

Method for Gel Permeation Chromatography Calibration and the Evaluation of Mark-Houwink Constants

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Synopsis

A novel and simple method is described for evaluation of the Mark-Houwink constants and developing of GPC calibration curve for a polymer where only broad molecular weight distribution samples are available. The method demands the GPC calibration curve for polystyrene and measurement of the intrinsic viscosity and GPC chromatogram of several samples. Results of applying the procedure to polystyrene and poly(methyl methacrylate) are presented.

INTRODUCTION

In order to interpret a gel permeation chromatograph (GPC) of any polymer sample in terms of its molecular weight distribution, it is necessary to establish a quantitative relationship between molecular weight M and elution volume v . It is well known that well-characterized narrow distribution polymer samples are the most appropriate for GPC calibration purposes. Such samples are, however, difficult to prepare with the exception of polystyrene, for which good standards are readily available. The M - v relationship for any other polymer can be obtained using the familiar universal calibration procedure^{1,2} and a reliable pair of k and α constants for the Mark-Houwink-Sakurada equation.

The evaluation of the Mark-Houwink constants k and α for a particular polymer-solvent system normally requires the preparation of a series of samples having a wide range of molecular weights and their subsequent characterization by light scattering and dilute-solution viscosity. However, gel permeation chromatography (GPC), i.e., size exclusion chromatography can provide a convenient alternative route to k and α .³⁻¹⁰ In this case k and α can be estimated using unfractionated polymer samples of known \bar{M}_n or \bar{M}_w and intrinsic viscosity.

In this work a new and simple method which permits the facile determination of the Mark-Houwink constant, and, therefore, the GPC calibration curve for an unfractionated polymer is presented. The method described uses a combination of gel permeation chromatography and intrinsic viscosity measurements for several samples. The samples used should have the same polydispersity index or have very broad molecular weight distribution.

The initial step in this procedure involves the calculation of hydrodynamic average molecular weight, \bar{M}_x ¹⁰ for each sample. Then, \bar{M}_x and in-

intrinsic viscosity data are combined to calculate one of the Mark-Houwink constants α . Finally, $[\eta]$, GPC distribution data, and the calculated value of α are used to estimate the value of the constant k . The method presented is applied to polystyrene (PS) and poly(methyl methacrylate) (PMMA).

CALCULATION OF \bar{M}_x

In a recent publication by Goldwasser et al.,¹⁰ the use of a new molecular weight average \bar{M}_x to characterize polymer samples of heterogeneous composition have been proposed. \bar{M}_x , the hydrodynamic volume average, is defined according to

$$\bar{M}_x = \frac{\sum \omega_i [\eta]_i M_i}{\sum \omega_i [\eta]_i} = \frac{\sum \omega_i J_i}{[\eta]} \quad (1)$$

where ω_i and $[\eta]_i$ are the weight fraction and intrinsic viscosity, respectively, of all species which exit the GPC columns with elution volume v_i . The denominator in eq. (1) is equal to the intrinsic viscosity $[\eta]$, of the whole sample in GPC solvent. The values in numerator are available from GPC chromatogram and universal calibration curve. $J_i = [\eta]_i M_i$ can be read directly from the universal calibration curve and ω_i is equated to the ratio of the area of the GPC detector response at elution volume v_i to the total area under the GPC chromatogram.

CALCULATION of k AND α

For a polydisperse polymer, the Mark-Houwink equation relates $[\eta]$ to the viscosity average molecular weight \bar{M}_v

$$[\eta] = k \bar{M}_v^\alpha \quad (2)$$

If the whole polymer is considered to be composed of a mixture of monodisperse species each with molecular weight M_i weight fraction ω_i , and intrinsic viscosity $[\eta]_i$ in GPC solvent, then⁹

$$\bar{M}_v = (k)^{-1/\alpha+1} \left(\sum \omega_i J_i^{\alpha/(\alpha+1)} \right)^{1/\alpha} \quad (3)$$

