JOURNAL OF APPLIED POLYMER SCIENCE VOL. 19, 2655-2665 (1975)

Method for Correcting Molecular Weight from Gel-Permeation Chromatography. I. Skewing and Concentration Corrections

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Synopsis

The purpose of this paper is to present a metod to calculate real molecular weight averages of polymer samples from GPC chromatograms where the instrumental spreading functions are skewed and the concentration effect exists. In this method, it is assumed that (1) the skewed chromatograms of monodisperse polymer samples can be represented as resultant of halves of two different Gaussians, (2) the resolution factors are regarded as constant in the case of low sample loading, and (3) the peak elution volume is independent of the presence of other components in the case of low sample loading. Adequate monodisperse polystyrenes and the mixtures (binary, seven and ten components) were examined for this purpose; and the molecular weight averages calculated by this method were compared with the ones obtained by Rosen and Provder's method. From the results in our study, it is found that this method can be available for correcting molecular weight from GPC chromatograms except for very narrow high molecular weight samples.

INTRODUCTION

On the study of Gel-Permeation Chromatography, the corrections of the instrumental spreading and the concentration effect have been interesting problems. When the spreading is taken into account, the GPC chromatogram has been generally given by the following integral equation:[1]

$$F(v) = \int_{v_a}^{v_b} \bar{W}(y) \times G(v,y)dy \tag{1}$$

where v and y are the interchangeable elution volume and v_a and v_b are, respectively, the initial elution volume and the final elution volume of the observed chromatogram $F(v)$. $\bar{W}(y)$ is the corrected chromatogram. $G(v,y)$ is the instrumental spreading function, which is generally expressed as the Gaussian:

$$G(v,y) = (h/\pi)^{1/2} \times \exp\{-h(v - y)^2\} \tag{2}$$

where h is the resolution factor.

It is well known, however, that the chromatograms of adequate monodisperse polymer samples are not necessarily expressed by the Gaussian. They become skew especially in the region of high molecular weight[2] and of high

sample loading.[3] Then, Tung and Runyon[4] proposed to use only the leading halves of the chromatograms to overcome the difficulty of fitting the Gaussian to the skewed chromatograms. Rosen and Provder[5] attempted to express $G(v,y)$ by the Gram-Charlier series. Balke and Hamielec[6] proposed the skewed factor sk. In this study, a simple and intuitive device to represent skewed chromatograms is proposed and, moreover, some investigations concerning the concentration effect are undertaken.

METHOD

A typical skewed chromatogram of adequate monodisperse polymer sample is illustrated in Figure 1a. It can be regarded as resultant of halves of two different Gaussians (1, 2) having identical peaks, but of different variances (Fig. 1b). That is,

$$G(v,y) = \begin{cases} A_l \times \left(\frac{h_l}{\pi}\right)^{1/2} \times \exp\{-h_l(v - y)^2\}; (v \leqq y) & (3a) \\ A_t \times \left(\frac{h_t}{\pi}\right)^{1/2} \times \exp\{-h_t(v - y)^2\}; (v \geqq y) & (3b) \end{cases}$$

$$A_l/A_t = (h_t/h_l)^{1/2} \quad (4)$$

where A is a correction factor related to the area under the chromatogram. Suffix $_l$ and suffix $_t$ express the leading half and the tailing half of the chromatogram, respectively. The area for a unit input of polymer samples should be unity except for the region in very small molecular weight.

$$\int_{v_a}^{v_b} G(v,y)dy = \frac{A_l + A_t}{2} = 1 \quad (5)$$

From eqs. (4) and (5)

$$A_l = \frac{2 \times h_t^{1/2}}{h_l^{1/2} + h_t^{1/2}} \quad (6a)$$

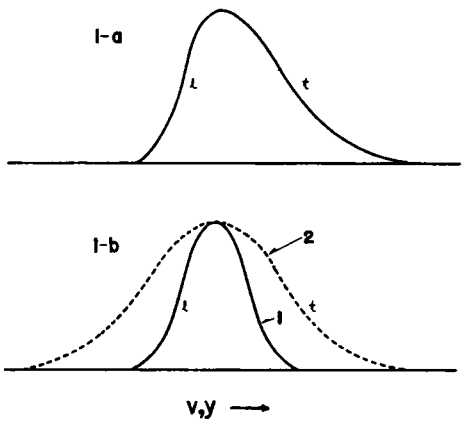

Fig. 1. Part a shows schematic skewed chromatogram; Part b, resultant of two Gaussians.

$$A_l = \frac{2 \times {h_l}^{1/2}}{{h_l}^{1/2} + {h_t}^{1/2}} \tag{6b}$$

are obtained.

