

A Graphic Procedure for Obtaining Average Molecular Weights from a Chromatogram

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Synopsis

A simple graphic method is described for obtaining average molecular weights of a continuously distributed polymer from its GPC chromatogram. The method is based on the assumption that the weight distribution of the polymer may be approximated by a Schulz distribution. As an example, a polystyrene sample is analyzed graphically, and the results are compared with the traditional method of calculation.

INTRODUCTION

It is well known that the weight concentration of a solute in a dilute solution is in many cases¹ found to be

$$c_w = \frac{n_s - n_1}{n - n_1} \quad (1)$$

where c_w is the weight concentration in grams per cm³ of solution and n is the refractive index. The subscript s and 1 refer to the solution and solvent, respectively, and the parameter lacking subscripts refers to the solute (eluent).

Inherent in eq. (1) is the assumption that the densities of the solution, solute, and solvent are equal and that the Gladstone-Dale equation holds for the system.¹

The difference between the index of refraction of the solution and the solvent, $(n_s - n_1)$, is proportional to the height of the chromatogram, $R(V)$. This assumes a linear relationship between the input signal and the output of the recorder.

From this, the area under a chromatogram peak can be expressed as

$$A = \int_0^{\infty} R(V)dV = kw_t(n - n_1) \quad (2)$$

where w_t is the total weight of solute and the constant k is independent of eluent species.

In general, the output signal of a chromatograph, $R(V)$, due to a mono-dispersed solute appears as a Gaussian peak, which can be expressed as

$$R(V) = \frac{A}{\sigma} \left[\frac{1}{2\pi} \right]^{1/2} \exp \left\{ - (\bar{V} - V)^2 / 2\sigma^2 \right\} \quad (3)$$

where the constant A has been evaluated in eq. (2) and σ^2 is the variance of the peak.

However, a polymer generally appears as a material consisting of a continuous spectrum of particles of varying molecular weights. For this system the equation for its chromatogram is a generalization of eq. (3), and is found to be

$$R(V) = k(n - n_1) \int \frac{w(\bar{V})}{\sigma(\bar{V})} \exp \left\{ -(\bar{V} - V)^2 / 2\sigma^2(\bar{V}) \right\} d\bar{V}. \quad (4)$$

Generally, for polymers, n is essentially independent of molecular weight; $w(M)$, the weight distribution, can be represented by any of a number of approximate functions. While eq. (4) is a rather cumbersome integral equation, its solution should reproduce the curve $R(V)$ for all V .

Tung, in a series of papers,^{2,3,4} has attempted to solve an integral equation equivalent to eq. (4) by making the assumption that the variance is a constant. Despite the known inaccuracy in such an assumption, he was able to obtain reasonable results. This suggests that a simpler approach is often justified.

The common method of calculating the weight- and number-average molecular weights from the chromatogram involves either a numerical integration or a large number of height measurements to solve the expressions⁵

$$\bar{M}_n = \frac{\sum M_i N_i}{\sum N_i}; \quad \bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}. \quad (5)$$

A rapid method has been found to resolve this problem and avoid the above procedure. Surprisingly, despite the assumption that the polymer can be represented by a Schulz distribution, the results compare well with other, more elaborate, methods.

EXPERIMENTAL

The Waters gel permeation chromatograph was used at a temperature of 135°C. Narrow fractions of polystyrene ($\bar{M}_w/\bar{M}_n < 1.06$) were eluted in trichlorobenzene at a flow rate of 1 ml/min. Figure 1 presents the calibration curve obtained.

A typical commercial sample of crystal polystyrene was eluted, and the chromatogram obtained is shown in Figure 2.

DISCUSSION

A convenient equation which may be used to approximate a continuously distributed polymer is the Schulz distribution⁶:

$$w(M) = \frac{p^{m+1} M^m e^{-pM}}{\Gamma(m+p)}; \quad (6)$$

where Γ is the gamma function and m and p are constants which characterize the distribution.