where

$$J_i = [\eta]_i M_i = k M_i^{\alpha+1} \quad (4)$$

Equation (2) can be written in terms of hydrodynamic volume average molecular weight, \bar{M}_x :

$$[\eta] = k_x \bar{M}_x^\alpha = \delta k \bar{M}_x^\alpha \quad (5)$$

Eliminating $[\eta]$ from eqs. (2) and (5) and using eqs. (1) and (3) gives

$$\delta = \left(\sum \omega_i J_i^{\alpha/(\alpha+1)} \right)^{\alpha+1} / \left(\sum \omega_i J_i \right)^{\alpha} \quad (6)$$

If the parameter δ remains constant through the change of $[\eta]$ and \bar{M}_x , then a log-log plot of $[\eta]$ vs. \bar{M}_x gives the expected straight line relationship. The constants α and k_x can be obtained from the slope and intercept such lines, respectively. Then constant $k = k_x/\delta$ can be estimated utilizing eq. (6).

In order to keep δ constant, through the change of $[\eta]$ and \bar{M}_x , polymer samples having the same polydispersity index or very broad MWD should be used (see the Appendix). By applying eqs. (5) and (6) to a series of polymers, having the same δ , constants k and α can be estimated precisely and accurately.

EXPERIMENTAL

Polystyrene (PS) standards of known MW used in this work (Pressure Chemical Co.) were narrow MWD, with M_{peak} values ranging from 800 to 1.8 million. A series of poly(methyl methacrylate) (PMMA) and PS having broad MWD were synthesized and characterized in-house. The solvent used for both GPC and $[\eta]$ measurements was tetrahydrofuran (THF).

Gel Permeation Chromatography

A Water Associates GPC equipped with a high pressure solvent delivery system (Model 150C) was used. Solutions of concentrations smaller than 2 mg/mL were used in order to minimize concentration effects on the peak positions. The flow rate, through a set of six μ styragel packed columns was 1 mL/min and the GPC temperature was 35°C. A calibration curve based on elution volumes of 11 polystyrene standards was constructed. The relation between molecular weight of PS and elution volume was obtained utilizing a third-degree polynomial. The coefficients of this polynomial were adjusted for axial dispersion using an optimization method reported in the literature.¹¹ Then the corrected relationship between M and elution of PS was transferred to universal calibration curve by using the intrinsic viscosity of PS standards.

Viscosity Measurements

The intrinsic viscosities of all polymers were measured with a Cannon-Ubbelohde viscometer equipped with a light detector unit.

RESULTS AND DISCUSSIONS

The hydrodynamic average molecular weight of polymers were estimated by using eq. (1). The right-hand side of eq. (1) was evaluated by treating the normalized GPC chromatogram data in a computer program. $\bar{M}_x \cdot [\eta]$ data of several polymer samples were utilized to estimate k_x and α , which were then used to calculate δ and therefore k .

The precision of the proposed method which uses $\bar{M}_x \cdot [\eta]$ data to calculate k and α according to eqs. (5) and (6) is tested here to show that the method

works well when polymer samples with the same polydispersity or very broad MWD ($\overline{M}_w/\overline{M}_n \geq 4$) were used and that the method works poorly when there are appreciable variances in the polydispersity of polymers with narrow MWD.

$\overline{M}_x \cdot [\eta]$ data for the polystyrene standards are reported in Table I. The log-log plot of the calculated \overline{M}_x of the standards and the measured $[\eta]$ values gives the expected straight line relationship (Fig. 1). A k_x value of 1.54×10^{-4} dL/g and an α value of 0.703, which defines the solid line shown in the figure were obtained. This α value is then used with the GPC curves of the standards to calculate δ and k . The results are reported in Table I. It is clear that the variation for the calculated k value is less than 2%. This was expected, since the polydispersity of all samples was the same. The mean value of k as obtained is 1.6×10^{-4} dL/g. This value of k and α are in good agreement with $k = 1.64 \times 10^{-4}$ dL/g and $\alpha = 0.702$ obtained from the log-log plot of the reported molecular weight of the standards and the measured $[\eta]$ values (Fig. 2).

