Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1084 (2005) 160–166
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Direct determination of band broadening in size exclusion chromatography

I. Schnöll-Bitai*

Institut für Physikalische Chemie, Währinger Str. 42, A-1090 Vienna, Austria

Abstract

A simple method to correct the measured extent of band broadening in size exclusion chromatography for the contribution of narrow (polydisperse) standards is presented. It is based on the assumptions that commercial polymer standards can be described by a Poisson distribution and the additivity of peak variances. Two sets of standards (polystyrene from two suppliers) were investigated under normal working conditions, i.e. a combination of four columns with different porosities and a flow rate of 1 ml/min. Furthermore, the polystyrene standards were used to determine the extent of band broadening for four additional combinations of columns (varying in their separation range and porosities) as a function of the elution volume. The assumption of a constant peak variance for band broadening turned out to be a (very) rough approximation for some combinations of columns, but all results taken together demonstrate that this assumption is not generally applicable. Qualitative agreement between theory and experiment was found with a rearranged van Deemter equation.

Keywords: Size exclusion chromatography; Band broadening; Poisson distribution; Van Deemter equation

1. Introduction

When measuring chain length distributions (CLD) of polymers with size exclusion chromatography the influence of band broadening (bb) on the CLD becomes obvious for monodisperse samples, narrow polymers and for "broad" multimodale distributions composed of narrow peaks. The determined number and mass average degrees of polymerization and polydispersities are slightly incorrect as a consequence. Furthermore, due to bb a shift of the location of the points of inflection (which are used for the direct determination of the rate constant of propagation, k_p, in free radical polymerization [1]) can be observed. In order to be able to correct this adulteration an experimentally simple, fast and straightforward method for the direct determination of the extent of bb as a function of elution volume is needed. Based on this knowledge correction routines can be developed. These problems are addressed in the IUPAC project *"Data treatment in size exclusion chromatography of polymers – Correction for band broadening and other systematic errors"* from G.R. Meira.

Knox and McLennan [2] already pointed out that the peak width of a measured distribution is composed of two contributions, namely the original width of the distribution (due to the fact that synthetic polymers are polydisperse) and the influence of bb. This fact is also expressed by the additivity of peak variances:

$$\sigma^2_{SEC} = \sigma^2_{peak} + \sigma^2_{bb} \quad (1)$$

σ^2_{SEC} is the measured peak variance, σ^2_{peak} and σ^2_{bb} represent the contributions of the peak and bb, respectively. The conventional direct determination of both contributions involves either a lot of experimental work or sophisticated mathematical inversion procedures. On the other hand, theoretical expressions can be derived for σ^2_{peak} for different types of distribution which are to be expected for either anionic or radical polymerizations.

Ideal anionic polymerization will lead to Poisson distributions, distributions with narrow peaks can be synthesized by either quasi living radical polymerization, pseudo-stationary or quenched instationary polymerizations. Anal-

* Tel.: +431 4277 52441; fax: +431 4277 9524.
E-mail address: irene.schnoell-bitai@univie.ac.at.

0021-9673/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2004.09.079

ysis of calculated narrow CLDs showed, that the location of the points of inflection is always influenced by experimental conditions. Poisson distributions and narrow distributions are characterized by the fact, that the relative peak width δ (defined as the ratio of the points of inflections i_{high}, i_{low}) is an invariant quantity with respect to the number, n, molar mass, w, and the so called hyper distribution, h [3,4]:

$$\frac{i_{high}}{i_{low}} = \delta_n \approx \delta_w \approx \delta_h > 1 \tag{2}$$

This is important as it means that the relative peak width is also independent of the detector type. The location of the extraordinary points can either be determined directly from the raw data or from those converted to the different types of distribution. The peak width, Δ_{SEC}, determined from the raw data is proportional to the relative peak width according to [5]:

$$\begin{aligned} 2\sigma_{SEC} &= \Delta_{SEC} = V_{R,low} - V_{R,high} \\ &= \frac{1}{k}\{\log M_{high} - \log M_{low}\} \\ &= \frac{1}{k}\log\frac{L_{high}}{L_{low}} = \frac{1}{k}\log\delta_h \end{aligned} \tag{3}$$

with k being the slope of a linear calibration: $\log(M) = a - kV_R$.

