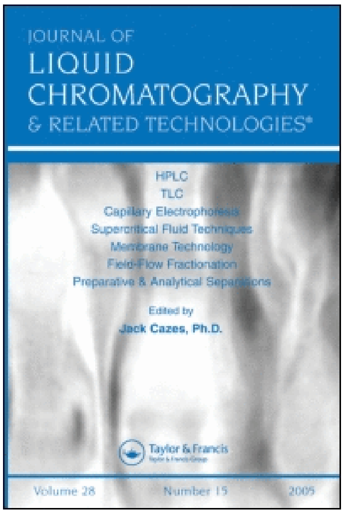

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Froment, P. and Revillon, A.(1987) 'Some Aspects of Analysis of Polymers by Steric Exclusion Chromatography and On-line Low Angle Laser Light Scattering (SEC-LALLS)', Journal of Liquid Chromatography & Related Technologies, 10: 7, 1383 — 1397
To link to this Article: DOI: 10.1080/01483918708066775
URL: http://dx.doi.org/10.1080/01483918708066775

JOURNAL OF LIQUID CHROMATOGRAPHY, 10(7), 1383-1397 (1987)

SOME ASPECTS OF ANALYSIS OF POLYMERS BY STERIC EXCLUSION CHROMATOGRAPHY AND ON-LINE LOW ANGLE LASER LIGHT SCATTERING (SEC-LALLS)

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ABSTRACT

Low angle laser light scattering as a second detector for size exclusion chromatography separation leads to true values of $\bar{M}_w$ but $\bar{M}_n$ and molecular weight distribution (MWD) are strongly dependent on axial dispersion σ and calibration system. Here, we discuss (i) on certain experimental parameters and (ii) on the influence of σ for two MWD and different calibrations on $\bar{M}_n$ values and calculated MWD.

INTRODUCTION

With our first results (1), we have already published the interest and the limits of light scattering detection in size-exclusion chromatography (SEC). We insist that the weight-average molecular weight $\bar{M}_w$ is always the true value whereas the number-average molecular weight $\bar{M}_n$ is affected by the efficiency of the chromatographic system and by the treatment of data. Additionally, the molecular weight distribution (MWD) is affected. Consequently, very few results are shown in the literature. Our study has been extended to other polymers. Yet, the results presented here are those of a fundamental approach, considering the axial spreading and the shape of the calibration curve for two computer-simulated distributions.

Let us recall that the main feature of the on-line coupling SEC-LALLS is to give a correct value of $\bar{M}_w$, as already published (2,3). The determination of the $\bar{M}_n$ and MWD values provides a further improvement in the characterization of polymers. A curve as a function of the elution volume, $\bar{M}_w(v)$, is obtained upon combination of the signals of the two detectors. It is expressed as (4,5):

$$\bar{M}_w(v) = M(v)\ F(v-D\sigma^2)/F(v)\ \exp(D^2\sigma^2/2)$$

where F(v) is the experimental chromatogram, σ is the variance of the spreading function assumed to be gaussian, D is the slope of the calibration curve LnM(v) (note that D is a function of v when this calibration is not linear).

$\bar{M}_w(v)$ appears to be dependent both on σ and on D, the key parameter being the term $D\sigma^2$. For low values of σ, it can be assumed that the calculated MWD value is a close approximation of the true one. Prior to plotting MWD, a smoothing procedure must be applied to the $\bar{M}_w(v)$ curve in order to minimize experimental errors, mainly low local extrema which generate strong oscillations in the conventional semi-log plot.

We attempted to determine the limits of such an approach by studying the theoretical $\bar{M}_w(v)$ curves corresponding to two MWD often encountered in polymerization processes: Wesslau and Schulz-Flory. We have tested different values of $D\sigma^2$, assuming for convenience σ to be independent of v. The other parameter to be varied is the calibration function which has been chosen of first and third degrees.

MATERIALS

The chromatographic system is composed of a 6000 A pump (Waters), an injection valve with a 23.4 µL loop (Rheodyne), a set of three Microbondagel columns (Waters, E125, E500, E1000, EHA) covering a wide molecular weight separation range. THF is used as solvent at a flow-rate of 0.5 ml min^{-1}, at room temperature. The two detectors are a differential refractometer R401 (Waters) and a low angle (6°) laser light scattering (LALLS) KMX 6 instrument (Chromatix), respectively. A Norsk-Data ND 100 computer is used with adequate programs developed for SEC analysis in the FFP laboratory. Osmometry measurements have been carried out using a Wescan membrane osmometer in DMF at 47°C.