Since narrow standards with the same polydispersity usually are not available for most polymers, it was decided to test the precision of the proposed method using polymer samples with broad molecular weight distribution.

The calculated values of \overline{M}_x and the measured $[\eta]$ values of a series of broad MWD polystyrene are reported in Table II and Figure 3. The experimental data of these samples were treated according to eqs. (5) and (6). A k_x value of 1.03×10^{-4} dL/g, an α value 0.704 and a k value of 1.58×10^{-4} dL/g were obtained. These results are in good agreement with k and α calculated from the data shown in Figures 1 and 2.

Mark-Houwink constants for PMMA were also estimated by applying the proposed method to PMMA samples with broad MWD ($\overline{M}_w/\overline{M}_n > 4$). The results are reported in Table III and Figure 4. A k value of 1.22×10^{-4} dL/g and an α value of 0.69 were found, which are in good agreement with $k = 1.28 \times 10^{-4}$ dL/g and $\alpha = 0.69$ reported in the literature.² The fact that δ is independent of MW and polydispersity of broad MWD polymers indicates that an accurate k and α can be estimated.

The results presented in Tables I-III indicate that the precision in the $\overline{M}_x \cdot [\eta]$ determined k and α values, when the $\overline{M}_w/\overline{M}_n$ of all polymer samples are the same or $\overline{M}_w/\overline{M}_n > 4$, is comparable to the actual k and α values, obtained by the more involved conventional viscometric technique using narrow standards. However, the method works poorly when there are appreciable variances in the polydispersity of polymer with $\overline{M}_w/\overline{M}_n < 3$. To

TABLE I
Viscosity- \overline{M}_x Data of PS Standards in THF at 35°C ($\overline{M}_w/\overline{M}_n = 1.06$)

$10^{-3} M_p$	$10^{-3} \overline{M}_x$	$[\eta]$ (dL/g)	$10^5 k$ (dL/g)
4.0	4.282	0.055	16.04
9.0	9.634	0.100	16.00
50.0	53.520	0.300	16.06
100.0	107.050	0.540	15.96
233.0	249.42	0.981	16.21
			$\overline{k} = 16.054 \times 10^{-5}$

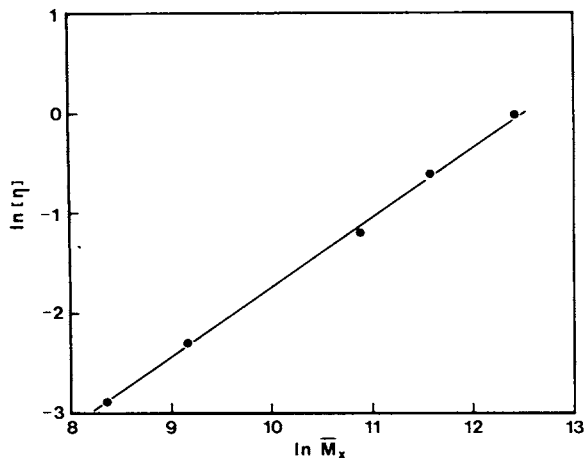


Fig. 1. $\ln[\eta]$ vs. $\ln \bar{M}_x$ for PS standards in THF at 35°C ($\bar{M}_w/\bar{M}_n = 1.06$).

show this, a series of polystyrene standards with \bar{M}_w/\bar{M}_n ranging from 1.06 to 2.3 was used. These samples were prepared by mixing different polystyrene standard from Pressure Chemical Company. \bar{M}_n - $[\eta]$ data for these samples are reported in Table IV. The log-log plot of \bar{M}_x and $[\eta]$ gives $k_x = 1.94 \times 10^{-4}$ dL/g and $\alpha = 0.678$. The data presented in Table IV indicate that calculated values of δ and therefore k varies. The mean value of k as obtained is 2.20×10^{-4} dL/g which is 36% higher than k obtained from data reported in Figure 2. The variation for the calculated α is about 4%. The error in the estimation of k and α in this case as expected is due to variation of δ with \bar{M}_w/\bar{M}_n of polymer.

