

# A Gel Permeation Chromatography Calibration Method for a Broad Molecular Weight Distribution Polymer

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## Synopsis

A novel, precise, and simple method is described for developing a GPC calibration curve for a polymer where only broad molecular weight distribution samples are available. The method demands a GPC calibration curve for another polymer (e.g., polystyrene) and measurement of the intrinsic viscosity and an average molecular weight for each of several samples of the broad molecular weight distribution polymer in addition to GPC measurements on those samples. Results of applying the procedure to poly(*n*-lauryl methacrylate) are presented.

## INTRODUCTION

The suggestion of Grubisic, Rempp, and Benoit<sup>1</sup> that the hydrodynamic volume can be used to establish a universal calibration curve in gel permeation chromatography (GPC) is now well accepted. A plot of  $\log [\eta]M$  versus elution volume is the same for various homopolymers and copolymers in a given solvent. Here,  $[\eta]$  is the intrinsic viscosity in the solvent of the polymer having molecular weight  $M$ . At a given elution volume, it is assumed that all polymers have the same hydrodynamic volume and, therefore, the same value of  $[\eta]M$ , so that we can write for any particular elution volume

$$\log [\eta]_{\text{PS}}M_{\text{PS}} = \log [\eta]_{\text{P}}M_{\text{P}} \quad (1)$$

where PS refers to polystyrene standards experimentally used to establish a calibration and P, to a polymer requiring analysis. It is also assumed that the various GPC parameters, e.g., flow rate, column combination, solvent, and temperature, remain constant. Equation (1), therefore, permits the determination of  $M_{\text{P}}$  from an experimental polystyrene calibration, providing the dependence of  $[\eta]_{\text{PS}}$  and  $[\eta]_{\text{P}}$  on elution volume can be established. Intrinsic viscosity and molecular weight are related by the familiar equation

$$[\eta] = KM^a \quad (2)$$

where  $K$  and  $a$  are the Mark-Houwink constants. Substitution of eq. (2) for the polymers into eq. (1) and rearrangement gives the following relation between the molecular weight of a polystyrene standard,  $M_{\text{PS}}$ , and that of another polymer,  $M_{\text{P}}$ , which will elute at the same volume as  $M_{\text{PS}}$ :

$$\log M_{\text{P}} = \left( \frac{1 + a_{\text{PS}}}{1 + a_{\text{P}}} \right) \log M_{\text{PS}} + \frac{1}{1 + a_{\text{P}}} \log \frac{K_{\text{PS}}}{K_{\text{P}}} \quad (3)$$

where  $K_{PS}$ ,  $a_{PS}$ , and  $K_P$ ,  $a_P$  are the Mark-Houwink constants for polystyrene and the other polymer, respectively. Equation (3) permits the determination of  $M_P$  from an experimental polystyrene calibration for any polymer whose Mark-Houwink constants are known. In this paper, we present a new procedure which permits the facile determination of the Mark-Houwink constants and, therefore, the GPC calibration curve for a polymer with a broad molecular weight distribution. To accomplish this procedure, we employ a rather small amount of GPC, membrane osmometry (MO), and intrinsic viscosity data. The initial step in this procedure involves the calculation of one of the Mark-Houwink constants,  $a$ . Then, the MO and the GPC distribution data are combined to calculate the value of the Mark-Houwink constant  $K$ . The Mark-Houwink constants are then combined with experimental polystyrene calibration to calculate the calibration curve of polymer. As an example of the use of this method, the Mark-Houwink constants of poly(*n*-lauryl methacrylate), poly(NLMA), in THF at 25°C were found and a calibration curve for this polymer constructed.

### CALCULATION OF $K_P$ AND $a_P$

For a polydisperse polymer, the Mark-Houwink equation relates  $[\eta]$  to the viscosity-average molecular weight:<sup>2,3</sup>

$$[\eta] = K_P \bar{M}_{v,P}^{a_P} \quad (2a)$$

where  $\bar{M}_{v,P}$  is the viscosity-average molecular weight of the polydisperse polymer (whose calibration curve is sought) and defined by eq. (4):

$$\bar{M}_{v,P} = [\sum W_{iP} M_{iP}^{a_P}]^{1/a_P} \quad (4)$$

The number-average molecular weight of the polydisperse polymer,  $\bar{M}_{n,P}$ , defined by

$$\bar{M}_{n,P} = \frac{1}{\sum (W_{iP}/M_{iP})} \quad (5)$$

where  $W_{iP}$  and  $M_{iP}$  are the weight fraction and molecular weight of the *i*th species, respectively.