Knowledge of the ideal peak variance suffices for correcting the measured peak variance for the contribution of polydispersity, thus enabling the direct determination of band broadening:

$$\sigma_{bb} = \sqrt{\sigma^2_{SEC} - \sigma^2_{peak}} = \frac{1}{2}\sqrt{\Delta^2_{SEC} - \{\log(\delta_{peak})/k\}^2} \tag{4}$$

For monodisperse samples, the relative peak width is independent of the molar mass and equal to one per definition. For a Poisson distribution, the relative peak width depends only on the value of the chain length at the peak maximum, i_{max}, according to theory [5]:

$$\delta = \frac{i_{max} + \sqrt{i_{max}}}{i_{max} - \sqrt{i_{max}}} \tag{5}$$

The experimental variance already corrected for the contribution of the polydispersity is still composed of several contributions, namely those of the injector, the connecting capillaries, the detector and the columns:

$$\sigma^2_{bb} = \sigma^2_{inj} + \sigma^2_{cap} + \sigma^2_{det} + \sigma^2_{col}\,(ml^2) \tag{6}$$

From capillary liquid chromatography [6], estimates for the first three quantities can be given:

$$\sigma^2_{inj} = \frac{V^2_{inj}}{D^2}\,(ml^2) \tag{7}$$

D^2 is a constant for the injection technique and equals 12 for a rectangular sample plug (this corresponds to the lowest possible contribution from the injection process). For an injection volume V_{inj} = 0.1 ml, the contribution from the injection is as small as $\sigma^2_{inj} = 8.3 \times 10^{-4}\,ml^2$.

$$\sigma^2_{cap} = \frac{r^4 l\pi F}{384 D_m}\,(ml^2) \tag{8}$$

For a flow rate F of 0.0167 ml/s, a radius of the capillary of r = 0.0125 cm and a diffusion coefficient of the solute $D_m = 3.4 \times 10^{-4} \times M^{-0.564}\,cm^2/s$ [7] (for polystyrene in THF at T = 25 °C) will give rise to about $5 \times 10^{-6}\,ml^2$ per cm capillary.

Depending on the detector type, injection mode and injection volume, this contribution can range from 0.00017 to 0.00372 ml^2 [6]. In all, the extra-column contributions to bb are pretty small and as the comparison with experimental results will show can be neglected without loss of accuracy.

$$\sigma^2_{bb} \approx \sigma^2_{col} \tag{6a}$$

Therefore, bb is dominated by the effects occurring in the columns. Van Deemter [8] presented a theoretical equation for the height equivalent of a theoretical plate H that takes into account the contributions of diffusion and mass resistance:

$$H = A + \frac{B}{u} + Cu\,(cm) \tag{9}$$

with a linear flow rate (cm/s).

The first term, A, represents the contribution from the eddy diffusion, whereas the extent of longitudinal diffusion of the solute in the mobile phase is described by the second term, B. The third term, C, stems from the mass transfer between the stationary phase in the pores and the mobile phase. The plate height is correlated to the peak variance by:

$$H = \left(\frac{\sigma_{col}}{V_R}\right)^2 L \tag{10}$$

with L being the length of the column(s).

2. Experimental

Standards: poly(styrene) (PS), poly(methyl methacrylate) (PMMA) were from Polymer Standard Service (PSS, Mainz Germany) and poly(styrene) from scientific products (SP, Ontario, New York, USA); *eluent*: THF (Merck, Vienna, Austria), 1 ml/min at 30 °C; *columns*: PSS-SDV, 10 μm (8 mm × 300 mm), 10^3, 10^4, 10^5, 10^6 A (a new set of columns was used and its performance was not completely identical with that used before) from Polymer Standard Service (Mainz, Germany); the columns were always connected in the order of decreasing porosity starting with the highest porosity after the injector. *Detector*: Waters RI (Waters 2410, Vienna, Austria). Between the injector were a pre-column filter and

a PSS-SDV 10 μm pre-column (8 mm × 50 mm) from Polymer Standard Service (Mainz, Germany). Mixtures of three or four standards were used; the concentration varied between 1 and 2 mg/ml for masses below 10^4, between 0.5 and 1 mg/ml for 10^4 < molar mass < 10^6 and was below 0.5 mg/ml for higher molar masses. Too high a concentration broadened the signal additionally. For each polymer type, a linear as well as a third order polynomial calibration curve was constructed. In the intermediate elution range, the two calibration curves coincided, deviations were observed at the low and high molar mass ends. The chromatographic data was numerically differentiated in order to determine peak maxima and points of inflection.