In summary, the proposed method, which uses \bar{M}_x - $[\eta]$ data to calculate k and α and therefore the GPC calibration curve, is simple and can be applied to polymers with the same polydispersities or very broad MWD. The unique feature of this approach is as follows:

1. Knowledge of the molecular weight of the polymers is not required:

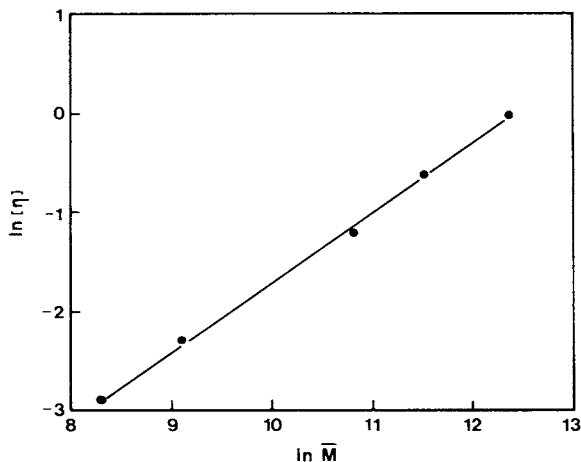


Fig. 2. $\ln[\eta]$ vs. $\ln \bar{M}_p$ for PS standards in THF at 35°C ($\bar{M}_w/\bar{M}_n = 1.06$).

TABLE II
Viscosity- \bar{M}_x Data of Broad MWD PS in THF at 35°C

\bar{M}_w/\bar{M}_n	$10^{-3} \bar{M}_x$	$[\eta]$ (dL/g)	$10^5 k$ (dL/g)
4.45	333.60	0.845	15.79
5.15	67.15	0.271	15.78
5.56	545.97	1.171	15.76
6.09	892.96	1.646	15.69
7.10	28.65	0.144	15.48

$\bar{k} = 15.80 \times 10^{-5}$

2. The method is not limited by the availability of narrow MWD samples, broad MWD samples are usually more readily available, or can be easily synthesized, for all polymer types.

CONCLUSIONS

The validity of a practical method for k and α calculation from GPC is demonstrated. The proposed method has the advantages of being fast and convenient, eliminates all fractionation problems related to monodisperse sample preparation, and should be very useful for the characterization of highly specialized polymer products. It can be applied to polymers having both narrow as well as broad MWD and requires just the determination of $[\eta]$ and GPC chromatograms.

APPENDIX

The parameter δ is defined by eq. (6), viz.,

$$\delta = \left(\sum \omega_i J_i^{\alpha/(\alpha+1)} \right)^{\alpha+1} \left/ \left(\sum \omega_i J_i \right)^\alpha \right. \quad (7)$$

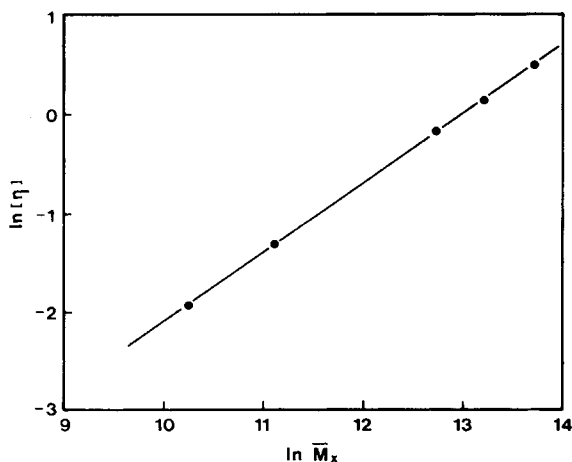


Fig. 3. $\ln[\eta]$ vs. $\ln \bar{M}_x$ for PS in THF at 35°C ($\bar{M}_w/\bar{M}_n \geq 4.45$).

