

Evaluation of GPC Methods for Estimation of Mark-Houwink-Sakurada Constants

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Synopsis

Constants for the Mark-Houwink-Sakurada relation can be established in principle from GPC measurements on broad distribution polymers. The method requires use of two samples with different intrinsic viscosities or a single polymer for which $[\eta]$ and \bar{M}_n or \bar{M}_w are known. The $[\eta]-\bar{M}_w$ combination is not reliable because \bar{M}_v and \bar{M}_w are often very similar in magnitude. The $[\eta]-\bar{M}_n$ method is likewise not recommended because of the influence of skewing and axial dispersion effects on the GPC measurement of \bar{M}_n . The simplest and safest way to use GPC data to estimate the MHS constants involves the measurement of GPC chromatograms of two polymer samples with different intrinsic viscosities. The method is not confined to the solvent used as the GPC eluant. The MHS constants derived from GPC appear to reflect the molecular weight range of the calibration samples and may not be as widely applicable as those from the more tedious classical methods which employ a series of fractionated samples.

INTRODUCTION

The Mark-Houwink-Sakurada (MHS) relation is very widely useful in polymer science. Here,

$$[\eta] = K\bar{M}_v^\alpha \quad (1)$$

where the viscosity-average molecular weight \bar{M}_v is linked to the intrinsic viscosity $[\eta]$ of the polymer solution through the constants K and α . The numerical values of K and α for a particular polymer/solvent system have generally been established by a laborious process in which a whole polymer sample is separated into sharp fractions, each of which is then characterized by a primary molecular weight measurement. If the fractions have narrow molecular weight distributions, any measured average molecular weight, say \bar{M}_w , can be equated to \bar{M}_v without serious error and the relationship of eq. (1) can be calibrated in terms of K and α by regression analysis of the data from a sufficient number of fractionated species.

Gel permeation chromatography (GPC)¹ provides a much more convenient route to K and α . These constants are in fact needed in order to use the familiar $[\eta]-M$ universal calibration procedure.^{2,3} Weiss and Cohn-Ginsberg⁴ have pointed out that whole polymer samples can be used to establish K and α for universal calibrations in GPC. This method requires the use of two samples of the same polymer type with different intrinsic viscosities or a single sample for which $[\eta]$ and \bar{M}_n or \bar{M}_w are known. The two-sample procedure can also provide Mark-Houwink-Sakurada constants for solvents that are not used in the actual GPC analysis. We are not aware of use of this variation, which is illustrated in

this article, although it is implicit in the basic concepts of this procedure for universal calibration.

This article focuses on the practical aspects of the application of the method of Weiss and Cohn-Ginsberg⁴ for the measurement of Mark-Houwink constants. Since all the data used in such calculations are subject to measurement errors and uncertainties, it is important to determine which method is the most reliable of the several variations that are all equally attractive in principle. We find, in fact, that the most practical procedure is clearly that one which involves measurement of the GPC chromatograms and intrinsic viscosities of two different samples of the same polymer type.

THEORY

The whole polymer is considered to be composed of a mixture of monodisperse species each with molecular weight M_i , weight fraction w_i , and intrinsic viscosity $[\eta]_i$ in the GPC solvent. A parameter J is defined as

$$J_i \equiv [\eta]_i M_i \quad (2)$$

Since the GPC elution volume is a function of $[\eta]_i M_i$,² the GPC chromatogram yields J_i and corresponding values of w_i (after normalization), provided all species elute effectively at infinite dilution.³ With suitable substitutions,⁴

$$[\eta] = K^{1/(\alpha+1)} \sum w_i J_i^{\alpha/(\alpha+1)} \quad (3)$$

$$\bar{M}_n = K^{-1/(\alpha+1)} / \sum w_i J_i^{1/(\alpha+1)} \quad (4)$$

and

$$\bar{M}_w = K^{-1/(\alpha+1)} \sum w_i J_i^{1/(\alpha+1)} \quad (5)$$

K can be eliminated by combining eqs. (3), (4), and (5):

$$[\eta] \bar{M}_n = \sum w_i J_i^{\alpha/(\alpha+1)} / \sum w_i J_i^{-1/(\alpha+1)} \quad (6)$$

$$[\eta] \bar{M}_w = \sum w_i J_i^{\alpha/(\alpha+1)} \sum w_i J_i^{1/(\alpha+1)} \quad (7)$$

$$[\eta]' / [\eta] = \sum w_i' J_i'^{\alpha/(\alpha+1)} / \sum w_i J_i^{\alpha/(\alpha+1)} \quad (8)$$

In eq. (8) the primed and unprimed terms refer to different samples of the same polymeric type. In principle, any one of eqs. (6), (7), or (8) can be used with the appropriate data to obtain an independent measure of α , and eq. (3) can then be used with the experimental $[\eta]$ and GPC chromatogram (i.e., w_i and J_i terms) to calculate K .