RESULTS AND DISCUSSION

The first distribution which has been examined is the so-called log-normal (or Wesslau) distribution:

$$w(M) = (\beta\pi^{1/2}M)^{-1} \exp\ (-\beta^{-2}Ln^2M/Mo)$$

with $\beta = 0.4366$ and $M_o = (\bar{M}_w\bar{M}_n)^{1/2} = 3.8 \times 10^5$, $(\bar{M}_w = 4 \times 10^5$ and $\bar{M}_n = 3.63 \times 10^5)$.

The second distribution is the Schulz-Flory distribution, using the gamma function Γ:

$$w(M) = \beta^{\alpha+1}M^{\alpha} \exp\ (-\beta M)\ \Gamma(\alpha+1)^{-1}$$

with $\alpha = 1$, $\beta = .5 \times 10^{-5}$, $\bar{M}_w = 4 \times 10^5$, $\bar{M}_n = 2.13 \times 10^5$.

The calibration functions are of third and first degrees in LnM, respectively, as follows:

$$LnM = A_0 + A_1v + A_2v^2 + A_3v^3$$

where $A_0 = 139$, $A_1 = -50.55$, $A_2 = 6.84$, $A_3 = -0.316$

or expressed as a linear approximation:

$$LnM = C - Dv$$

where $C = 24.97$ and $D = 1.86$.

w(M) is transformed into w(v) which is the chromatogram without axial spreading, whereas the experimental chromatogram F(v) is obtained through the well-known relationship:

$$F(v) = \int_{-\infty}^{\infty} w(y)\ (2\pi\sigma^2)^{-1/2}\ \exp\ -(v-y)^2/2\sigma^2\ dy.$$

Practically, to reduce memory space, the integration is performed between the limits v -3σ and v $+3\sigma$. Extending the interval of integration does not increase the accuracy of F(v). Moreover, values of F(v) and w(V) below 1% of their maximal values are discarded. This troncature gives a more realistic picture of experimental chromatograms. As an example, Figure 1 presents the chromatogram F(v) and the