On the other hand, it is well known that the chromatograms of polydisperse samples can be assumed as resultant of the chromatograms of each component,[7] as shown in Figure 2. Ouano[8] reported that the chromatograms of mixtures could be expressed by superimposition of those of each component, provided that the sample loading had been low. Therefore, we can express the chromatograms by the following equation, when the Gaussian quadrature approximation[1] is employed for eq. (1):

$$F(v_i) = \frac{v_b - v_a}{2} \times \left[\sum_{j=1}^{i} G_j \times \overline{W}(y_i) \times K_j \times \exp\{-h_{l_j}(v_i - y_j)^2\} + \sum_{j=i+1}^{n} G_j \times \overline{W}(y_i) \times K_j \times \exp\{-h_{t_j}(v_i - y_j)^2\} \right] \tag{7}$$

where

$$y_j = [(v_b - v_a)/2] \times x_j + [(v_b + v_a)/2]$$

$$K_j = \frac{2 \times {h_{l_j}}^{1/2} \times {h_{t_j}}^{1/2}}{\pi^{1/2} \times ({h_{l_j}}^{1/2} + {h_{t_j}}^{1/2})}$$

G_j and x_j are the weight coefficient and the abscissas for the Gaussian quadrature, respectively. Both resolution factors, h_l and h_t, can be determined from eq. (3) by employing the method of least-squares if n pairs of $G(v)$ and v values are selected from the leading halves and the tailing halves

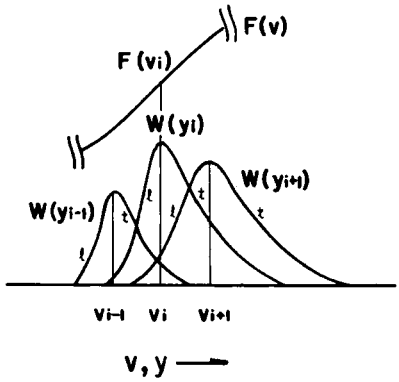

Fig. 2. Resultant of chromatograms.

of the observed chromatograms of narrow polystyrenes, respectively. The corrected chromatogram is therefore obtained from eq. (7) by employing linear programing[1] where n pairs of $F(v)$ and v values selected at the abscissas of the Gaussian quadrature are employed as input data. The molecular

weight averages and the limiting viscosity number are calculated by the following equations:

$$\langle M \rangle_N = \frac{\sum_{i=1}^{n} G_i \times \overline{W}(y_i) \times M_i}{\sum_{i=1}^{n} G_i \times \overline{W}(y_i)/M_i} \tag{8}$$

$$\langle M \rangle_W = \frac{\sum_{i=1}^{n} G_i \times \overline{W}(y_i) \times M_i}{\sum_{i=1}^{n} G_i \times \overline{W}(y_i)} \tag{9}$$

$$[\eta] = \frac{K \times \sum_{i=1}^{n} G_i \times \overline{W}(y_i) \times M_i^{\alpha}}{\sum_{i=1}^{n} G_i \times \overline{W}(y_i)} \tag{10}$$

where K and α are constants in the Mark–Houwink equation. M_i (the molecular weight of the eluted species at volume y_i) depends upon the concentration of the species. This concentration dependence of M_i will be subsequently discussed in detail.

EXPERIMENTS

GPC

Measurements were performed on a Water's Model 200 GPC, where polystyrene-gel columns (10^7, 10^6, 10^5, and 10^3 A) were installed in the normal ordering, i.e., high- to low-permeability limit. The operation conditions were as follows:

solvent	1,2,4-trichlorobenzene (TCB)
flow rate	1 ml/min
temperature	130°C
input solution concentration (C)	6∼1 mg/ml
injection time	2 min
samples	narrow polystyrenes (from the Pressure Chemical Co. and NBS) and the mixtures.

Viscosity

Measurements were made for TCB solutions at 130°C. A Cannon–Fenske Viscometer with flow time of solvent exceeding 200 sec over was used. The viscosity data were extrapolated to infinite dilution by the following equation:

$$\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C + \ldots \tag{11}$$

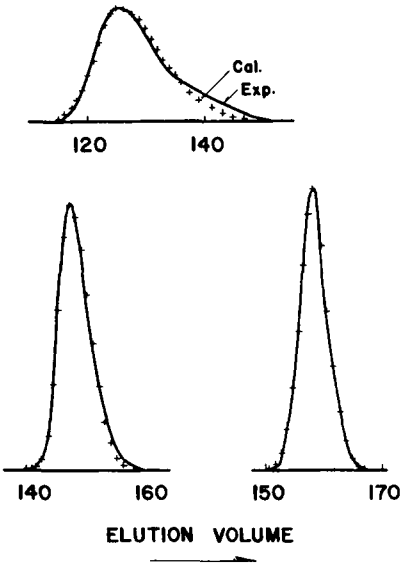

Fig. 3. Comparison of observed and calculated chromatograms.

where η_{sp} is the specific viscosity, k' is constant, C is the sample concentration, and $[\eta]$ is the limiting viscosity number.