3. Results and discussion

The use of a linear calibration curve is a simplification which might only be justified in the intermediate region of a calibration curve. In most cases, a distinct curvature can be observed at both ends of the calibration range. When a linear calibration is used or the calibration curve is replaced by a polygon, the peak variances seem to increase at high values of the peak maximum (cf. Fig. 1 "local slope"). On the other hand, if at a certain retention volume the slope is assigned the value of the first derivative:

$$k = \frac{d \log M}{\mathrm{d}V} = \sum_{i=1}^{j} i a_i V_R^{i-1} \tag{11}$$

it becomes obvious that the choice of the slope will influence the results considerably where the calibration curve deviates from linearity. In Fig. 1, the results are compared for two sets of polystyrene standards, one from PSS and the other from SP. Below a molecular mass of 10,000 (i.e. $\log i_{\max} < 2$) the variances become smaller and below 5000 negative values were obtained in some cases. Neglecting this low molecular mass region, it seems to be justified to interpret the peak variances as almost constant for a molecular weight range of 10,000 to 3,000,000 without any theoretical background. A constant variance was also found by Busnel et al. [7] for different columns. A distinct reduction in the peak variances below a degree of polymerization for the peak maximum $i_{\max}$ of 100 does not disappear when the slope is assigned the value of the first derivative. A similar behaviour was observed when PMMA standards were analyzed. The scatter in the data is comparable for the PS standards from both suppliers, it seems to be slightly larger for the PMMA standards (even when neglecting one standard with M_n = 22,200 which does not at all comply with the other data).

An increase in band broadening is expected near the exclusion limit, but according to the specification of the supplier all standards should lie within the separation range of the columns. When the column 10^6 A is taken away, the standards with the highest molar masses should lie outside of the separation range. In Fig. 2, a maximum in the σ^2 values can be observed at $\log(i_{\max}) \sim 3.5$ and the variances drop drastically at even higher degrees of polymerization (lower retention volumes). Most variances are smaller than for the combination of four columns which is intuitively expected. The location of the maximum is shifted to lower $\log(i_{\max})$ values when the separation range is further reduced by taking away the column with 10^5 A; the peak variances become smaller in the separation range. At first glance, a decreasing variance with increasing $\log(i_{\max})$ seem to be in contradiction with the results given in Fig. 1 but the trend can already be observed in Fig. 2.

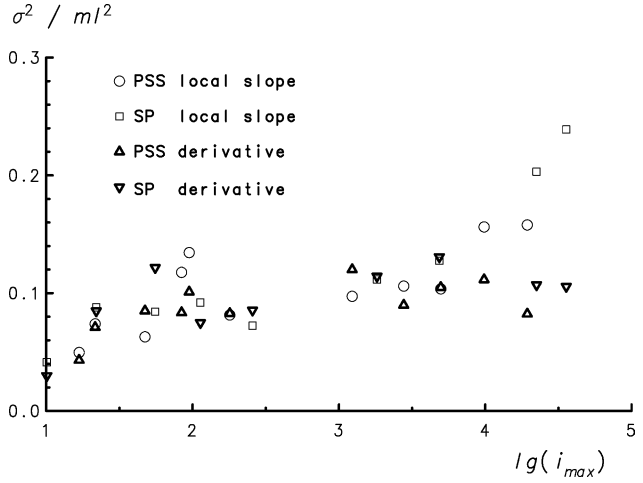

Fig. 1. Comparison of σ^2 values as a function of the degree of polymerization $i_{\max}$ of the peak maximum determined with either a local slope (polygon calibration) or the slope calculated via the first derivative of the calibration curve (Eq. (11)); columns: $10^6 + 10^5 + 10^4 + 10^3$ A.