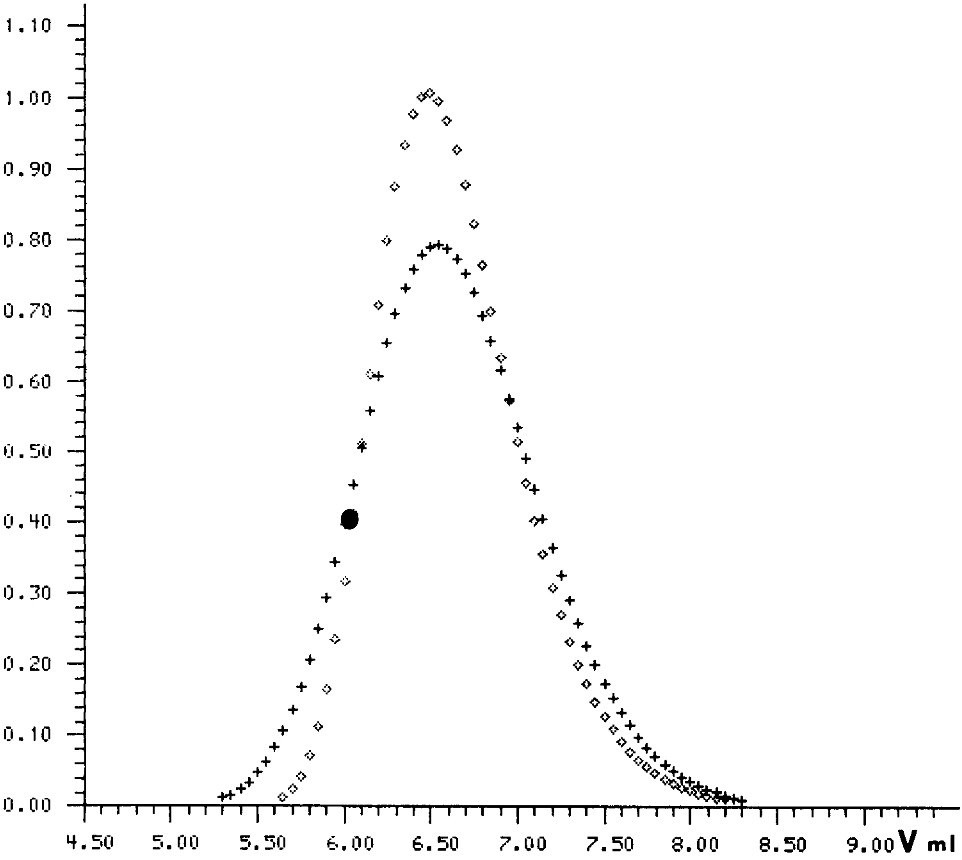

FIGURE 1. Weight differential distribution curve W(v) (◊) and chromatogram F(v) (++) with Schulz-Flory MWD and linear calibration ($D\sigma^2$ = 0.167).

weight differential distribution W(v) for a Schulz-Flory distribution and a linear calibration ($D\sigma^2$ = 0.167), where the effect of axial spreading may be seen.

Before examining the interpretation of theoretical distributions, let us consider the effect of some experimental parameters.

I. Under good experimental conditions, the light scattering signal is correct, i.e. stable, reproducible, without drift or spurious peaks. This results is a true $\bar{M}_w$ signal, since it depends only on

TABLE 1
Influence of Volume Increment on Calculated Molecular Weight Averages

number of values	volume increment, Δv ml	$10^{-5}\ \bar{M}_w$	$10^{-5}\ \bar{M}_n$
9	0.4	4.29	2.46
12	0.3	4.29	2.44
18	0.2	4.28	2.50
36	0.1	4.27	2.48

this detector without taking into account the column system efficiency and the shape of the chromatogram:

$$\bar{M}_w = (\Delta v/m)\ \Sigma((K/\Delta R_{\theta i})-2A_2{}^{-1}$$

where Δv is the incremental volume for measurements of signals, m is the injected mass of the polymer sample, $\Delta R_{\theta i}$ is the difference between the Rayleigh ratios of the solvent and the solution of the polymer fraction eluted at v_i, A_2 is the second virial coefficient, K is the light scattering constant (vide infra, c).

We have compared static and on-line measurements for 15 different polymer samples: all values are in close agreement (better than 5%). Yet, we have investigated the effect of several parameters appearing in the above formule on $\bar{M}_w$.

a) Number of Values Used for the Calculation

This parameter plays a little role since a low number of values is sufficient for securing a constant result for number and weight averages, as already stated in conventional SEC.

b) Second Virial Coefficient A_2

In a good solvent, A_2 generally varies from 10^{-4} to 10^{-3}, depending on the system polymer/solvent. It also varies with the molecular weight, according to:

$$A_2\ \alpha\ M^{-0.2}$$

which means a factor of 4 when M varies from 10^3 to 10^6. For a polymer sample, A_2, if unknown, can be determined by static measurements. Yet this value is an average, for the whole sample, and the variation of A_2 with the molar weight remains unknown. So, at best, the calculation of $\bar{M}_w$ is carried out with a constant value of A_2. It appears of a sufficient accuracy, since we obtained only a slight increase of $\bar{M}_w$ (2%) and $\bar{M}_n$ (1.4%) for a four-fold increase of A_2: 2 to 8 10^{-4} mol.ml.g^{-1} (6).

Kim et al. (7) have also claimed that setting $A_2 = 0$ introduces a small error (less than 2%).

c) Light Scattering Constant K Value

The expression of K is $4\pi^2 n^2 \lambda^4 N^{-1} (dn/dc)^2$ where the refractive index increment dn/dc must be measured at the temperature and wavelength λ of the experiment (generally 6328 Å). Several factors affect the values of dn/dc, e.g. molecular weight, purity of the solvent... These factors may explain the discrepancies observed in published data, even for the conventional system polystyrene/tetrahydrofuran (8-10), so that a 5% error leads to a 10% error on K and $\bar{M}_w$.

d) Concentration of the Sample and Related Chromatogram

Errors on peak ends lead to larger changes of average values: it is well known that the front peak refers to the $\bar{M}_w$ value, whereas the rear peak affects the $\bar{M}_n$ value. Errors of a few % on the base line may lead to a similar error on $\bar{M}_w$ but four times larger for $\bar{M}_n$ (11). Concentration of the sample may be varied in the domain 0.1 to 1 mg, without change of the calculated $\bar{M}$ values. Since two detectors are necessary to derive $\bar{M}_n$ values,

$$\bar{M}_n = \Sigma c_i / \Sigma (c_i / \bar{M}_{wi})$$

the volume connecting them has to be considered: its uncertainty on the volume connecting the two detectors has a very limited effect, since simulated changes of this volume up to 3 times the assumed value affect $\bar{M}_n$ only by 12%. This is due to the small volume - less than 0.1 ml here –, although, in other experimental conditions, different consequences may be derived. The same remark may be applied to coupled SEC-viscometry measurements (12).

