

An Approach to a Simplified Universal Calibration for Gel Permeation Chromatography

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Synopsis

Criteria for establishing a universal GPC calibration for poly-1,2-butadiene on the basis of polystyrene standards are considered. The number-average molecular weights of the two polymers are related by a linear expression on the assumption that their respective Mark-Houwink exponents are equal. The coefficient C_n of this expression, determined from GPC and viscosity measurements, remained constant for a considerable range of molecular weights and polydispersities. The applicability of C_n beyond the interval of present measurements is considered on the basis of results in the literature. The results are comparable to those obtained from a universal calibration based on the unperturbed dimension of polymer chains, but do not agree with those obtained from a model based on extended length.

INTRODUCTION

The interpretation of data in gel permeation chromatography requires the evaluation of the molecular weight distribution of a particular polymer on the basis of known molecular weight distributions of a series of standard samples. As standard samples are not available for most polymers, a considerable experimental and theoretical effort has been expended to obtain universal calibration techniques based on polystyrene standards. This, in fact, requires the transformation of the primary calibration curve so that it can be used for polymers structurally different from the standard.

The use of the extended length of polymer chains was originally suggested.^{1,2} A calibration curve was constructed by plotting the logarithm of the extended chain length against the elution volume. The molecular weight was calculated by applying the Q factor, representing the molecular weight corresponding to 1 Å of projected chain length. Such factors can be determined by consideration of chain geometry.

It is not surprising, in view of the considerable simplifications involved, that the extended length concept has been found inapplicable to many polymers. Its validity is most likely limited to polymers with close structural similarity. Heller and Moacanin³ recently reported good agreement for poly-1-vinylnaphthalene, poly-2-vinylnaphthalene and poly-4-vinylbiphenyl.

Obviously a more general scheme could be that based on the effective volume of the chains in solution. The feasibility of utilizing the hydrodynamic

volume ($M[\eta]$) as a universal parameter was demonstrated by Benoit and co-workers⁴ and confirmed by other workers.⁵ The product ($M[\eta]$) is proportional to the cube of the hydrodynamic radius R_H , which can be considered as the actual separation parameter in GPC:

$$M[\eta] = 10\pi N_A R_H^3 \quad (1)$$

A plot of either R_H or ($M[\eta]$) against the elution volume of standard samples then provides a universal calibration curve applicable to other polymers.

When two monodisperse polymers possess the same hydrodynamic radius in solution, their molecular weights are related through their limiting viscosity numbers:

$$\frac{M_1}{M_2} = \frac{[\eta]_2}{[\eta]_1} \quad (2)$$

It should be noted that this relationship cannot be used directly to evaluate the molecular weight distribution of a polydisperse sample. Additional information is required to relate the limiting viscosity number of each polymer to its molecular weight. This relationship is expressed quantitatively by the Mark-Houwink equation

$$[\eta] = KM^a \quad (3)$$

Combination of eqs. (2) and (3) yields

$$\log M_2 = \frac{1}{1+a_2} \log \frac{K_1}{K_2} + \frac{1+a_1}{1+a_2} \log M_1. \quad (4)$$

A primary polystyrene calibration curve can be employed for other polymers through eq. (4).

The calibration proposed by Coll and Gilding⁶ employs the expression ($M[\eta] / f(\epsilon)$) as the universal parameter, where $f(\epsilon)$ is solely dependent on the Mark-Houwink exponent a . This leads to an expression similar to eq. (4):

$$\log M_2 = \frac{1}{1+a_2} \log \frac{K_1 f(\epsilon_2)}{K_2 f(\epsilon_1)} + \frac{1+a_1}{1+a_2} \log M_1 \quad (5)$$

Equations (4) and (5) utilize Mark-Houwink constants of both polymers. However, such constants are frequently unavailable for the solvents and temperatures employed in GPC. Furthermore, listed values in the literature are often insufficiently reliable and their applicability to the present problem is difficult to assess.

