$$\ln \overline{M}_k(V, \text{uc}) = k \ln \overline{M}_w + (1-k) \ln \overline{M}_n + E_3 \tag{B.2}$$

where:

$$E_3 = \frac{(V'_{k-1} - V)^2 - (V'_k - V)^2}{2\sigma^2 + (\beta/B)^2} \tag{B.3}$$

where, according to Eq. (18):

$$V'_k = V_0 + \frac{k\beta^2}{2B} + \delta \tag{B.4}$$

and (cf. the discussion following Eq. (19) Section 3.2)

$$V'_{k-1} = V_0 + \frac{(k-1)\beta^2}{2B} \tag{B.5}$$

The quantity E_3 can be expressed:

$$E_3 =$$
$$- \frac{[(\beta/B)^2 + 2\delta/B] \times [\ln M_0 - A - BV + (2k-1)\beta^2/4 + \delta B/2]}{2\sigma^2 + (\beta/B)^2} \tag{B.6}$$

which is, by using Eqs. (4) and (5):

$$E_3 = \frac{[(\beta/B)^2 + 2\delta/B][A + BV - k\ln\overline{M}_w + (k-1)\ln\overline{M}_n] - \delta^2 - (\delta/B)\ln\overline{M}_w/\overline{M}_n}{2\sigma^2 + (\beta/B)^2} \tag{B.7}$$

Inserting E_3 from Eq. (B.7) into Eq. (B.2), we have:

$$\ln \overline{M}_k(V) = \ln[\overline{M}_n(\overline{M}_w/\overline{M}_n)^k]$$
$$+ \frac{(\beta^2/B^2 + 2\delta/B)(A + BV - k\ln\overline{M}_w + (k-1)\ln\overline{M}_n) - \delta^2 - (\delta/B)\ln(\overline{M}_w/\overline{M}_n)}{2\sigma^2 + (\beta/B)^2} \tag{B.8}$$

which, by using the identities:

$$\overline{M}_n(\overline{M}_w/\overline{M}_n)^k = \overline{M}_k \tag{B.9}$$

and

$$\ln \overline{M}_k + \ln \sqrt{\overline{M}_w/\overline{M}_n} = \ln \sqrt{\overline{M}_k\overline{M}_{k+1}} \tag{B.10}$$

the formula (Eq. (20)) results.

Appendix C

Derivation of Eqs. (36) and (37)

The MWD averages are defined by Eq. (33). By use of Eq. (6) (for both uncorrected MWD and chromatogram) and employing the definition of local molecular weight by Eq. (19), it can be shown that the alternative expression for uncorrected averages is:

$$\overline{M}_l(k, \text{uc}) = \frac{\displaystyle\int_{-\infty}^{\infty} \overline{M}_k^l(V, \text{uc})F_0(V)\,\mathrm{d}V}{\displaystyle\int_{-\infty}^{\infty} \overline{M}_k^{l-1}(V, \text{uc})F_0(V)\,\mathrm{d}V} \tag{C.1}$$

where for $l = 0$, 1 and 2, respectively, the definitions of $\overline{M}_n(\text{uc})$, $\overline{M}_w(\text{uc})$ and $\overline{M}_z(\text{uc})$, respectively, is obtained, for $k = 0$, 1 and 2 denoting the n-, w- and z-detection according to Eq. (19). The integrals in Eq. (C.1).

$$I_{i,k} = \int_{-\infty}^{\infty} \overline{M}_k^i(V, \text{uc})F_0(V)\,\mathrm{d}V \tag{C.2}$$

where $i = l$ and $l - 1$, can be, according to definition of local molecular weight, (Eq. (19)), expressed as:

$$I_{i,k} = \int_{-\infty}^{\infty} \left(\frac{F_k(V)}{F_{k-1}(V)} \right)^i F_0(V)\, dV \tag{C.3a}$$

Inserting $F_k(V)$ and $F_{k-1}(V)$ from Eq. (14), the integration can be performed. The result is (details are given below):

$$I_{0,k} = 1 \tag{C.3b}$$

$$I_{i,0} = P_{i,0} \sqrt{\frac{\pi}{p}} \exp[pi(i+1)(V_1 - v_0)^2] \tag{C.4}$$

$$I_{i,1} = P_{i,1} \sqrt{\frac{\pi}{p}} \exp[pi(i-1)(V_1 - V_0)^2] \tag{C.5}$$

$$I_{i,2} = P_{i,2} \sqrt{\frac{\pi}{p}} \exp\{p[i^2(V_1 - V_2)^2$$
$$- i(V_1 - V_2)(V_0 - V_1 + V_0 - V_2)]\} \tag{C.6}$$

where:

$$p = 1/(2\sigma^2 + \beta^2/B^2) \tag{C.7}$$

and the constant term is evaluated:

$$P_{i,k} = \sqrt{\frac{p}{\pi}} \left(\frac{\mu_k'}{\mu_{k-1}'} \right)^i = \sqrt{\frac{p}{\pi}} \overline{M}_k^i \tag{C.8}$$