II. Now, we consider the theoretical distributions in different experimental conditions.

a) Linear Calibration Curve

The Wesslau distribution has been examined in detail by Kotaka (13): we only recall here that $\mathrm{Ln}\bar{M}_w(v)$ is a linear function of v. If M(v) is unknown, the $\bar{M}_n$ values may be corrected according to the method of He et al. (14), provided several samples are available. Their formula can be written:

$$\bar{M}_n = \bar{M}'_n \exp D_w(D_w - D)\sigma'^2$$

where D_w is the slope of $\mathrm{Ln}M_w(v)$, D is the slope of LnM(v) as stated above, σ' is the variance of the experimental chromatogram F(v) and $\bar{M}'_n$ is the experimental value.

This method has been applied to samples of cellulose tricarbanilate (15) with chromatograms showing a good symetry. The calculated values are compared with those obtained by membrane osmometry in Table 2.

The results are in excellent agreement although care must be taken both for osmometric measurements and selection of curves as Gaussian as possible.

Although $\bar{M}_w(v)$ is theoretically linear, distortion occurs in experimental chromatograms when $D\sigma^2$ increases. As shown in Fig. 2,

TABLE 2
Comparison of Number Averages

	Experimental $\bar{M}_n$	Corrected $\bar{M}_n$	$\bar{M}_n$ from osmometry
Sample 1	120,000	102,000	105,000
Sample 2	75,000	62,000	64,000

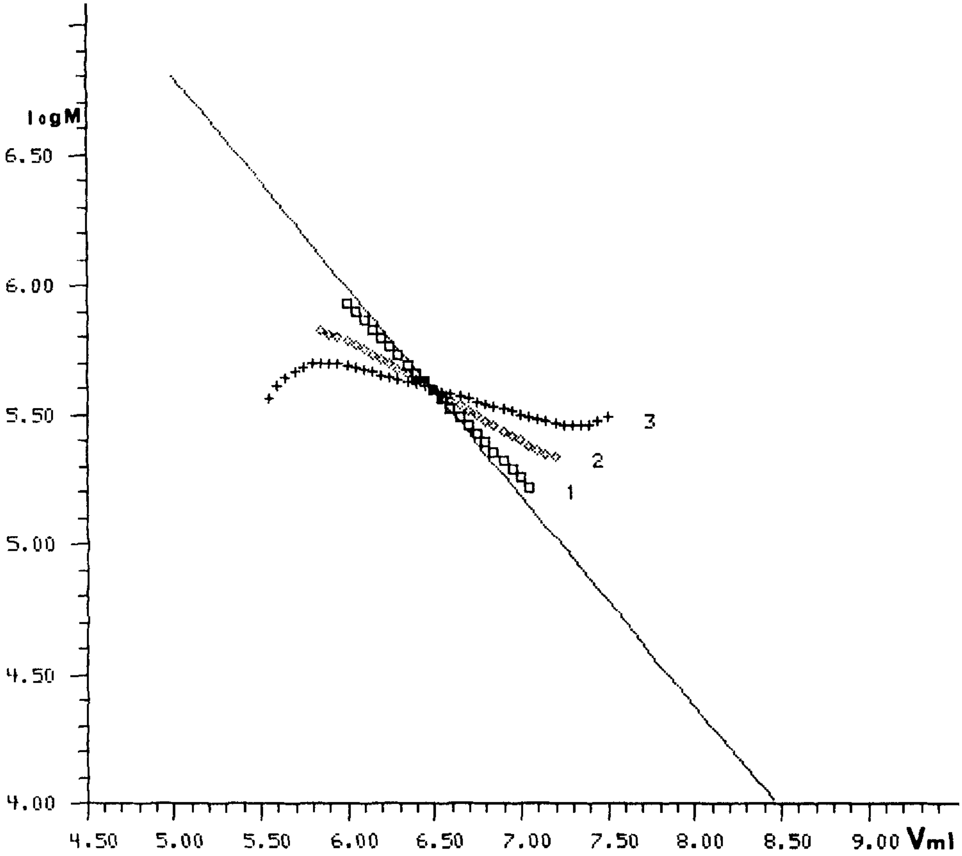

FIGURE 2. M(v) and evolution of the $\bar{M}_w(v)$ curve with $D\sigma^2$ value for linear calibration and Wesslau MWD. 1, 2, 3, respectively for $D\sigma^2$ = 0.01, 0.05, 0.17.