Cheng et al. [9] demonstrated that a maximum in the spreading function σ^2 should appear which is due to the inverse proportionality of the column spreading function to the diffusion coefficient D_m of the solute. Rearrangement of the van Deemter equation and insertion of the respective terms

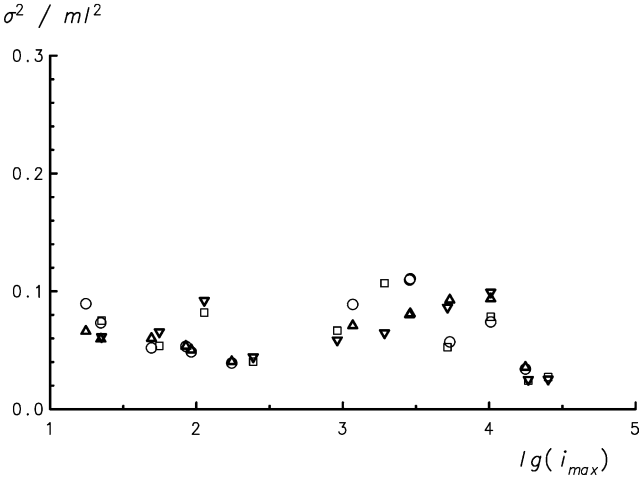

Fig. 2. σ^2 values for a column combination with a smaller separation range; columns $10^3 + 10^4 + 10^5$ A; symbols as in Fig. 1.

[10] for the different contributions will lead to:

$$\frac{HV_R^2}{L} = \lambda\frac{2d_p}{L}V_R^2 + \gamma\frac{2D_m}{L}\frac{1}{u}V_R^2 + q\frac{V_0}{L}\frac{d_p^2}{D_s}u(V_R - V_0) = \sigma_{col}^2 \quad (10a)$$

This equation is more complete than the one used by Cheng et al. It gives information of how the particle diameter d_p and the interstitial volume V_0 will influence the peak variance as a function of elution volume. D_s is the diffusion coefficient of the solute in the pores and is expected to be smaller due to obstructed diffusion effects within a pore [11] according to:

$$\frac{D_m}{D_s} = \exp\left\{\beta\frac{R_s}{R_{1/2}}\right\} \quad (12)$$

where β is either 5.5 for a ratio of the Stokes radius of the polymer to the pore radius $R_s/R_{1/2}$ below 0.05 or $\beta = 7.4$ for $R_s/R_{1/2}$ above 0.05. If this ratio is set constant as an approximation:

$$D_s = cD_m = cc'M^{-\varepsilon} \quad (13)$$

c is called the obstruction factor. When a linear calibration in the form

$$\ln M = a' - k'V_R$$

is used Eq. (10a) takes the form

$$\sigma_{col}^2 = \lambda A V_R^2 + \gamma B_1 \exp\{B_2 V_R\}V_R^2 + \frac{1}{c}C_1 \exp\{C_2 V_R\}V_0(V_R - V_0) \quad (10b)$$

with

$$A = \frac{2d_p}{L}$$

$$B_1 = \frac{2}{L}\frac{c' \exp\{-\varepsilon a'\}}{u}$$

$$B_2 = \varepsilon k' = -C_2$$

$$C_1 = q\frac{d_p^2}{L}\frac{u}{c' \exp\{-\varepsilon a'\}}$$

for a constant flow rate. In Table 1 the different combinations of columns are compiled together with the calculated coefficients for polystyrene by making use of the diffusion coefficient of styrene as given before and a geometrical factor of $q = 1/30$ as derived by Giddings [12]. It was not possible to determine the interstitial volume V_0 with a polymer standard with a molecular weight higher than the exclusion limit as there seemed to be still some separation (this was deduced from the calibration curves). Therefore, from the standard with the highest molecular weight the retention volume belonging to the beginning of the elution curve was chosen as a substitute. This value was slightly higher than the separation limit given by the supplier for the column with the highest porosity (10^6 A), but definitely higher than those with lower porosities. Nevertheless, the qualitative agreement between experiment and theory seems to justify this choice. A sensible data fit was not possible when the exclusion limit as given from the supplier [19] for the different columns were converted into retention volumes.