RESULTS AND DISCUSSION

Resultant of Two Gaussians

Some observed chromatograms of narrow polystyrenes are represented in Figure 3 with the chromatograms determined by this resultant method. The agreement between both chromatograms is fair for low molecular weight samples; but with the increase of the molecular weight it becomes progressively poor, especially at the base of the chromatogram. This discrepancy for narrow high molecular weight samples predicts the limit of this method.

Concentration Effect

Table I gives the values of h and v_o (peak elution volume) for narrow polystyrenes at some concentrations (sample loading, $w = 2 \times C$). Figure 4 represents the relation between h and v_o. It is seen from Figure 4 that the instrumental spreading and the skewing become progressively greater as v_o decreases; in other words, the molecular weight increases. Figure 5 gives the relation between h and the sample loading. It is found from Figure 5 that h gradually increases as w decreases and finally approaches to a constant value. Moore[9] reported a similar observation. This experimental fact suggests that the concentration dependence of h should be considered in solving eq. (7). However, fortunately, it becomes possible to determine $\bar{W}(y)$ from eq. (7), provided that GPC measurements were carried out in low sample loading satisfying the constant of h. Figures 6 and 7 represent the relations between v_o and w, and between v_o and M (i.e., calibration curves), respectively. It is seen from Figure 7 that the calibration curves deviate from a linear relation.

TABLE I
Chromatogram Characteristics of Narrow Polystyrenes

Sample	$\langle M \rangle_w$[a]	Q[a]	Sample loading, mg	V_o, ml	h_l	h_t
10a	600	1.10>	9.96	167.4	2.58	1.86
11b	4,000	1.10>	10.84	158.0	1.67	1.73
2b	20,400	1.06>	9.84	146.6	2.15	1.14
4b	110,000	1.06>	10.42	136.1	2.25	0.745
			5.52	135.6	2.55	0.965
			2.68	135.8	2.50	0.953
1c	200,000	1.06>	10.72	133.1	1.75	0.461
			4.80	132.5	2.25	0.723
			2.44	132.8	2.25	0.760
hp	394,000	1.06>	9.80	128.1	0.985	0.385
			5.80	127.6	1.67	0.435
			3.00	127.2	1.96	0.420
13a	670,000	1.10>	10.56	125.6	0.583	0.160
			5.52	124.7	1.30	0.211
			2.66	123.8	1.61	0.220

[a] Nominal value.

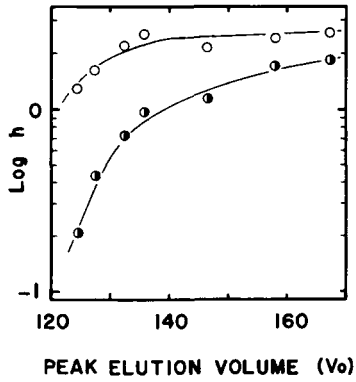

Fig. 4. Relation between resolution factor and peak elution volume: (○) leading half (◑) tailing half.

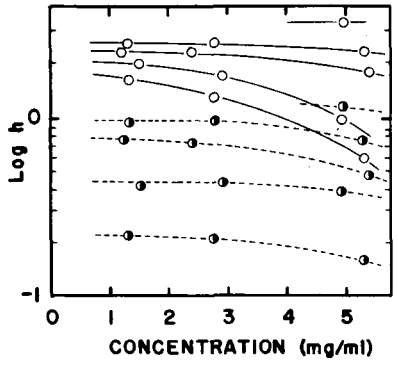

Fig. 5. Relation between resolution factor and input sample concentration: (○) leading half (◑) tailing half.

This well-known concentration effect[10–12] must be worthy of remark in calculating molecular weight from GPC chromatograms, in analogy with the instrumental spreading. However, almost all studies in this field until now have separately performed the instrumental spreading and the concentration corrections. In this paper we intend to carry out both corrections together.