The form of his equation is rather convenient. For example, the R -th average molecular weight, for the above distribution, reduces to

$$\bar{M}_R = \frac{\sum N_i M_i^R}{\sum N_i M_i^{R-1}} = \frac{(m + R - 1)}{p}.$$

Thus,

$$\begin{aligned} \bar{M}_n &= \bar{M}_1 = \frac{m}{p} \\ \bar{M}_w &= \bar{M}_2 = \frac{m + 1}{p} = \frac{(m + 1)\bar{M}_n}{m} \\ \bar{M}_z &= \bar{M}_3 = \frac{m + 2}{p} = \left(\frac{m + 2}{m}\right)\bar{M}_n \end{aligned} \quad (7)$$

By a similar calculation,

$$\bar{M}_v^a = \frac{\Gamma(m + a + 1)}{p^a \Gamma(1 + m)}. \quad (8)$$

The $w(M)$ can be related to $w(V)$ through a knowledge of the chromatogram's calibration curve. Benoit⁷ has shown that a universal calibration curve can be obtained having the form

$$\log [\eta] \bar{M}_w = A - BV \quad (9)$$

where A and B are constants varying from column to column; $[\eta]$ is the intrinsic viscosity of the polymer and is related to the viscosity-average molecular weight by the well-known expression $[\eta] = k \bar{M}_v^a$. The constant a is a function of solvent, solute, and temperature. Generally, for good solvents, $a \sim 0.75$. The universal calibration relationship, eq. (9), can therefore be expressed as

$$\log k \bar{M}_n^a \bar{M}_w = \log k \bar{M}_w^2 \frac{\Gamma(m + a + 1)}{p^{a-1} \Gamma(m + 1 + 1)} = A - BV. \quad (10)$$

Equation (10) can be expressed in a more revealing form by solving for the weight-average molecular weight. This yields

$$\begin{aligned} \log \bar{M}_w &= \frac{1}{1 + a} \left\{ A - \log k \right. \\ &\quad \left. - \log \left[\frac{\Gamma(m + a + 1)}{\Gamma(m + 2)} (m + 1)^{1-a} \right] \right\} - \left(\frac{B}{1 + a} \right) V. \end{aligned} \quad (11)$$

Both a and k are independent of molecular weight and depend only on the eluent components and conditions. The term $\log [\Gamma(m + a + 1) (m + 1)^{1-a} / \Gamma(m + 2)]$ approaches zero for all realistic values of m (i.e., $m >$

0.11 or, equivalently, $\bar{M}_w/\bar{M}_n < 10$), assuming reasonable values for a ($a > 0.7$). Therefore, eq. (11) predicts that for a wide range of conditions, a linear relationship exists between $\log \bar{M}_w$ and the elution volume V . This has been observed in numerous cases.

For polystyrene, a reasonably linear correlation exists between $\log \bar{M}_w$ versus V . It is then logical to assume that the weight-average molecular weight of a polymer corresponds to the peak elution volume. Thus, \bar{M}_w can be determined by inspection after proper calibration with narrow fraction polymer of known molecular weight; \bar{M} can be found from the following relationship:

$$w(b\bar{M}_w) = \frac{p^{m+1}b^m \bar{M}_w^m e^{-pb\bar{M}_w}}{\Gamma(m+p)} \quad (12)$$