Combining eqs. (3), (4), and (5) yields

$$\bar{M}_{v,P} = \bar{M}_{n,P} [\sum (W_{iP} M_{iPS}^{\beta a_P})]^{1/a_P} [\sum (W_{iP}/M_{iPS}^{\beta})] \quad (6)$$

where  $M_{iPS}$  is the molecular weight of the *i*th species of polystyrene and  $\beta = (1 + a_{PS})/(1 + a_P)$ . It is emphasized that  $M_{iPS}$  has the same elution volume as  $M_{iP}$ .

Combining eqs. (2a), (3), (4), and (5) gives

$$\frac{[\eta] \bar{M}_{n,P}}{K_{PS}} = [\sum (W_{iP}/M_{iPS}^{\beta})] / [\sum (W_{iP} M_{iPS}^{\beta a_P})] \quad (7)$$

The approach to the calculation of Mark-Houwink constants of a broad molecular weight distribution polymer can be described as follows: First,  $a_P$  is determined using eq. (7), the intrinsic viscosity-membrane osmometry data, and the GPC distribution curve for the broad molecular weight distribution polymer and the polystyrene GPC calibration. This value of  $a_P$  is then used in eq. (6),

along with the GPC distribution curve for a broad molecular weight distribution polymer and the polystyrene GPC calibration, to determine  $\bar{M}_v$  from the MO values of  $\bar{M}_n$  for each sample. The  $\bar{M}_v$  values are then used with the corresponding  $[\eta]$  values to determine  $K_P$  in eq. (2a). The values of  $a_P$  and  $K_P$  can then be used with the polystyrene calibration curve in eq. (3) to construct a calibration curve suitable for any molecular weight distribution of the polymer.

## EXPERIMENTAL

### Materials

Polystyrene GPC molecular weight calibrations were established with standards supplied by Waters Associate, and the values quoted for peak molecular weight. Standards having molecular weights of 900, 10,000, 19,800, 97,200, and 1,800,000 were obtained from Pressure Chemical Company.

N-Lauryl methacrylate (NLMA) monomer (from Polysciences Inc.) was purified by washing with sodium hydroxide (NaOH) solution and distilling under reduced pressure. NLMA was polymerized at 80°C with different concentration of benzoyl peroxide under a reduced pressure of nitrogen. Then, the polymer samples were purified using methanol, and the purity of polymer samples were checked by GPC.

### Osmometry

Osmotic pressure measurements were made with toluene solvent in a Model 502 high membrane osmometer (MO) thermostatted at 25°C. The membrane, Type S & S08, was carefully conditioned with solvent at the same temperature before use. Four polymer concentrations less than 1.2 g/dl were employed.

### Viscometry

Measurements were made with an Ubbelohde-type viscometer. Data at five concentrations, up to 1 g/dl in tetrahydrofuran (THF) at 25°C, were extrapolated linearly by the Huggins and Kraemer method to a common intercept to find the intrinsic viscosity  $[\eta]$ .

### Gel Permeation Chromatography

A Waters Associates Model 301 gel permeation chromatograph (GPC) was used with THF solvent at 25°C. Sample concentrations were 0.2% w/v, and the volume of polymer injected was 2 ml. The GPC column combination was  $10^6$ ,  $10^5$ ,  $8 \times 10^3$ ,  $3 \times 10^3$ , and  $10^3$  Å. Elutions were conducted with a solvent flow rate of 1 ml/min. Calculation of average molecular weights from GPC elution curves were performed by the Chang and Huang<sup>4</sup> method.

## RESULTS AND DISCUSSION

The experimental intrinsic viscosity–molecular weight data for poly(NLMA) in tetrahydrofuran (THF) at 25°C are shown in Table I. Figure 1 shows a plot

TABLE I  
Experimental and Calculated Data for Poly(NLMA) Samples

Sample no.	$[\eta]$ , dl/g	$\bar{M}_n \times 10^{-5}$ (MO)	$\bar{M}_v \times 10^{-5}$ calculated from eq. (6)	$\bar{M}_n \times 10^{-5}$ calculated from Fig. 2
1	2.43	22.200	35.120	21.837
2	0.785	4.291	6.827	4.296
3	0.380	1.500	2.380	1.498
4	0.25	0.896	1.3	0.898
5 <sup>a</sup>	0.13	0.315	0.51	0.3126

<sup>a</sup> Standard sample supplied by Cellomer Associates, Inc., as having  $\bar{M}_n = 31,300$ .

of  $[\eta]$  versus  $\bar{M}_v$  obtained by using the procedure outlined above. The  $\bar{M}_v$  values from Figure 1 are tabulated in Table I, and the Mark-Houwink constants obtained from Figure 1 are  $a_P = 0.69$ ,  $K_P = 0.73 \times 10^{-4}$ .