Experimental determination of K and a based on the measurements of \bar{M}_w or other molecular weight averages is also subject to substantial errors. This led us to assess alternative approaches to the problem.

Consider two polymers which are structurally different but not radically dissimilar. Their thermodynamic behavior is characterized by the exponents a_1 and a_2 . At the same temperature and in the same solvent, one can

assume that $a_1 \simeq a_2$. Then eqs. (4) and (5) reduce to the simple expression

$$\log M_2 = \log C + \log M_1 \quad (6)$$

or

$$M_2 = C \cdot M_1 \quad (7)$$

where C is a constant.

The exponential relationship is thus replaced by a simple linear equation. To prove the feasibility of such a simplification for a particular pair of polymers, it is necessary to examine the underlying assumptions and to assess the errors introduced in the case where a_1 and a_2 are not identical.

We were spurred in our attempts by the necessity to characterize polymers formed by electrochemical techniques and to compare these to conventionally polymerized macromolecules. Here, we establish the validity of the foregoing simplified calibration scheme for polystyrene and 1,2-polybutadiene.

EXPERIMENTAL

A Model 301A chromatograph manufactured by Waters Associates was employed with a differential refractometer as the detecting device. The chromatograph was equipped with five Styragel columns of the following pore dimensions: 2000–5000 Å, 2000–7000 Å, 2×5000 –15000 Å, and 15000–50000 Å. All measurements were carried out in tetrahydrofuran. The instrument was in an air-conditioned room maintained at 20°C. Constant flow rate of approximately 1 ml/min was used throughout.

Samples containing approximately 0.25 g polymer per 100 ml solution were used for the analysis. All solutions were filtered under pressure through a fine Teflon filter to remove impurities and undissolved polymer particles. Two milliliters of the sample solution were injected via the sample loop.

The separating efficiency of the instrument was checked regularly by recording the chromatogram of a 4- μ l sample of toluene. The number of plate counts calculated from such chromatograms was found to remain reasonably constant.

The columns were calibrated by a series of narrow-molecular-weight-distribution polystyrene samples supplied by Waters Associates. The calibration graph plots the peak molecular weights of standards against their GPC peak elution volume; it is shown in Figure 1. Using this calibration curve, raw chromatograms of polystyrene samples could be evaluated in terms of molecular weights and molecular weight distributions. University of Waterloo MWD I computer program* was used for this purpose. The analysis of polystyrene standards indicated a very good agreement between the values of molecular weight and polydispersity supplied by the manufac-

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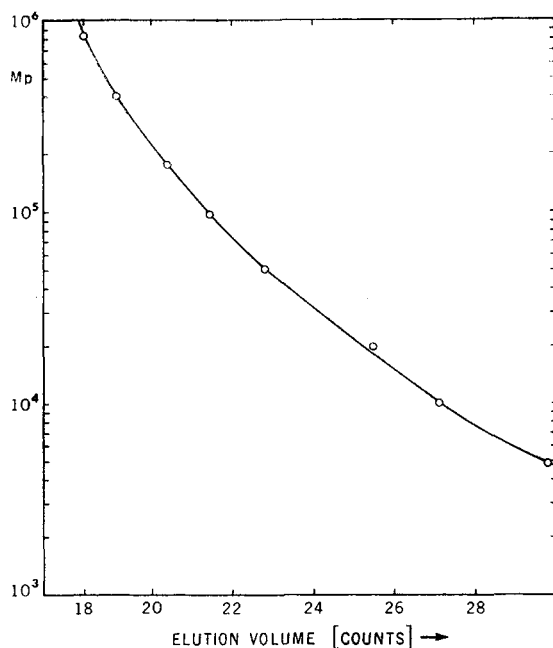


Fig. 1. Primary polystyrene calibration curve.