TABLE III
Viscosity- \bar{M}_x Data of Broad MWD PMMA in THF at 35°C

\bar{M}_w/\bar{M}_n	$10^{-3} \bar{M}_x$	$[\eta]$ (dL/g)	$10^5 k$ (dL/g)
4.2	26.98	0.095	12.02
4.7	121.52	0.269	12.13
5.5	219.34	0.40	12.31
6.0	407.53	0.611	12.37
4.5	522.43	0.743	12.11
			$\bar{k} = 12.19 \times 10^{-5}$

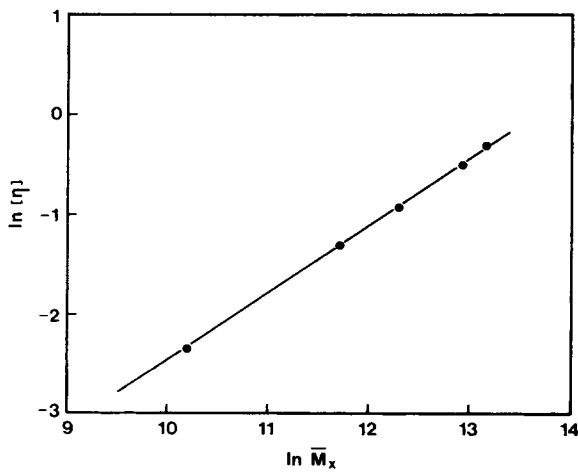


Fig. 4. $\ln[\eta]$ vs. $\ln \bar{M}_n$ for PMMA at 35°C ($\bar{M}_w/\bar{M}_n \geq 4.2$).

TABLE IV
Viscosity- \bar{M}_x Data of PS Standards in THF at 35°C

\bar{M}_w/\bar{M}_n	$10^{-3} \bar{M}_x$	$[\eta]$ (dL/g)	$10^5 k$ (dL/g)
1.06	110.21	0.54	20.10
1.1	434.21	1.40	20.53
1.28	73.43	0.38	21.92
1.75	140.25	0.536	24.34
2.26	233.27	0.72	25.87
1.06	37.47	0.26	20.21
1.15	353.27	1.19	20.86
			$\bar{k} = 21.98 \times 10^{-5}$

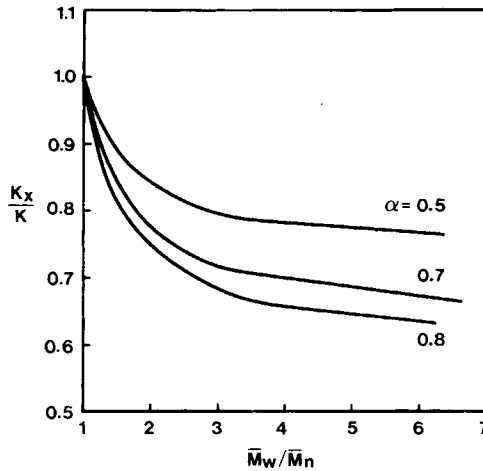


Fig. 5. K_x/K vs. $\overline{M}_w/\overline{M}_n$ for exponential type distribution.

where

$$J_i = kM_i^{\alpha+1} \quad (8)$$

Equation (7) can be written as

$$\delta = \left(\sum \omega_i M_i^\alpha \right)^{\alpha+1} \left(\sum \omega_i M_i^{\alpha+1} \right)^\alpha \quad (9)$$