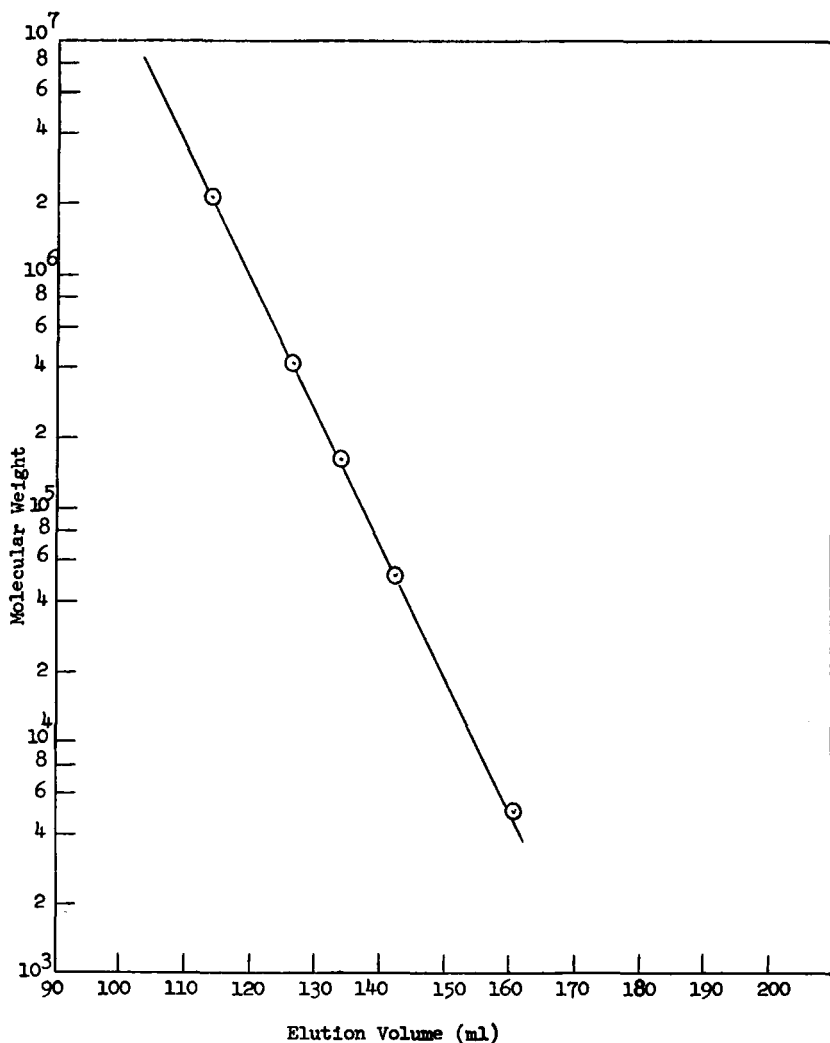


Fig. 1. Calibration curve for polystyrene in trichlorobenzene at 135°C.

where b is a constant, typically 1,2,3,4,... or $1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \dots$. Since for a continuous polymer distribution the vertical displacement is proportional to the grams of material present,

$$\log \frac{w(\bar{M}_w)}{w(b\bar{M}_w)} = \log \frac{R(\bar{M}_w)}{R(b\bar{M}_w)} = \frac{m}{2.3} (b - 1 - \ln b). \quad (13)$$

Therefore, a graph of $R(\bar{M}_w)/R(b\bar{M}_w)$ versus $(b - 1 - \ln b)$ should yield a straight line on semilog paper with a slope equal to $m/2.3$. From this, using the relation for \bar{M}_n in eq. (7), the number-average molecular weight can be determined, as well as any other weighted average.

RESULTS

Figure 2 presents a chromatogram of a typical polystyrene sample. Table I presents a simple method of analyzing this chromatogram. \bar{M}_w

TABLE I
Sample Calculation to Determine the Points in Figure 3

b	$(b - 1 - \ln b)$	$b\bar{M}_w$	$b\bar{V}$	$R(b\bar{V})$	$R(\bar{M}_w)/R(b\bar{M}_w)$
1	0	2.1×10^6	126.0	41	1.00
$\frac{1}{2}$	0.194	1.05×10^6	136.5	37	1.11
$\frac{1}{3}$	0.433	0.7×10^6	139.5	31	1.32
$\frac{1}{4}$	0.64	0.525×10^6	142.0	26.5	1.55
$\frac{1}{5}$	0.81	0.42×10^6	143.5	23.0	1.78
$\frac{1}{6}$	0.96	0.35×10^6	145.0	20.5	2.0

is initially found from the maximum peak height by use of Figure 1. Values of b have been selected to give peak height values in the midrange of the curve; $b\bar{V}$ is found using Figure 1, and $R(b\bar{V})$ can then be measured