TABLE I
Evaluation of Polystyrene Standards by the MWD I Computer Program

Sample no.	\bar{M}_n	\bar{M}_w/\bar{M}_n	
		Manufacturer	Computed
41984	163,000	1.055	1.070
41995	96,200	1.021	1.066
25170	49,000	1.041	1.047
25168	19,650	1.010	1.085
25171	9,700	1.062	1.085
25169	4,600	1.087	1.067

turer and those computed by the program. Table I compares the values of polydispersity ratio \bar{M}_w/\bar{M}_n for six polystyrene samples.

The MWD I program does not correct the chromatographic data for instrumental peak spreading. Such a correction was attempted employing the MWD II computer program of Chang and Huang.⁷ However, this program seemed to overcorrect the results regardless of the value of the resolution coefficient h , and we therefore did not apply the spreading correction.

RESULTS AND DISCUSSION

The hydrodynamic volume concept⁴ implies that if a polymer other than polystyrene is evaluated by the polystyrene calibration curve, the resulting

average molecular weight can be considered equivalent to that of a hypothetical sample of polystyrene possessing the same hydrodynamic volume as the polymer analyzed. From the values of $[\eta]$ and \bar{M}_n of standard polystyrene fractions, we have calculated the products $\bar{M}_n(\text{PS})[\eta(\text{PS})]$. Their logarithms were plotted against $\log \bar{M}_n(\text{PS})$. The relationship was linear and is shown in Figure 2.

The polybutadiene samples were characterized by their limiting viscosity numbers, and their GPC chromatograms were recorded. From the computer program, one obtains values of $\bar{M}_n(\text{PS})$, and the corresponding average values of hydrodynamic volume $\bar{M}_n(\text{PS})[\eta(\text{PS})] = \bar{M}_n(\text{PB})[\eta(\text{PB})]$ can be extrapolated from Figure 2. Finally, the value of $\bar{M}_n(\text{PB})$ is obtained by dividing the extrapolated hydrodynamic volume by the limiting viscosity number of the polybutadiene sample. If the assumption described in the previous text is correct, the coefficient

$$C_n = \frac{\bar{M}_n(\text{PB})}{\bar{M}_n(\text{PS})} \quad (8)$$

should be a constant.

Data compiled in Table II demonstrate that coefficient C_n remains practically constant for polybutadiene samples of various molecular weights and polydispersities. The uncertainty involved in the determination of C_n is remarkably small as reflected by the standard deviation of $\sigma = 0.013$. It should be noted that the 1% confidence limit gives $\lambda = 0.035$.

TABLE II
Test of Simplified Universal Calibration in GPC

$\bar{M}_n(\text{PS})$	$\bar{M}_n(\text{PB})$	$[\eta]$	\bar{M}_w/\bar{M}_n	C_n	C_w
15,480	9,420	0.2165	1.29	0.6077	0.6155
20,600	12,400	0.2651	1.18	0.6155	0.7436
21,960	13,340	0.2753	1.31	0.6075	0.6855
28,000	17,100	0.3209	1.23	0.6119	0.6471
29,000	17,800	0.3240	1.28	0.6138	0.6684
29,200	17,600	0.3385	1.49	0.6037	0.7208
30,500	19,480	0.3314	1.20	0.6394	0.6579
39,500	25,130	0.3976	1.28	0.6358	0.7010

For comparison, the last column of Table II lists the values of coefficients C_w obtained with a modified procedure utilizing \bar{M}_w averages instead of \bar{M}_n averages. It is evident that the values of C_w vary from sample to sample and are dependent on the molecular weight distribution.