the linearity is maintained when the values of $D\sigma^2$ are low, whereas with higher values, the curvature becomes more pronounced so that the linear part of the curve diminishes. This is very sensitive in the narrow distribution, as shown in Fig. 2.

With a non-linear calibration curve, which means D to be variable, the $D\sigma^2$ parameter varies by a factor of 3 (from 0.05 to 0.14 for σ = 0.2), in the range of elution volumes covered by the curve.

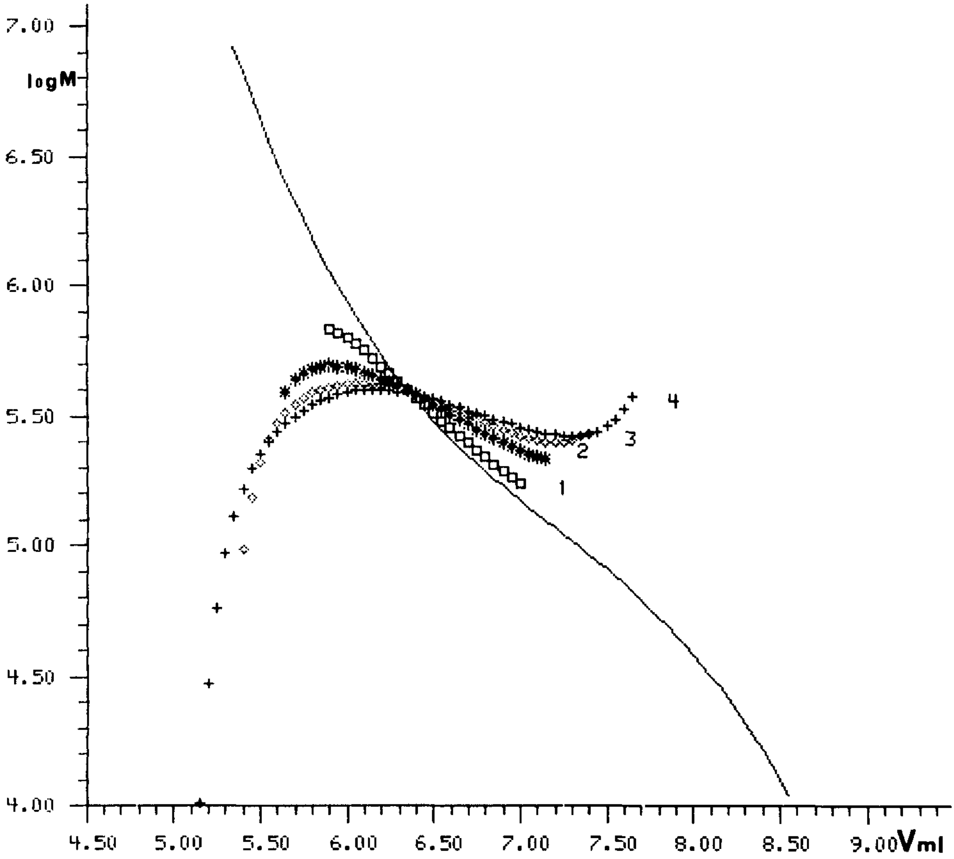

FIGURE 3. M(v) and evolution of the $\bar{M}_w(v)$ curve with $D\sigma^2$ value for non-linear calibration and Wesslau MWD. 1, 2, 3, 4 respectively for $D\sigma^2$ = 0.019, 0.073, 0.165, 0.293.

The curvature of $\bar{M}_w(v)$ is rather pronounced so that it is sometimes ambiguous to draw the MWD (Fig. 3).

Under the same conditions, similar patterns occur experimentally as shown by the $\mathrm{Ln}\bar{M}_w(v)$ curve of a polystyrene standard (Fig. 4). In such a case, it is not very interesting to know the MWD.