Experimental

The polymers used were commercial poly(methyl methacrylate) samples. \bar{M}_n was calculated from osmometric pressure measurements of toluene solutions, using deacetylated cellulose acetate membranes. \bar{M}_w was obtained from light scattering in toluene with a Brice-Phoenix light-scattering photometer modified according to the design of Roche and Tanner.⁵ Turbidity measurements were made at angles between 45° and 142.5° to the incident beam, and \bar{M}_w was calculated by Zimm's procedure.⁶

Intrinsic viscosities were measured with Ubbelohde suspended-level glass

viscometers and were calculated by the single concentration method of Rudin and Wagner.⁷ Estimations at different concentrations did not produce exactly the same values of $[\eta]$, and so the measured $[\eta]$ points for each polymer/solvent system were extrapolated to zero concentration. The resulting $[\eta]$ values always agreed closely with those from classical plots according to the Huggins⁸ and Kraemer⁹ equations.

Table I lists the measured values of \overline{M}_n , \overline{M}_w , and \overline{M}_v in various solvents. The \overline{M}_v values were obtained with the MHS constants determined in this work, as described below.

Gel permeation chromatography involved tetrahydrofuran (THF) solutions with 2 mg/ml concentrations. The flow rate was 2.5 ml/min through a set of 14 2-ft-long polystyrene gel columns. Nominal exclusion sizes (in Å) of these packings were 60, 200, 500, 10^3 , 10^4 , 10^5 , and 10^6 .

A universal calibration curve based on elution volumes of anionic polystyrene standards was constructed in terms of hydrodynamic volumes.^{3,10} For this purpose, the concentrations of the standards were taken to be equal to their nominal injection concentrations, while the components of polydisperse samples were assumed to elute at infinite dilution.³

RESULTS

The general approach for calculation of K and α involved the use of one of eqs. (6), (7), or (8). The right-hand side of the equation was evaluated by treating the normalized GPC chromatogram data in a reiterative computer program which "plugged in" values of α between 0.5 and 1.0. These results were then compared with the magnitude of the left-hand side term which consisted of a product or ratio of independently measured parameters. The α value which matched the

TABLE I
Characteristics of Poly(methyl Methacrylate) Samples

Sample A	B	C	
Osmometry $\overline{M}_n \times 10^{-4}$	1.93	4.30	11.00
GPC ^a $\overline{M}_n \times 10^{-4}$	1.86	3.91	8.66
Light scattering $\overline{M}_w \times 10^{-4}$	—	10.50	—
GPC ^a $\overline{M}_w \times 10^{-4}$	3.96	9.28	24.34
$\overline{M}_v \times 10^{-4}$ in THF ^a	3.05	7.24	19.27
$\overline{M}_v \times 10^{-4}$ in chloroform ^b	2.40	5.49	13.78
$\overline{M}_v \times 10^{-4}$ in acetone ^c	3.75	—	27.45
$\overline{M}_v \times 10^{-4}$ in benzene ^d	2.59	—	18.32
$[\eta]$ THF, cm ³ /g	18.13	32.07	61.21
$[\eta]$ chloroform, cm ³ /g	23.72	44.33	88.76
$[\eta]$ acetone, cm ³ /g	14.06	—	40.77
$[\eta]$ benzene, cm ³ /g	20.56	—	61.78

^a GPC in THF; calibration from $[\eta] = 1.99 \times 10^{-2} \overline{M}_v^{0.660}$ cm³/g.

^b Chloroform: $[\eta] = 1.17 \times 10^{-2} \overline{M}_v^{0.755}$ cm³/g.

^c Acetone: $[\eta] = 5.02 \times 10^{-2} \overline{M}_v^{0.535}$ cm³/g.

^d Benzene: $[\eta] = 6.81 \times 10^{-2} \overline{M}_v^{0.562}$ cm³/g.

GPC data to this left-hand side term was used to calculate K from

$$K = ([\eta]/\sum w_i J_i^{\alpha/(\alpha+1)})^{\alpha+1} \quad (3a)$$

Evidently, two K values could be calculated if eq. (8) were used to establish α . They proved to be identical in this work.