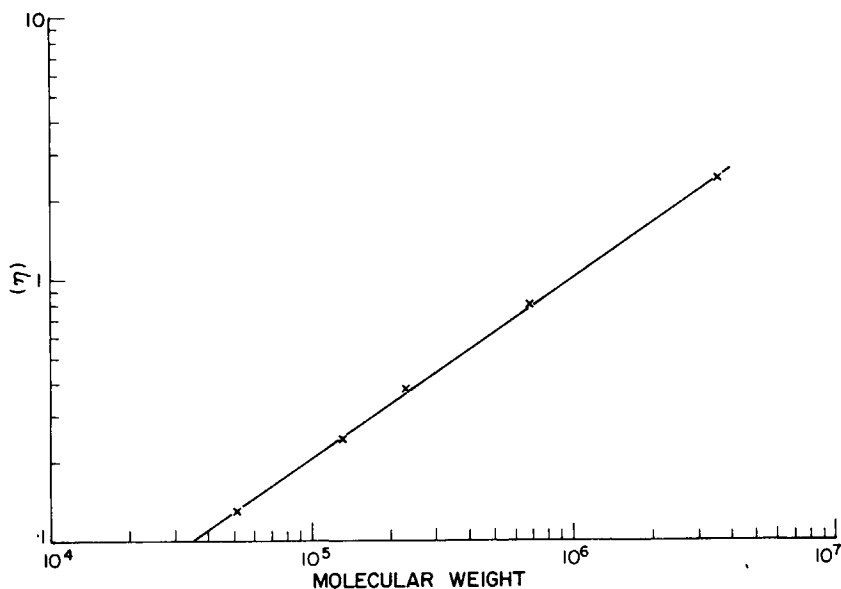


Fig. 1. Intrinsic viscosity vs. molecular weight for poly(NLMA) in THF at 25°C: (x)  $\bar{M}_v$  calculated as described in text.

The calculated GPC calibration curve of poly(NLMA) which was generated using these constants and eq. (3) is shown along with the experimental polystyrene calibration curve in Figure 2. The  $\bar{M}_n$  values of the poly(NLMA) samples obtained from this calibration are listed in Table I.

Substituting values of  $a_P = 0.69$ ,  $K_P = 0.73 \times 10^{-4}$ ,  $a_{PS} = 0.706$ , and  $K_{PS} = 1.6 \times 10^{-4}$  in eq. (3)<sup>5,6</sup> yields

$$\log M_P - 1.01 \log M_{PS} = 0.203 \quad (8)$$

The difference in slope in the  $M_P$  and  $M_{PS}$  calibration is small because the polymer-solvent interactions for polystyrene and poly(NLMA) in THF at 25°C are quite similar.

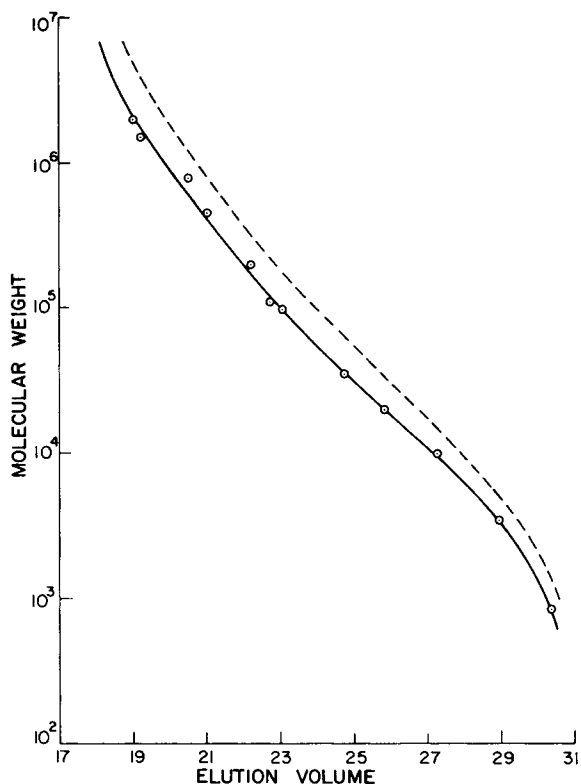


Fig. 2. GPC calibration curve experimentally determined for polystyrene samples ( $\ominus$ ) and (dashed line) calculated for poly(NLMA) as described in text.

If weight or other average molecular weight data are available instead of number average, then an equation analogous to eqs. (6) and (7) can readily be derived by using the proper moments in eq. (5).

In conclusion, the method described here is a simple and useful calibration procedure for a new polymer when well-characterized, narrow molecular weight distribution samples are not available. The method does not depend on the nature of the MWD of the samples used.

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Received December 2, 1975

Revised April 13, 1976