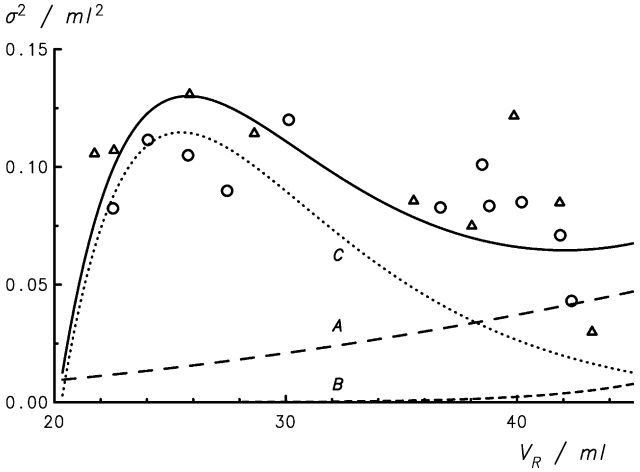

Fig. 3. σ^2 values as a function of the retention volume V_R; circles: results from PSS standards, triangles: results from SP standards; columns: $10^6 + 10^5 + 10^4 + 10^3$ A. The full line is the sum of the three contributions (A, B and C) as given by the van Deemter Eq. (10b).

The values listed in Table 1 demonstrate that the contribution of the longitudinal diffusion (B term) is far smaller than those from eddy diffusion and mass transfer and can therefore be neglected in most cases; only for high elution volumes a non negligible contribution will appear. This is in agreement with the observation of Striegel for the B-term broadening below 30,000 [13]. This can also be observed in the Figs. 3–7, where the determined variances are compared with the theoretical predictions (Eq. (10b)); the different contributions are also included. For a qualitative agreement between theory and experiment, $\gamma = 1$ and $\lambda = 1.4$ was used in all cases. The latter constant represents the quality of packing and ranges from 1 (very well packed) to 10 (faulty packing) [14]. With respect to

Table 1
The particle size for all columns was 10 μm, the linear flow rate was 0.0332 cm/s

Combination	Length (cm)	a'	$-k'$ (ml^{-1})	V_0 (ml)	A (10^{-5})	B_1 (10^{-10})	$B_2 = -C_2$	C_1 (10^{-3})
10^6, 10^5, 10^4, 10^3	120	22.117	0.3421	20.3	1.67	6.5	0.193	7.11
10^5, 10^4, 10^3	90	21.425	0.4486	15.0	2.22	12.8	0.253	6.41
10^4, 10^3	60	21.425	0.6797	10.2	3.33	19.2	0.383	9.62
10^6, 10^5	60	23.378	0.6646	11.5	3.33	6.4	0.375	28.95
10^6, 10^5, 10^4	90	22.419	0.4396	16.5	2.22	7.3	0.248	11.23

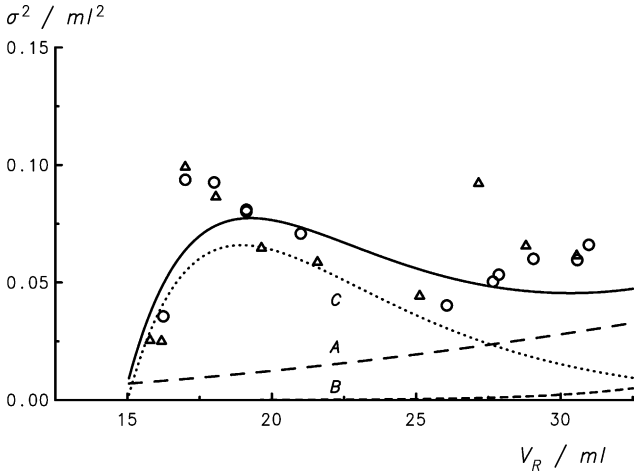

Fig. 4. σ^2 values as a function of the retention volume V_R; symbols as in Fig. 3; columns: $10^5 + 10^4 + 10^3$ A.

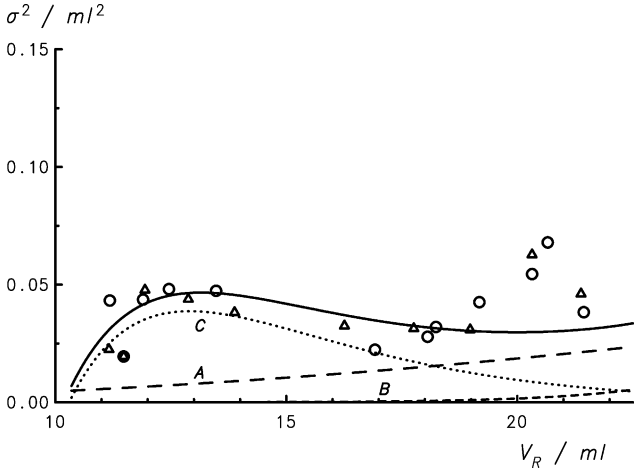

Fig. 5. σ^2 values as a function of the retention volume V_R; symbols as in Fig. 3; columns: $10^4 + 10^3$ A.