We found that eq. (7) was not suitable for calculation of K and α because no reasonable α value made the calculated right-hand terms of this equation converge onto the experimental value of $[\eta]\bar{M}_w$. This is probably because \bar{M}_v and \bar{M}_w are often too highly correlated, as suggested by Weiss and Cohn-Ginsberg.⁴

Equation (6) was, however, also not effective in the present case. In most cases the range of $[\eta]\bar{M}_n$ values that can be generated with different values of α in this equation is quite small. Uncertainties in the low-molecular-weight tail of the GPC chromatogram and in the osmometric value of \bar{M}_n can be large enough to prevent convergence of the terms on both sides of eq. (6). The membrane leakage error can be serious with lower molecular weight polymers¹¹ such as our sample A. Axial dispersion errors can also affect the GPC calculation of \bar{M}_n , although this uncertainty is often reported to be negligible with whole polymers. Skewing of the chromatogram toward the low-molecular-weight end is a more serious problem in this connection. Skewing not only distorts the true molecular weight distribution but also makes it impossible to correct for axial dispersion with a Gaussian function.

Skewing which becomes more serious with high-molecular-weight polymers reflects laminar flow effects in the intracolumn tubing^{12,13} and nonuniform flushing of detector cells.¹⁴ In our case, chromatograms of anionic polystyrene standards were observed to be skewed when the GPC columns were bypassed and the sample was eluted directly from the inlet port through connecting tubing to the detector cell.

Several procedures have been suggested for simultaneous correction for axial dispersion and skewing.^{15,16} They involve independent measurements of \bar{M}_w and \bar{M}_n of a broad distribution polymer and correction of the chromatogram to bring the GPC values of these two molecular weight averages into coincidence with \bar{M}_w from light scattering and \bar{M}_n from membrane osmometry. The skewing correction can vary with molecular weight distribution. In order to estimate K and α from GPC data which are adjusted to compensate for skewing, one would need to measure \bar{M}_n , \bar{M}_w , and $[\eta]$ in the GPC solvent for a particular polymer sample. We have not pursued this approach because the employment of eq. (8) seems to circumvent the problems caused by errors in measurement of \bar{M}_n and axial spreading and skewing problems in GPC.

For polymer A, the measured value of $[\eta]\bar{M}_n$ is 3.500×10^5 cm³/mole (Table I). The uncorrected GPC chromatogram for this polymer produced $[\eta]\bar{M}_n = 2.43 \times 10^5$ cm³/mole with $\alpha = 0.5$, and $[\eta]\bar{M}_n = 3.53 \times 10^5$ cm³/mole with $\alpha = 1.0$. The "true" value of α is 0.985 according to these data. The estimated magnitude of α would have decreased if \bar{M}_n were actually lower than the osmometric value listed in Table I, and it is likely that this would be the case with this low-molecular-weight sample.¹¹

No convergence between the two sides of eq. (6) was obtained for $0.5 \leq \alpha \leq 1.0$ with samples B and C. In both cases the $[\eta]\bar{M}_n$ values generated from the uncorrected GPC chromatograms and α in the range $0.5 \leq \alpha \leq 1.0$ occupied narrow ranges below the measured parameter.

Peak tailing due to skewing is apparently an important contributor to the failure of eq. (6) to converge with these higher molecular weight samples. To test this idea, the GPC chromatograms were arbitrarily adjusted for peak tailing by reducing peak heights on the low-molecular-weight side of the chromatogram. Not surprisingly, it was found that an adjustment sufficient to change the GPC value of \bar{M}_n substantially and to cause eq. (6) to converge would produce only minor changes in the GPC estimate of \bar{M}_w of the polymer. More important was the observation that such adjustments had almost no effect on the $[\eta]'/[\eta]$ ratio in eq. (8). This is because skewing affects the low-molecular-weight portion of the distribution particularly and because \bar{M}_v of whole polymers is always much closer to \bar{M}_w than to \bar{M}_n .

The useful conclusion from this investigation is that the simplest and safest way to use GPC data to estimate K and α and to avoid complications from zone broadening and skewing effects involves reliance on eq. (8) with measured intrinsic viscosities of two samples of the same polymer type.

Table II lists the K and α values for tetrahydrofuran solutions from ratios of intrinsic viscosities in this solvent. The choice of samples for the ratio of intrinsic viscosities produces somewhat different pairs of α and K values. This is as ex-

TABLE II
Mark-Houwink-Sakurada Constants from Intrinsic Viscosity Ratios and GPC Chromatograms

Solvent	Samples ($[\eta]$, cm ³ /g)	$[\eta]_1'/[\eta]_2$		α from eq. (12)	$K \times 10^2$, cm ³ /g, from eq. (3a)
		Exp.	From GPC and eq. (8)		
THF	<u>C(61.21)</u> A(18.13)	3.376	3.382	0.660	1.99
	<u>C(61.21)</u> B(32.07)	1.909	1.908	0.650	2.25
	<u>B(32.07)</u> A(18.13)	1.769	1.771	0.670	1.79
HCCl ₃	<u>C(88.76)</u> A(23.72)	3.742	3.743	0.755	1.17
	<u>C(88.76)</u> B(44.33)	2.002	2.003	0.735	1.49
	<u>B(44.33)</u> A(23.72)	1.869	1.870	0.780	0.90
Acetone	<u>C(40.77)</u> A(14.06)	2.900	2.900	0.535	5.02
Benzene	<u>C(61.78)</u> A(20.56)	3.005	3.007	0.562	6.81

pected. A higher value of one constant always coincides with a lower value of the other, and all three pairs of MHS constants will give practically the same value of \bar{M}_v in eq. (1) for any given $[\eta]$ which is within the range of intrinsic viscosities used to establish K and α .