In the second example of Schulz-Flory MWD, the curves $\bar{M}_w(v)$ have been represented in Fig. 5 in the hypothesis of a linear calibration.

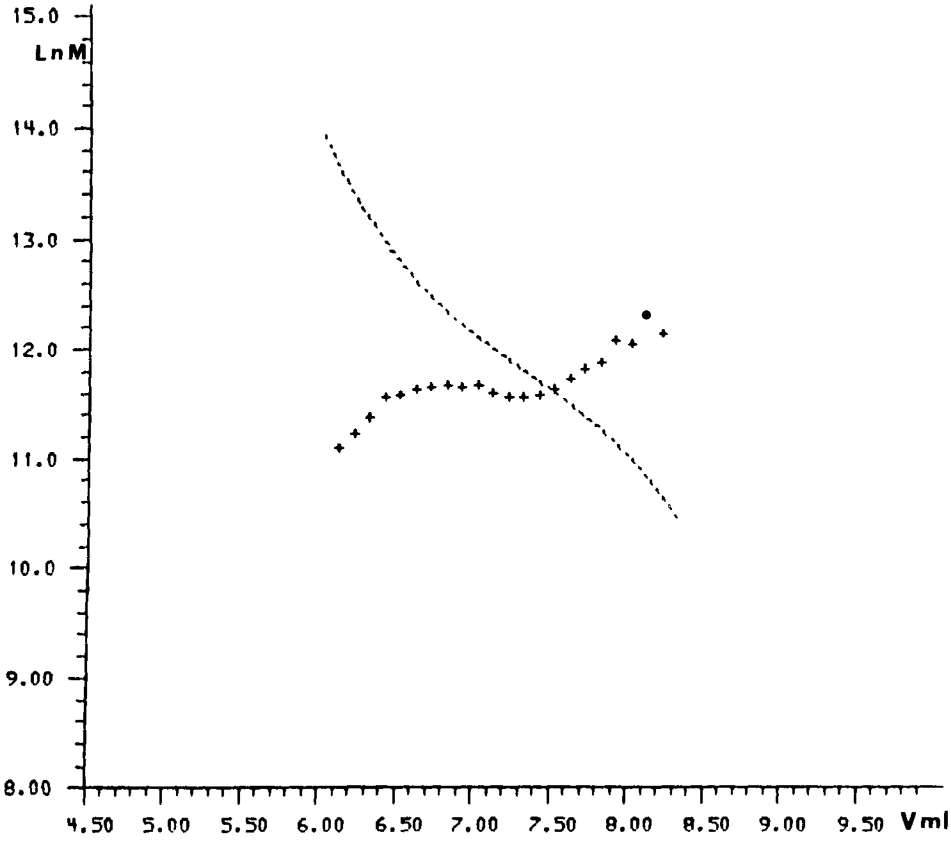

FIGURE 4. M(v) and $\bar{M}_w(v)$ for a narrow molecular weight distribution polystyrene (M = 97000).

For $D\sigma^2$, it may be seen that $\bar{M}_w(v)$ is quasi linear and extremely close to M(v). It is quite different when $D\sigma^2$ is increased, so that $\bar{M}_w(v)$ shows a curvature and deviates from M(v).

For the same distribution, but with a non-linear calibration, Fig. 6 shows the evolution of $\bar{M}_w(v)$ with $D\sigma^2$. Increasing values of $D\sigma^2$ lead to a severe distortion of the $\bar{M}_w(v)$ curves, especially with low and high values of v. Similar curves have been published by other authors (4). An identical effect - perhaps less marked - may be expected with linear calibration and σ varying with v.

