

Notes

Use of Broad Distribution Polymers and GPC Methods for Estimation of Mark-Houwink-Sakurada Constants

A recent article from this laboratory¹ contained an error in analysis which we are correcting herein. The cited paper considered the use of gel permeation chromatography (GPC) to determine the Mark-Houwink-Sakurada (MHS) constants for polymers in various solvents. The procedure outlined earlier for the GPC solvent^{1,2} requires no correction, but the reported extension of this method to solvents other than that used in the GPC analysis is more properly applied as follows.

THEORY

A parameter J is defined as

$$J_i = [\eta]_i M_i \quad (1)$$

Since the GPC elution volume is a function of $[\eta]_i M_i$,³ the GPC analysis yields J_i and the corresponding values of weight fraction, w_i , (after normalization) of the eluting species. A reasonable assumption here is that all species elute at infinite dilution.⁴ It can then be shown^{1,2} that

$$[\eta]' / [\eta] = \sum w_i' J_i'^{\alpha / (\alpha + 1)} / \sum w_i J_i^{\alpha / (\alpha + 1)} \quad (2)$$

where the primed and unprimed terms refer to different samples of the same polymeric type and the intrinsic viscosities ($[\eta]$) and GPC analyses are all obtained in the same solvent. In eq. (2) the exponent α is the MHS exponent in the familiar expression

$$[\eta] = K \bar{M}_v^\alpha \quad (3)$$

The right-hand side of eq. (2) is evaluated by treating the normalized GPC chromatogram in a reiterative computer program which tests values of α between 0.5 and 1.0 and compares the results with the magnitude of the left-hand side term which is a ratio of independently measured intrinsic viscosities. The α value which matches the GPC data to this left-hand side term is then used to calculate K from

$$K = ([\eta] / \sum w_i J_i^{\alpha / (\alpha + 1)})^{\alpha + 1} \quad (4)$$

The same general approach can be used to determine the MHS constants in a solvent other than the GPC solvent. In the following paragraphs all values in the non-GPC solvent are subscripted 2, while those in the GPC solvent are left without a subscript. In the second (non-GPC) solvent

$$J_{i2} \equiv [\eta]_{i2} M_i \quad (5)$$

For a species of given molecular weight, M_i , eqs. (1) and (5) give

$$J_{i2} = [\eta]_{i2} J_i / [\eta]_i \quad (6)$$

With eq. (3)

$$J_{i2} = J_i (K_2 / K) M_i^{\alpha_2 - \alpha} \quad (7)$$

Then, for the non-GPC solvent the analogue of eq. (2) is

$$\frac{[\eta]'_2}{[\eta]_2} = \frac{\sum w_i' J_i'^{\alpha_2 / (\alpha + 1)}}{\sum w_i J_i^{\alpha_2 / (\alpha + 1)}} \quad (8)$$

As above, the w_i and J_i values are available from the GPC experiment, and the intrinsic viscosities of the two polymer samples are measured in the GPC solvent. The exponent α for the GPC solvent is calculated as described above.¹ It then remains to estimate the MHS exponent for the non-GPC

solvent α_2 from a reiterative computer fit to eq. (8), which uses the w_i , J_i , and α values from GPC and the ratio of intrinsic viscosities measured in the non-GPC solvent.

Equation (4), which is used to estimate K in the GPC solvent from the intrinsic viscosity of a single polymer also contains the parameter J , which is valid only for the GPC solvent. To estimate K_2 for the non-GPC solvent, one proceeds from the expression in Ref. 1:

$$[\eta]_2 = K_2^{1/(\alpha_2+1)} \sum w_i J_i^{\alpha_2/(\alpha_2+1)} \quad (9)$$

With eqs. (5), (7), and

$$M_i = (J_i/K)^{1/(\alpha+1)} \quad (10)$$

it then follows that

$$K_2 = ([\eta]_2 K^{\alpha_2/(\alpha+1)}) / (\sum w_i J_i^{\alpha_2/(\alpha+1)}) \quad (11)$$

Thus, once K and α for the GPC solvent are obtained, the ratio of intrinsic viscosities of two polymers in a second solvent can be used to calculate the MHS constants for the latter solutions from eqs. (8) and (11).