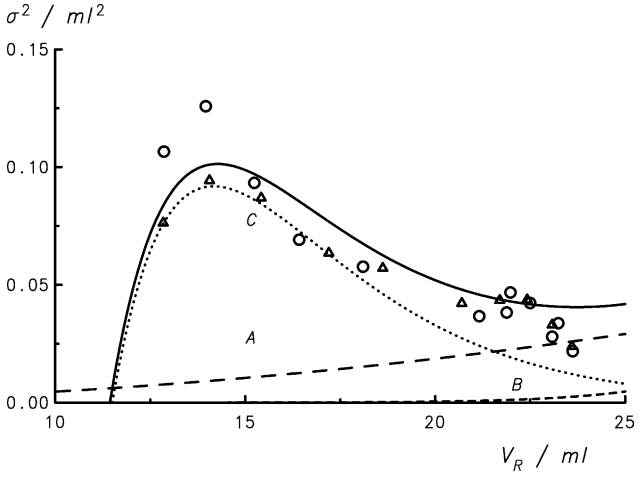

Fig. 6. σ^2 values as a function of the retention volume V_R; symbols as in Fig. 3; columns: $10^6 + 10^5$ A.

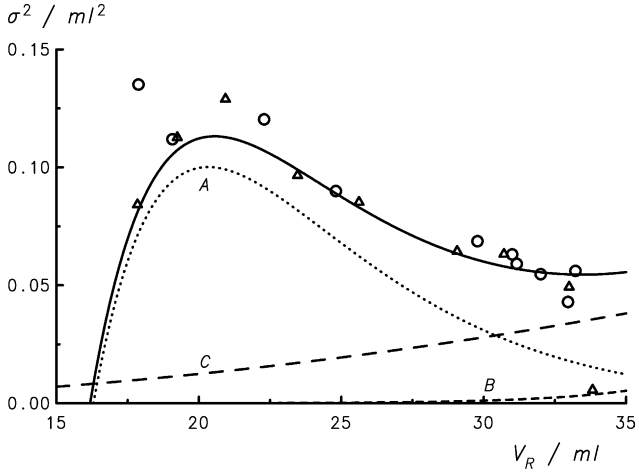

Fig. 7. σ^2 values as a function of the retention volume V_R; symbols as in Fig. 3; columns: $10^6 + 10^5 + 10^4$ A.

the mass transfer term c^{-1} was set equal to 21 for all column combinations. This would correspond to an obstruction factor of about 0.05. This is far smaller than the expected value of 0.7 for a small molecule (e.g. toluene) and also smaller than 0.12 as determined for polystyrene with a molecular weight of 160,000 [14]. Taking into account that the obstruction factor strongly depends on the molecular mass, a still smaller value is feasible for molecular masses over 10^6. Whether this value is physically preposterous or not can be decided with the following estimate.

As separation is said to occur because of the size of the solute, the radius of an equivalent sphere can be derived from the hydrodynamic volume V_h:

$$V_h = \frac{4\pi}{3} R_{sphere}^3 \tag{14a}$$

$$V_h \approx \frac{K M^{1+\alpha}}{N_L} \tag{14b}$$

With the Kuhn–Mark–Houwink–Sakurada coefficients for polystyrene in THF at $T = 25\,^\circ$C of $K = 0.011\,\mathrm{cm^3\,g^{-1}}$ and $\alpha = 0.725$ [15], the radii of the analyzed polymer standards range from 0.9 to 70 nm. The pore radius for the different columns are given in Table 2 together with the obstruction factor calculated with Eq. (12) for the standards with the highest molecular mass in the respective separation range. Thus, it is demonstrated that the values used to fit the experimental results are in a physically sensible range.