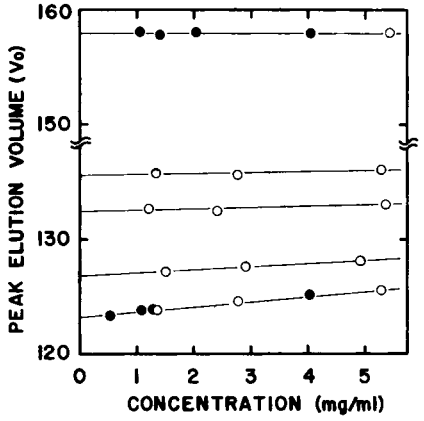

Fig. 6. Relation between peak elution volume and input sample concentration: (●) from the binary mixtures.

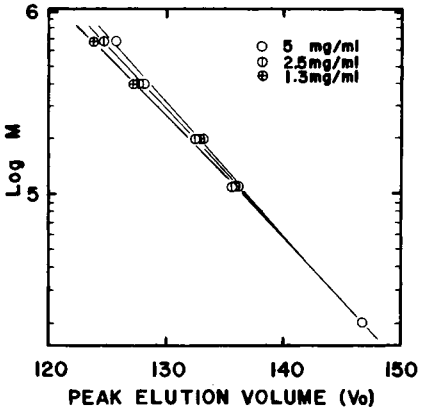

Fig. 7. Relation between peak elution volume and molecular weight (calibration curves).

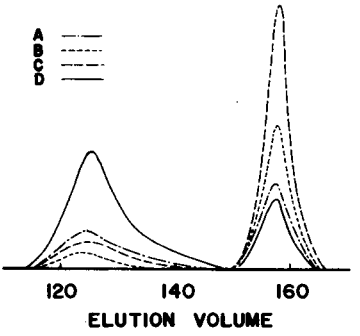

Fig. 8. Chromatograms of binary mixtures.

TABLE II
Binary Mixtures

Sample	Sample loading, mg			V_o, ml	
	Total	13a	11b	13a	11b
A (13a + 11b)	4.10	(2.52 + 2.58)		123.9	157.8
B (13a + 11b)	5.12	(1.04 + 4.08)		123.4	158.1
C (13a + 11b)	10.22	(2.16 + 8.06)		123.8	158.0
D (13a + 11b)	10.20	(8.04 + 2.16)		125.2	158.1

In considering the concentration correction, first of all, two narrow polystyrenes (samples 13a and 11b), of which v_o are far apart from each other, were admixed at different fractions in order to clarify the effect of the presence of other components upon v_o. Figure 8 shows the observed chromatograms of the mixtures, and Table II gives v_o and the concentration of each component. The data are plotted in Figure 6. (See the solid cycles.) They are just on the lines obtained from the individual chromatogram. It is therefore concluded

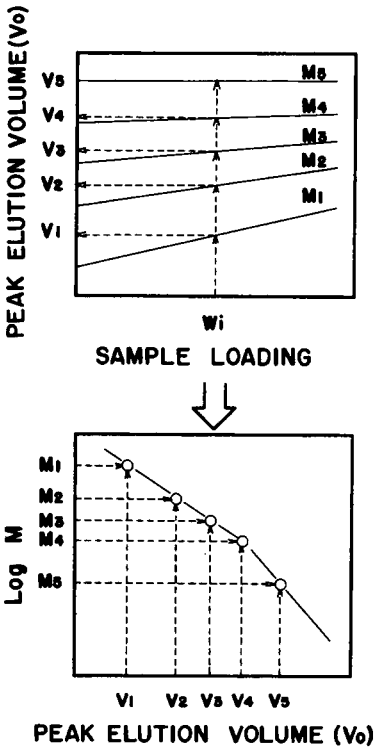

Fig. 9. Transformation for determining calibration curve at arbitary concentration.

that v_o is not affected by the presence of other components (no interaction between different molecular species), but depends only upon the concentration of the individual components.

Then, we can propose the following program for the concentration correction:

1. Determination of the concentration of component eluted at $y_i(v_o)$: This can be determined from

$$w \times \frac{\overline{W}(y_i)}{\sum_{i=1}^{n} \overline{W}(y_i)}$$

2. Determination of the relation between v_o and M at the above-mentioned concentration: This is performed by transforming the relation between v_o and w according to the sequence schematically described in Figure 9.

3. Determination of the equation satisfying the above mentioned relation: It can be expressed as two different equations for larger and smaller region than the elution volume, where the concentration effect appears.