The average value of the coefficient C_n can be used to calculate number-average molecular weights of unknown samples of the same polymer:

$$\bar{M}_n(\text{PB}) = 0.617\bar{M}_n(\text{PS}). \quad (9)$$

The applicability of eq. (9) beyond the region of our measurements is ques-

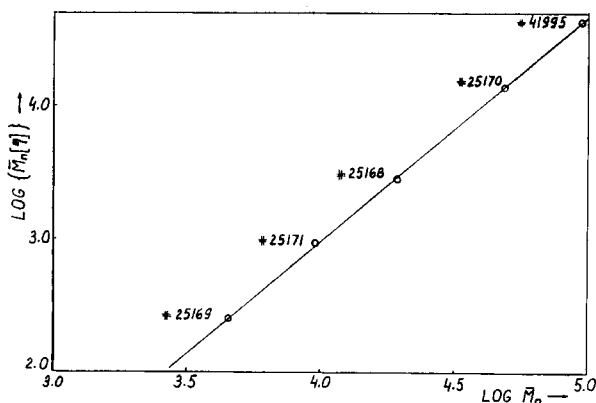


Fig. 2. Dependence of hydrodynamic volume on molecular weight for polystyrene standards.

tionable, but an estimate of errors involved may be inferred from data published by other workers.

For example, Coll and Gilding⁶ found the following exponential calibration curve for poly(α -methylstyrene):

$$\log M_{\text{PAMS}} = -0.058 + 1.021 \log M_{\text{PS}} \quad (10)$$

where PAMS and PS denote poly(α -methylstyrene) and polystyrene, respectively. The values of coefficient C obtained when eq. (10) is replaced by a linear relationship, eq. (7), are shown in Table III.

TABLE III
Application to α -Methylstyrene Data of Coll and Gilding⁶

M_{PS}	M_{PAMS}	C
10,000	10,620	0.94
50,000	54,900	0.91
100,000	111,500	0.90
500,000	576,000	0.87
1,000,000	1,170,000	0.86

It is evident that C varies with molecular weight. However, for an average value of C for polymers with molecular weights from 10^4 to 10^6 , the deviation is only +5% for the lowest and -5% for the highest molecular weight. It is therefore evident that unless the Mark-Houwink constants for two polymers differ significantly, the results obtained by using an exponential expression correspond to those obtained by a simplified linear relationship in eq. (7). The simple proportionality between the molecular weights of the two polymers may therefore be employed over a molecular weight range considerably greater than that investigated in our experiments.

Dawkins^{8,9} suggested the use of the unperturbed dimensions as a basis for universal calibration. The molecular weights of the polymers were related by the expression

$$\log M_2 = \log M_1 + \log \frac{A_1}{A_2} \quad (11)$$

where $A = \langle L_0^2 \rangle / M$ is a constant characteristic for each polymer. Insofar as eq. (11) is formally identical with eq. (7) used by us, it is interesting to compare the coefficient C_n determined on our experiments with the factor $A(\text{PS})/A(\text{PB})$ based on tabulated values of $A^{1/2}$.¹⁰ For polystyrene, $A^{1/2}(\text{PS}) = 0.67 \text{ \AA}$. The value for 1,2-polybutadiene is not available in the literature, but it can be estimated with a good accuracy from the unperturbed dimensions of similar vinyl polymers such as atactic poly-1-butene and atactic polypropylene. The effective value was calculated as the sum of the relative contributions of 1,2- and 1,4-components (90% and 10%, respectively), which gives $A^{1/2}(\text{PB}) = 0.80 \text{ \AA}$. From this we obtained $A(\text{PS})/A(\text{PB}) = 0.70$, which compares with a C_n value of 0.617. This result indicates the general validity of Dawkins' concept for this particular pair of polymers.

On the other hand, an application of the extended length calibration yields a transformation coefficient $Q(\text{PB})/Q(\text{PS}) = 0.44$, which is substantially smaller than C_n . According to Dawkins,⁹ two polymers are comparable via their extended lengths if their $A \cdot Q$ products are equal. In our case, $A(\text{PS}) \cdot Q(\text{PS}) = 21.1$ and $A(\text{PB}) \cdot Q(\text{PB}) = 13.0$, and the extended length concept is therefore not applicable. Thus, a calibration is required and the technique described here represents a simple alternative approach.

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