RESULTS

We use the raw data quoted earlier¹ for three poly(methyl methacrylate) (PMMA) samples in various solvents. Table I lists the intrinsic viscosities reported in our previous article along with the MHS constants which were estimated for tetrahydrofuran (THF), the GPC solvent, with eqs. (2) and (4).

These THF constants were used as inputs (K and α) in eqs. (8) and (11) to calculate K_2 and α_2 for the other solvents. The results of these procedures are summarized in Table II. The first entry is a check in which THF was treated as the second solvent. The MHS constants generated for the fictitious second solvent coincide within round-off error with the input values generated from eqs. (2) and (4). The three viscosity ratios obtained in chloroform produce sets of K and α values in which the lower values of one constant are compensated by higher values of the other, as expected.

The values of K_2 and α_2 calculated from eqs. (8) and (11) can evidently be influenced by the choice of K and α for the particular polymer in the GPC solvent. This effect is slight, however, as shown by the entries in Table III, where the MHS constants in THF were those measured by the present

TABLE I
Intrinsic Viscosities of PMMA Samples¹ (cm³ g⁻¹)

Sample	A	B	C
THF ^a	18.13	32.07	61.21
Chloroform	23.72	44.33	88.76
Acetone	14.06	—	40.77
Benzene	20.56	—	61.78

^a In THF $[\eta] = 1.99 \times 10^{-2} \bar{M}_v^{0.660}$.

TABLE II
Mark-Houwink-Sakurada Constants from GPC Chromatograms and Intrinsic Viscosity Ratios in Non-GPC Solvents $[\eta']/[\eta]$

Solvent	Ratio ^a	Experimental	GPC and eq. (8)	α [eq. (8)]	$K \times 10^2$ (cm ³ /g) [eq. (11)]
THF	C/A	3.376	3.376	0.659	2.01
CHCl ₃	C/A	3.742	3.742	0.714	1.47
	C/B	2.002	2.001	0.702	1.71
	B/A	1.869	1.870	0.727	1.28
Acetone	C/A	2.900	2.901	0.578	3.66
Benzene	C/A	3.005	3.006	0.597	4.38

^a Sample codes from Table I.

TABLE III
Effects of MHS Constants in GPC Solvent on MHS Constants Calculated in Other Solvents

Solvent	Samples	Ref. 1	Ref. 4	Ref. 5
Input constants (THF)	—	$K = 1.99 \times 10^{-2}$ $\alpha = 0.660$	$K = 1.28 \times 10^{-2}$ $\alpha = 0.690$	$K = 1.04 \times 10^{-2}$ $\alpha = 0.697$
THF	C/A	$K_2 = 2.01 \times 10^{-2}$ $\alpha_2 = 0.659$	$K_2 = 1.69 \times 10^{-2}$ $\alpha_2 = 0.671$	$K_2 = 1.55 \times 10^{-2}$ $\alpha_2 = 0.677$
CHCl ₃	C/A	$K_2 = 1.47 \times 10^{-2}$ $\alpha_2 = 0.714$	$K_2 = 1.22 \times 10^{-2}$ $\alpha_2 = 0.727$	$K_2 = 1.11 \times 10^{-2}$ $\alpha_2 = 0.730$
Acetone	C/A	$K_2 = 3.66 \times 10^{-2}$ $\alpha_2 = 0.578$	$K_2 = 3.19 \times 10^{-2}$ $\alpha_2 = 0.587$	$K_2 = 2.95 \times 10^{-2}$ $\alpha_2 = 0.590$
Benzene	C/A	$K_2 = 4.38 \times 10^{-2}$ $\alpha_2 = 0.597$	$K_2 = 3.73 \times 10^{-2}$ $\alpha_2 = 0.608$	$K_2 = 3.49 \times 10^{-2}$ $\alpha_2 = 0.610$

method¹ and several sets of values reported by other workers who used the classical procedure involving fractionated polymer samples.