In the calculation of $I_{i,0}$ through $I_{i,2}$, the following identities were used:

$$- pi(V - V_0)^2 - p(V - V_0)^2 + pi(V - V_1)^2 =$$
$$- p(V - (i+1)V_0 + iV_1)^2$$
$$+ pi(i+1)(V_1 - V_0)^2 \tag{C.9}$$

in the calculation of $I_{i,0}$:

$$- pi(V - V_1)^2 - p(V - V_0)^2 + pi(V - V_1)^2 =$$
$$- p(V + (i-1)V_0 - iV_1)^2$$
$$+ pi(i-1)(V_1 - V_0)^2 \tag{C.10}$$

in the calculation of $I_{i,1}$, and

$$- pi(V - V_1)^2 - p(V - V_0)^2 + pi(V - V_1)^2 =$$
$$- p(V - V_0 + i(V_1 - V_2))^2 + pi^2(V_1 - V_2)^2$$
$$- pi(V_1 - V_2)(V_0 - V_1 + V_0 - V_2) \tag{C.11}$$

in the calculation of $I_{i,2}$.

Inserting $F_k(V)$ and $F_{k-1}(V)$ given by Eq. (14) into integrals (Eqs. (C.3a) and (C.3b)) results in the integration of a constant term, given by Eq. (C.8),

multiplied by an exponential term. The argument in the exponential term is in each case rearranged using Eq. (C.9) through Eq. (C.11). The integration (over V in the limits from $-\infty$ to ∞) is then easily performed, using the Poisson integral, and Eq. (C.4) through Eq. (C.6) result.

The exponential terms in Eq. (C.4) through Eq. (C.6) are calculated using the following expressions derived from Eq. (17).

$$V_1' - V_2' = -\beta^2/2B \tag{C.12}$$

$$V_0' - V_1' = -\beta^2/2B - \delta \tag{C.13}$$

$$V_0' - V_2' = V_0' - V_1' + V_1' - V_2'$$
$$= -\beta^2/B - \delta \tag{C.14}$$

The integrals (Eq. (C.4)) are calculated as:

$$I_{i,0} = \overline{M}_n^{-1} \exp[pi(i+1)(\beta^2/2B + \delta)^2]$$
$$= \overline{M}_n^{-1} \exp\left[pi(i+1)\left(\frac{\beta^2}{2B} + \frac{2\delta}{B} \right) \ln(\overline{M}_w/\overline{M}_n) + \delta^2 \right]$$
$$= \overline{M}_n^{-1} (\overline{M}_w/\overline{M}_n)^{\frac{i(i+1)}{2}(\Sigma + \Delta)} \exp\left[\frac{i(i+1)}{2} Z \right] \tag{C.15}$$

The integrals $I_{i,1}$ are calculated in the same way as $I_{i,0}$ [with $i(i-1)$ instead of $i(i+1)$]. The result is:

$$I_{i,1} = \overline{M}_w (\overline{M}_w/\overline{M}_n)^{\frac{i(i-1)}{2}(\Sigma + \Delta)} \exp\left[\frac{i(i-1)}{2} Z \right] \tag{C.16}$$

and the integrals $I_{i,2}$ are calculated as:

$$I_{i,2} = \overline{M}_z^2 \exp\left[i^2 p \frac{\beta^2}{B^2} \frac{\beta^2}{4} - \frac{i}{p}\left(\frac{3\beta^2}{2B} - 2\delta \right) \right]$$
$$= \overline{M}_z^2 \exp\left[i(i-3)p \frac{\beta^2}{B^2} \ln\sqrt{\overline{M}_w/\overline{M}_n} - ip \frac{4\delta}{B} \ln\sqrt{\overline{M}_w/\overline{M}_n} \right]$$
$$= \overline{M}_z^2 (\overline{M}_w/\overline{M}_n)^{\frac{i(i-3)}{2}\Sigma - \frac{i}{2}\Delta} \tag{C.17}$$

The uncorrected number-, weight-, and z-average molecular weights are, respectively, calculated as

$I_{0,0}/I_{-1,0}$, $I_{1,0}/I_{0,0}$, and $I_{2,0}/I_{1,0}$, in the n-detection, and, as $I_{0,1}/I_{-1,1}$, $I_{1,1}/I_{0,1}$, and $I_{2,1}/I_{1,1}$ in the w-detection. In both cases, the results can be expressed as Eq. (36). In the z-detection, the averages are respectively calculated as $I_{0,2}/I_{-1,2}$, $I_{1,2}/I_{0,2}$, and $I_{2,2}/I_{1,2}$, and the results can be expressed as Eq. (37).

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