Similar conclusions apply to the K and α values calculated for chloroform, acetone and benzene solutions. These results, which are also summarized in Table II, were obtained from eqs. (8) and (3a) with intrinsic viscosities measured in the particular solvent and corresponding GPC J_i and w_i data in tetrahydrofuran.

DISCUSSION AND CONCLUSIONS

Mark-Houwink-Sakurada constants can be readily established from GPC chromatograms and the ratio of intrinsic viscosities of two samples of the same polymeric type. Intrinsic viscosities can be measured more accurately than molecular weight averages like \bar{M}_n or \bar{M}_w , and the estimations of such ratios from eq. (8) are relatively unaffected by axial dispersion or skewing problems which may influence GPC measurement of \bar{M}_n in particular. The entire procedure requires much less time than the classical process, which involved a regression analysis of intrinsic viscosities of characterized fractionated samples. The method can be further abbreviated if intrinsic viscosities are estimated from single concentration measurements of relative viscosities. It is probably most accurate, however, to rely on multipoint viscosity data and to calculate $[\eta]$ by methods such as that in ref. 17.

The constants calculated by this method can be expected to apply well only over the molecular weight range (or intrinsic viscosity range) for which they have

TABLE III
Mark-Houwink-Sakurada Constants for Poly(methyl Methacrylate)

THF			
$K \times 10^2, \text{cm}^3/\text{g}$	1.99	1.04	1.28
α	0.660	0.697	0.690
Molecular weight range ($M \times 10^{-4}$)	4-24	>3	5-80
Ref.	this work	(15)	(3)
Chloroform			
$K \times 10^2, \text{cm}^3/\text{g}$	1.17	0.581	0.48
α	0.755	0.79	0.80
Molecular weight range ($M \times 10^{-4}$)	4-24	5-41	8-137
Reference	this work	(19)	(20)
Acetone			
$K \times 10^2, \text{cm}^3/\text{g}$	5.02	0.618	0.75
α	0.535	0.72	0.70
Molecular weight range ($M \times 10^{-4}$)	4-24	5-41	3-98
Ref.	this work	(19)	(21)
Benzene			
$K \times 10^2, \text{cm}^3/\text{g}$	6.81	0.674	0.627
α	0.562	0.75	0.76
Molecular weight range ($M \times 10^{-4}$)	4-24	5-41	4-73
Ref.	this work	(19)	(22)

been determined. This stipulation applies also to MHS constants obtained by the classical fractionation method. Since K and α are inversely correlated,¹⁸ it is not to be expected that the constants measured from a particular ratio of intrinsic viscosities will necessarily coincide with those from another ratio or from classical multisample procedures. They should, however, combine to give equivalent \bar{M}_v values for the molecular weight range in which they are determined.

Table III lists MHS constants from this work and earlier studies with fractions in approximately the same molecular weight range as the broad distribution samples of the present study. In general, our α values are lower, and the K values are correspondingly higher than those produced by the other workers cited. These differences reflect the particular samples chosen for use in eq. (8) and the choice of fractions in the linear least-squares fit to eq. (1) which was used by the other authors. The K and α values determined in this work are valid for GPC measurements of molecular weight distributions of the particular broad polymers. This is shown in Table I by the good coincidence of average molecular weights estimated by GPC and osmometry or light scattering.

The K and α values determined from GPC do not, however, compare as closely as might be wished with the results of multifraction studies cited in Table III. The two literature values quoted for each solvent give reasonably consistent \bar{M}_v figures for the poly(methyl methacrylate) polymers used in this work. The constants derived from eq. (8) give significantly different viscosity-average molecular weights, however, and these discrepancies are particularly strong with the low-molecular-weight polymer, sample A.

We conclude that the use of broad distribution polymers for calibration of GPC analyses is best carried out by using two samples with different intrinsic viscosities and eq. (8). Extension of this process to give MHS constants in other solvents yields K and α values with very much less work than alternative methods that employ fractionated polymers. The GPC constants appear, however, not to be as reliable as those from the classical procedure, which uses more samples to establish the relation between $[\eta]$ and \bar{M}_v .

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