According to the equations it therefore becomes possible to estimate real molecular weight of component eluted at y_i with the concentration of

$$w \times \frac{\overline{W}(y_i)}{\sum_{i=1}^{n} \overline{W}(y_i)}.$$

EVALUATION OF THIS CORRECTION METHOD

Multicomponent mixtures and narrow polystyrenes were examined for this purpose. The composition of the mixtures is summarized in Table III with

TABLE III
Composition of Multicomponent Mixtures

	Component	$M_i \times 10^{-4}$	$[\eta]_i$	W_i, %	
PSM-1					
	12b	0.21	0.030	2.3	
	11b	0.40	0.047	3.1	
	8b	1.00	0.089	9.9	
	2b	2.04	0.146	12.0	$\langle M \rangle_n$*1 = 2.34 × 10⁴
	7b	3.70	0.211	17.9	
	4b	11.0	0.468	25.9	$\langle M \rangle_w$*2 = 16.3 × 10⁴
	1c	20.0	0.708	14.9	
	hp	39.4	1.13	8.0	$[\eta]$*3 = 0.515
	13a	67.0	1.63	4.0	
	14a	180	3.23	2.0	
PSM-2					
	11b	0.40	0.047	2.0	
	8b	1.00	0.089	8.0	$\langle M \rangle_n$*1 = 2.79 × 10⁴
	2b	2.04	0.146	20.0	
	7b	3.70	0.221	40.0	$\langle M \rangle_w$*2 = 6.56 × 10⁴
	4b	11.0	0.468	20.0	
	1c	20.0	0.768	8.0	$[\eta]$*3 = 0.298
	hp	39.4	1.13	2.0	

*1 $\langle M \rangle_n = \dfrac{\Sigma M_i W_i}{\Sigma W_i / M_i}$

*2 $\langle M \rangle_w = \Sigma M_i W_i$

*3 $[\eta] = \Sigma [\eta] i W_i$

TABLE IV
Molecular Characteristics of Experimental Test Samples

	From the composition			From this method			Rosen and Provder	
Sample	$\langle M\rangle_n$ 10^{-4}	$\langle M\rangle_w$ 10^{-4}	$[\eta]$	$\langle M\rangle_n$ 10^{-4}	$\langle M\rangle_w$ 10^{-4}	$[\eta]$	$\langle M\rangle_n$ 10^{-4}	$\langle M\rangle_w$ 10^{-4}
PSM-1	2.34	16.3	0.515	2.39[a]	18.9	0.530	2.54	18.4
				2.45[b]	24.6	0.536		
				2.40[c]	16.0	0.501		
PSM-2	2.79	6.56	0.298	2.60[a]	7.93	0.334	2.77	6.80
				2.74[b]	7.03	0.310		
				2.79[c]	6.44	0.308		
NBS706	13.6[d]	25.8[d]		9.65[a]	29.8		11.1	28.7
				10.6[b]	33.7			
				10.0[c]	25.8			
13a		67.0[d]		16.6[c]	57.4			
1c		11.0[d]		7.23[c]	9.27			
12b		2.04[d]		1.93[c]	2.07			

[a] Instrumental spreading correction only.
[b] Concentration correction only.
[c] Instrumental spreading + Concentration corrections.
[d] Nominal values.

the calculated molecular characteristics. All experiments were carried out below the sample loading of 4.0 mg to keep h constant and to avoid interaction between different molecular species. Table IV gives the molecular characteristics corrected by this method. It is found from Table IV that the instrumental spreading and the concentration corrections proposed in this paper are not individually enough; but that when both corrections are carried out, the corrected molecular characteristics are in fair agreement with the ones calculated from the composition. The discrepancy in narrow high molecular weight samples mainly contributes to imperfectibility of resultant of two different Gaussians and to uncertainty of the calibration curves in the small quantity of elution volume. To demonstrate the value of this method, we compared it with Rosen and Provder's method.[5,13] In carrying out the correction by use of Rosen and Provder's method, values of h and μ_3 against elution volume were first determined from the chromatograms of narrow polystyrenes according to eqs. (34) and (35) in ref. 13. The molecular weight averages were calculated by eqs. (36) and (37) in the same reference, employing the values of h and μ_3 corresponding to the peak elution volume of the chromatograms of polymer samples. The results are listed in the last column of Table IV. It is found from the table that this method (double Gaussian instrumental spreading correction + concentration correction) is somewhat better than Rosen and Provder's method with regard to agreement with the molecular weight averages calculated from the composition. From the results in this study we can propose a simple method for correcting molecular characteristics from GPC chromatograms where the instrumental spreading functions are skewed and the concentration effect exists.

The authors wish to thank Mitsubishi Petrochemical Company for permission to publish this work.

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Received October 22, 1974
Revised January 17, 1975