Table 2
Compilation of the pore radii [19] of the columns, the molar mass of the standard closest to the upper separation limit and the calculated c^{-1} values

Column	Radius (nm)	Molar mass	c^{-1}
10^6	182	2057000	16
10^5	74.4	512000	21
10^4	58.8	295000	16
10^3	10.3	18100	25

In all, the variances obtained for the different column combinations can be described by the van Deemter equation with only two adjustable parameters. The first belonging to the *A* term, describes the quality of the packing, the second gives information about the obstructed diffusion in the pores (*C* term). This is surprising as in all cases a combination of different porosities was used and no information was found of how this fact will influence the variances. Furthermore, instead of a size dependent obstructive factor (as given in Eq. (12)) a constant value was used to fit the data in order to keep the theoretical equation as simple as possible. Close inspection of the results from the combinations containing the lowest porosity (10^3 A) reveals that the variances for those standards with low molecular weight masses are higher than the theoretical ones, whereas such an effect seems to be missing for the two combinations without this column. Inclusion of a second *C* term with a higher interstitial volume (for the 10^3 column) improved the quality of the fit slightly. Thus, the van Deemter equation in its most simple formulation suffices to describe the experimental results and does not support the view of a constant variance independent of the retention volume. On the other hand, in some cases this assumption turned out be a possible approximation. Therefore, it will always be necessary to determine the variances of band broadening directly for a given column combination whenever the application of any kind of correction procedure is intended. These results also demonstrate very clearly that the combination of columns with different porosities have a very pronounced influence on the dependence of the variances on the retention volume. On the first sight contradictory experimental results found in the literature of either a constant variance [7] or an increasing variance [16] with decreasing retention volume become compatible by the van Deemter equation.

Another trial to link existing theories with experimental results was done by the investigation of the reduced plate height which lead to the following results: For the column set with the largest nominal separation range, the slope of log *h* versus log i_{max} is close to 0.25 but slight deviations can be observed in the low molecular mass regime. The obtained slope is in agreement with the results obtained by Glöckner [17] where a slope of 0.24 is expected according to theory and was measured for a set of columns packed with LiChrospher®. For the column combination 10^3 and 10^4 A alone, the reduced plate height decreased with increasing P_{max} in the low molar mass region followed by an increase. Vander Heyden et al. [18] reported a similar behaviour for a PL-Gel 5 μm column with 10^3 A. These results cannot be interpreted by the approach presented by Glöckner as a more complex pattern for the reduced plate height as a function of molar masses was obtained when different combinations of columns were used. From this, it can be concluded that the extrapolation procedure suggested by Glöckner is not applicable in all cases and it is therefore essential to determine directly the band broadening occurring in a given set of columns.

This can be done either by making use of commercially available polymer standards as shown in this contribution or by polymers synthesized independently. Multimodale distributions with narrow peaks can be obtained by radical pseudostationary polymerization (either rotating sector with a fixed sector speed or pulsed laser polymerization) in microemulsion [20,21].

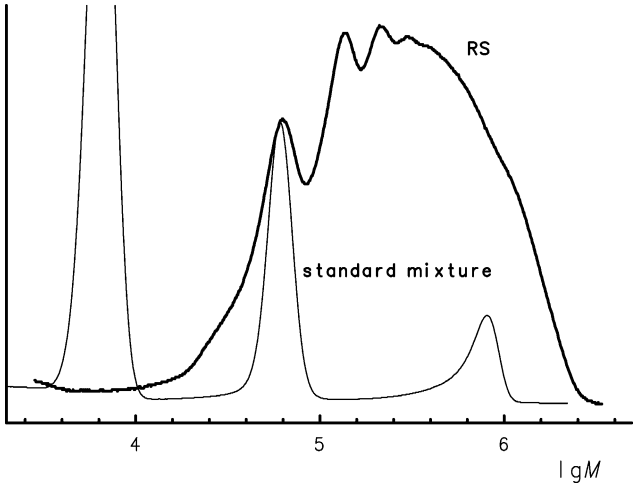

Fig. 8. RI signals of a PMMA standard mixture and a PMMA prepared by radical polymerization in microemulsation with intermittent illumination (RS = rotating sector with a light to dark ratio = 1:5). The location of the first peak maximum in the RS-signal corresponds to a molar mass of 62,500 and the respective value from the standard mixture is 61,000.