It is clear that δ is a dimensionless parameter which is equal to 1 for monodisperse samples. For a given distribution function $\delta_M = \delta_{c \cdot M} = \delta_M^c$, where c is a constant. This indicates that δ is independent of M . For example in case of exponential distribution function δ can be written

$$\delta = \frac{\Gamma(\alpha + 1 + h)/\Gamma(1 + h)}{(\alpha + 1 + h)^\alpha} \quad (10)$$

where

$$h = \frac{1}{\overline{M}_w/\overline{M}_n - 1}$$

A plot of δ vs. $\overline{M}_w/\overline{M}_n$ according to eq. (10) is presented in Figure 5. It is clear that δ for a given polymer-solvent system depends only on the polydispersity of polymer. The calculated values of δ for a series of polystyrene standards are summarized in Table V. Samples PS-7-PS-10 are prepared by mixing standard polystyrene and some of them have bimodal or trimodal distribution. The results presented in Table V indicate that, irrespective of distribution function, δ is only a function of $\overline{M}_w/\overline{M}_n$. Similar data for a series of broad MWD polystyrene and polymethacrylate

TABLE V
 δ as a Function of $\overline{M}_w/\overline{M}_n$ for Polystyrene in THF at 35°C

Sample ^a	$10^{-3} \overline{M}_p$	$\overline{M}_w/\overline{M}_n$	δ^b
PS-1	4.0	1.06	0.960
PS-2	35.0	1.06	0.962
PS-3	50.0	1.06	0.959
PS-4	100.0	1.06	0.965
PS-5	233.0	1.06	0.950
PS-6	390.0	1.1	0.945
PS-7	281.37 ^c	1.15	0.927
$(\frac{1}{2} \text{ PS-6, } \frac{1}{2} \text{ PS-5})$			
PS-8	49.73 ^c	1.28	0.885
$(\frac{1}{3} \text{ PS-2, } \frac{1}{3} \text{ PS-3, } \frac{1}{3} \text{ PS-5})$			
PS-9	61.78 ^c	1.75	0.797
$(\frac{1}{4} \text{ PS-2, } \frac{1}{4} \text{ PS-3, } \frac{1}{4} \text{ PS-4, } \frac{1}{4} \text{ PS-5})$			
PS-10	74.194 ^c	2.26	0.750
$(\frac{1}{5} \text{ PS-2, } \frac{1}{5} \text{ PS-3, } \frac{1}{5} \text{ PS-4, } \frac{1}{5} \text{ PS-5, } \frac{1}{5} \text{ PS-6})$			

^a Polystyrene standards from Pressure Chemical Co.

^b δ calculated from eq. (7) using $\alpha = 0.7$.

^c \overline{M}_n .

are presented in Table VI. It can be seen that δ for broad MWD samples is almost constant. This is in agreement with data shown in Figure 5.

From the results presented here, several conclusions can be stated:

1. δ is independent of M .
2. δ , for a given polymer-solvent system, is only a function of polydis-

TABLE VI
 Calculated Values of δ^a for PS^b and PMMA^b in THF at 35°C

Sample	$10^{-3} \overline{M}_n^c$	$\overline{M}_w/\overline{M}_n^c$	δ
PS	48.000	4.45	0.649
PS	8.600	5.15	0.641
PS	63.000	5.56	0.650
PS	94.00	6.09	0.653
PS	2.560	7.10	0.662
PMMA	4.300	4.20	0.690
PMMA	16.700	4.70	0.684
PMMA	25.400	5.50	0.685
PMMA	43.000	6.00	0.671
PMMA	75.400	4.50	0.685

^a δ calculated from eq. (7) using $\alpha = 0.7$ for PS and $\alpha = 0.69$ for PMMA.⁹

^b PS and PMMA synthesized using free radical polymerization.

^c Obtained from GPC.

persity of polymer. It decreases as $\overline{M}_w/\overline{M}_n$ increases from 1 and approaches an asymptotic limit for $\overline{M}_w/\overline{M}_n > 4$.

3. δ for a series of polymers having the same polydispersity or very broad MWD is the same.

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