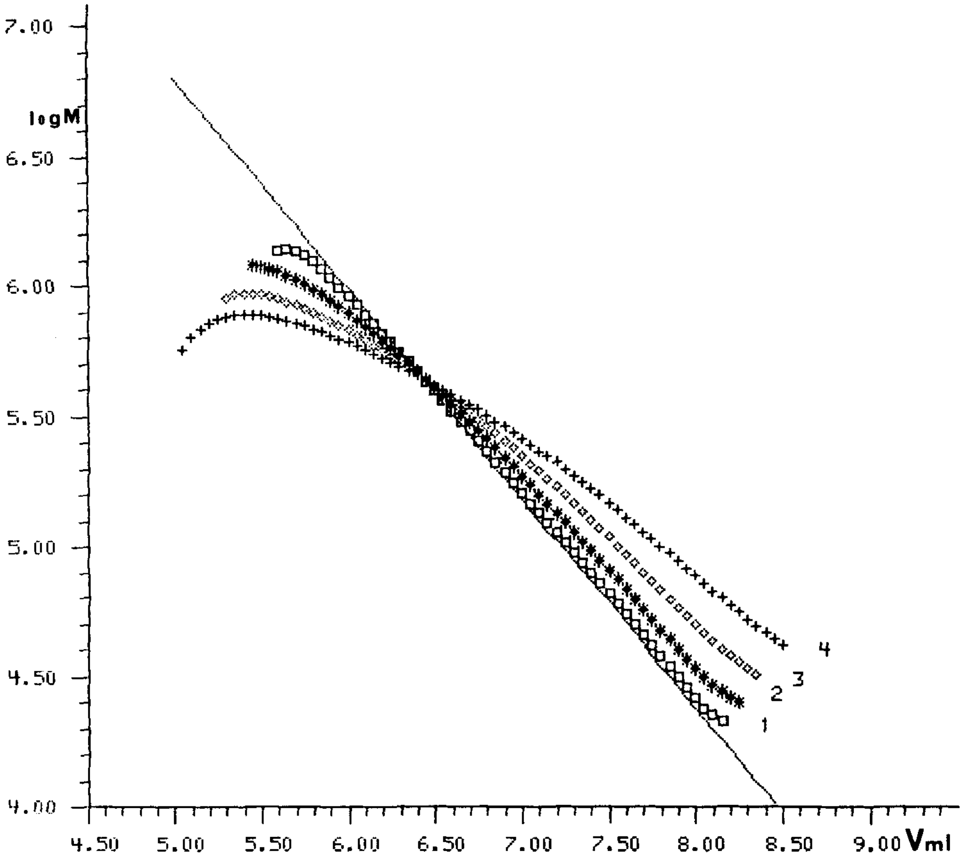

FIGURE 5. M(v) and evolution of the $\bar{M}_w$(v) curve with Dσ^2 value for linear calibration and Schulz-Flory MWD. 1, 2, 3, 4 respectively for Dσ^2 = 0.019, 0.074, 0.167, 0.298.

TABLE 3
Effect of Dσ^2 Values on Number Averages

Linear calibration				Non-linear calibration			
Wesslau		Schulz-Flory		Schulz-Flory		Wesslau	
Dσ^2	10^{-5} $\bar{M}_n$	Dσ^2	10^{-5} $\bar{M}_n$	Dσ^2*	10^{-5} $\bar{M}_n$	Dσ^2*	10^{-5} $\bar{M}_n$
0	3.63	0	2.13	0	2.13	0	3.63
0.01	3.68	0.019	2.25	0.020	2.21	0.019	3.70
0.05	3.80	0.074	2.45	0.080	2.35	0.073	3.73
0.17	3.89	0.167	2.73	0.172	2.52	0.165	3.62
		0.298	3.01	0.293	2.71	0.293	3.35