In the first case [20], narrow peaks are obtained with theoretical relative peak widths δ of 1.2 and 1.09 for the first and second peak for a light to dark ratio of 1:5 (based on distributions simulated for instationary polymerization conditions). For polymers prepared by pulsed laser polymerization [20], Eq. (5) is valid. In Fig. 8, the qualitative comparison between the peak width of PMMA prepared by pseudostationary polymerization in microemulsion and a standard (prepared by anionic polymerization) demonstrates that the peak width of the first is broader. The variance obtained from the first and second peaks of this sample by taking into account the proper theoretical peak variance is in agreement with that obtained from the standards [21]. Comparison of the variances determined from polymers prepared by different techniques can be used to judge the quality of polymer standards. In this way, we were able to show that the PMMA standard with M_n = 22,200 is too broad in comparison with a Poisson distribution and must therefore lead to a to high σ^2 value [21].

4. Conclusion

The determination of σ^2 of band broadening in size exclusion chromatography was based on the assumption that commercial polymer standards are almost Poisson distributed. The measured peak widths (defined via the points of inflection) are related to the variances and can be corrected for the variance stemming from the polymer distribution itself. Comparison of the results obtained with PS standards from

two suppliers showed good agreement for all measurements. Therefore, most of the investigated polymer standards can be used for the direct determination of the extent of band broadening following the procedure outlined in this contribution. On the other hand, polymers prepared by pseudostationary radical polymerization techniques can also be used to determine σ^2. Comparison of the results with those obtained from polymer standards is useful to discriminate standards as being close to or deviating appreciably from a Poisson distribution.

The study also demonstrates that no general recommendation concerning the dependence of σ^2 on the retention volume and therefore the degree of polymerization can be given. Sometimes the variances will be almost constant, or increase with decreasing retention volume or show even a more complicated behaviour depending on the separation range and the porosities of the columns. Consequently, σ^2 must be determined for each combination of columns for the intended experimental conditions. Depending on the combination of columns (partial) agreement with results from Busnel et al. [7], Cheng et al. [9], Glöckner [17] and Vander Heyden et al. [18] was observed. It was possible to interpret the experimental results by a rearranged van Deemter equation where only two parameters needed to be adjusted. It became evident that a general theory explaining how the combination of different porosities can be taken into account properly is needed.

References

[1] O.F. Olaj, I. Bitai, F. Hinkelmann, Makromol. Chem. 155 (1987) 177.
[2] J.H. Knox, F. McLennan, J. Chromatogr. 185 (1979) 289.
[3] I. Schnöll-Bitai, Macromol. Theor. Simul. 11 (2002) 199.
[4] I. Schnöll-Bitai, Macromol. Theor. Simul. 11 (2002) 770.
[5] I. Schnöll-Bitai, Macromol. Chem. Phys. 203 (2002) 1754.
[6] A. Prüß, C. Kempter, J. Gysler, T. Jira, J. Chromatogr. A 1016 (2) (2003) 129.
[7] J.P. Busnel, F. Foucault, L. Denis, W. Lee, T. Chang, J. Chromatogr. A 930 (2001) 61.
[8] J.J. van Deemter, F.J. Zuiderweg, A. Klinkenber, Chem. Eng. Sci. 5 (1956) 271.
[9] R.-S. Cheng, Z.-L. Wang, Y. Zhao, ACS Symp. Ser. 352 (1987) 281.
[10] O. Chiantore, M. Guaita, J. Liq. Chromatogr. 5 (4) (1982) 643.
[11] M. Potschka, J. Chromatogr. 648 (1993) 41.
[12] J.C. Giddings, Dynamics of Chromatography, Marcel Dekker, New York, 1965.
[13] M. Striegel, J. Chromatogr. A 932 (2001) 21.
[14] R. Tijssen, Handbook of HPLC (Chromatographic Science Series Vol. 78), Marcel Dekker, New York, 1998, p. 72.
[15] M. Kurata, Y. Tsunashima, Polymer Handbook, 4th ed., John Wiley & Sons, 1999, p. 68.
[16] J. Billani, G. Rois, K. Lederer, Chromatographia 26 (1988) 372.
[17] G. Glöckner, J. Liq. Chromatogr. 7 (1984) 1769.
[18] Y. Vander Heyden, S.-T. Popovici, B.B.P. Staal, P.J. Schoenmakers, J. Chromatogr. A 986 (2003) 1.
[19] P. Kilz, personal communication.
[20] I. Schnöll-Bitai, C. Pfeisinger, Macromol. Chem. Phys. 204 (2003) 384.
[21] C. Pfeisinger, K.-J. Su, G. Wagner, I. Schnöll-Bitai, in preparation.