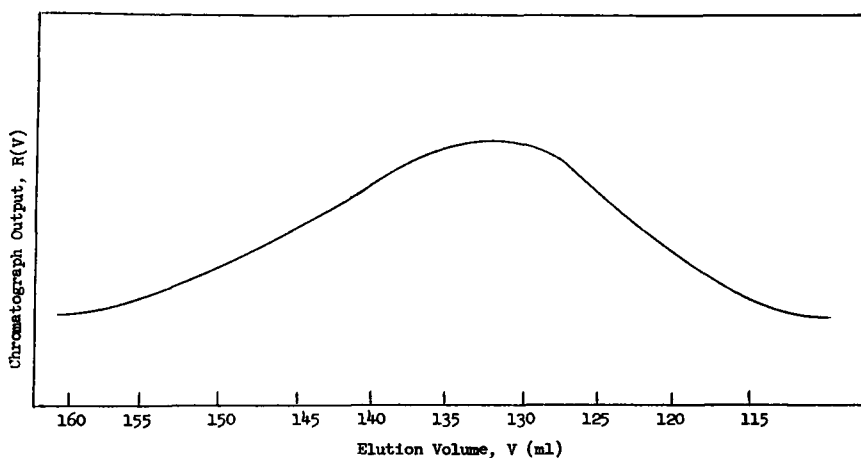


Fig. 2. Typical polystyrene chromatogram.

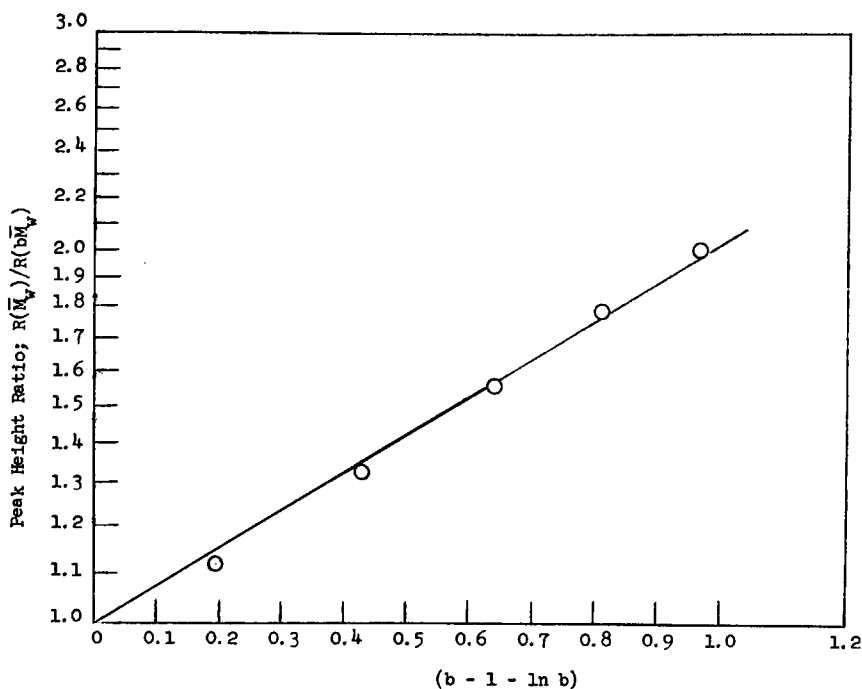


Fig. 3. Graphical procedure for determining m .

in Figure 2. The ratio of peak heights, $R(\bar{M}_w)/R(b\bar{M}_w)$, is then plotted as a function of $(b - 1 - \ln b)$ as in Figure 3. As shown by eq. (13), if the polymer can be approximated by a Schulz distribution, then the data should plot as a straight line passing through the (1.0, 0) point. For the chromatogram presented here, this is indeed the case. From the

TABLE II
Comparison of Results Obtained Graphically with Those
Obtained by the Peak Height Method

	Graphic results	Peak height results
\bar{M}_w	2.1×10^6	2.1×10^6
\bar{M}_n	8.75×10^4	9.1×10^4
\bar{M}_z	3.32×10^5	5.0×10^5
Q	2.4	2.3

slope of the line, m is found to be 0.71. Using this value, a number of the parameters used to characterize polymer distributions have been calculated, using eq. (7), and are compared in Table II, with a peak height method of solution shown in eq. (5). As can be seen, the method of solution outlined above gives reasonable values rapidly.

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