* Values at the top of the curve

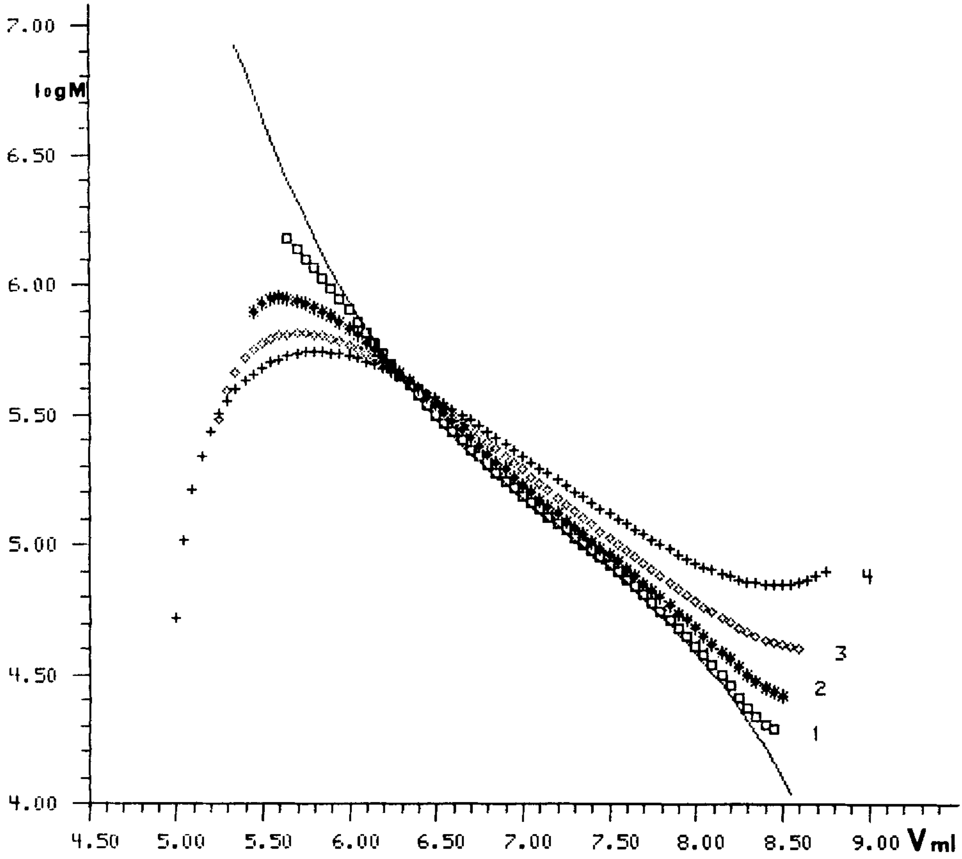

FIGURE 6. M(v) and evolution of the $\bar{M}_w(v)$ curve with $D\sigma^2$ value for non-linear calibration and Schulz-Flory MWD. 1, 2, 3, 4 respectively for $D\sigma^2$ = 0.020, 0.080, 0.172, 0.291.

From the examination of these different sets of curves, we infer that for $D\sigma^2 < 0.15$, it is possible to draw valid distribution curves by using $\bar{M}_w(v)$ and F(v). For higher values of σ, prior to drawing MWD, it seems necessary to correct for axial spreading, with all the inherent difficulties. Turning now to $\bar{M}_n$ values, a quantitative appreciation of the effect of $D\sigma^2$ on $\bar{M}_n$, calculated directly from the raw data ($\bar{M}_w(v)$ and F(v)) is given in Table 3.

$\bar{M}_n$ increases with $D\sigma^2$, as expected, for Schulz-Flory distributions, whereas it is rather unaffected for Wesslau distributions (except for high $D\sigma^2$ values or for narrow distributions). For Schulz-Flory distributions and non-linear calibration curves, the slightly better recovery of $\bar{M}_n$ for a given σ value is a consequence of the variation of $D\sigma^2$ with the elution volume. In our example, the parameters $D\sigma^2$ passes through a minimum between the peak maximum and the end of the F(v) curve. This part of the curve determines largely the $\bar{M}_n$ value.

For Wesslau distributions, $D\sigma^2$ continuously decreases when v increases. This variation explains the good recovery of $\bar{M}_n$. More surprising are the values of $\bar{M}_n$ lower than the true value. This is not in agreement with the commonly assumed statement that the $\bar{M}_n$ values obtained by SEC-LALLS are always higher than the true ones. Yet, this result is coherent with the shape of the $\bar{M}_w(v)$ curve. We have found values of $\bar{M}_n$ approximatively equal to those of $\bar{M}_w$ for a series of polystyrene standards, as already pointed out by Ouano (16).

CONCLUSION

In order to avoid duplication of other studies on the same subject, we only present some new results which may discuss the accuracy of the determination of molecular mass characteristics by the SEC-LALLS technique. We will focus our attention on the value of $\bar{M}_n$ and MWD curves. A correct value of $\bar{M}_n$ may be defined as having an accuracy of the same order as that obtained from absolute measurements. So, from our results, it is clear that $D\sigma^2$ must be below 0.15, except for narrow distributions.

The validity of MWD curves is not so easy to estimate, since $\bar{M}_w(v)$ is a function of the resolution, the calibration, and the molecular weight distribution of the sample. If the above requirement for $D\sigma^2$ is satisfied, F(v) is close to w(v). Nevertheless, one must search for a linear set of columns, since it allows a valid extrapolation of the experimental central part of $\bar{M}_w(v)$ and, consequently, discarding the extreme values. With non-linear calibration curves, extrapolation is less straightforward.

ACKNOWLEDGMENTS

The authors are indebted to J.-M. Lauriol, whose contribution has already been mentioned (1).

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