Table IV compares the MHS constants from this method with literature figures obtained with fractions in approximately the same molecular weight range as the broad distribution samples of the present study. There are many more sets of reported constants which can be used for comparison. The figures chosen here are those used in our earlier report,¹ where the constants calculated by our method did not match the results of previous workers. The comparison given here with the present corrected calculation method are much closer to literature figures.

Table V shows the \bar{M}_v values [from eq. (3)] from the various MHS constants quoted here. The differences are slight except for some estimates of the viscosity average molecular weights of sample A, which is at the lower edge of the range of molecular weights used in all the studies cited. The discrepancies between the various results are no worse than would be expected from comparisons of MHS constants produced by different studies involving characterization of fractionated polymer samples.

When the \bar{M}_v values from the present set of MHS constants are plotted against the corresponding α values the data points are linear and extrapolate to an estimated \bar{M}_w at $\alpha = 1$.¹⁰ These \bar{M}_w figures

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

THF			
$K \times 10^2 \text{ cm}^2/\text{g}$	1.99	1.28	1.04
α	0.660	0.690	0.697
Mol wt range ($M \times 10^{-4}$)	4-24	5-80	>3
Ref.	this work	4	5
Chloroform			
$K \times 10^2 \text{ cm}^2/\text{g}$	1.47	0.581	0.48
α	0.714	0.79	0.80
Mol wt range ($M \times 10^{-4}$)	4-24	5-41	8-137
Ref.	this work	6	7
Acetone			
$K \times 10^2 \text{ cm}^2/\text{g}$	3.66	0.618	0.75
α	0.578	0.72	0.70
Mol wt range ($M \times 10^{-4}$)	4-24	5-41	3-98
Ref.	this work	6	8
Benzene			
$K \times 10^2 \text{ cm}^2/\text{g}$	4.38	0.674	0.627
α	0.597	0.75	0.76
Mol wt range ($M \times 10^{-4}$)	4-24	5-41	4-73
Ref.	this work	6	9

TABLE V
Viscosity Average Molecular Weights of PMMA Samples with Different MHS Constants

Solvent	\bar{M}_v Values ($\times 10^{-4}$)		
	A (Ref.)	B (Ref.)	C (Ref.)
THF	3.1 (this work)	7.2 (this work)	19.3 (this work)
	3.7 (4)	8.4 (4)	21.5 (4)
	4.5 (5)	10.1 (5)	25.6 (5)
Chloroform	3.1 (this work)	7.5 (this work)	19.7 (this work)
	3.7 (6)	8.2 (6)	19.8 (6)
	4.1 (7)	9.1 (7)	21.6 (7)
Acetone	3.0 (this work)	—	18.7 (this work)
	4.6 (6)	—	20.2 (6)
	4.7 (8)	—	21.7 (8)
Benzene	3.0 (this work)	—	18.9 (this work)
	4.4 (6)	—	19.2 (6)
	4.2 (9)	—	18.0 (9)

are reasonably close to those reported¹ from light scattering for the same sample. This is further circumstantial evidence that all sets of MHS constants are consistent.

Since the GPC method provides reliable MHS constants fairly quickly and conveniently the cited procedure for estimating \bar{M}_w from intrinsic viscosity figures is made more attractive. Single point intrinsic viscosities¹¹ can be used for the data which are used to extrapolate to $\alpha = 1$ and $\bar{M}_v = \bar{M}_w$. The weight average molecular weight of a polymer sample can thus be approximated fairly well from two or three relative viscosities in different solvents. Multipoint intrinsic viscosities are probably best used to establish the MHS constants in the GPC method, however, since this procedure hinges on the use of a ratio of such data which should be as accurate as possible.

CONCLUSIONS

The GPC analysis of broad distribution polymers can be used conveniently to estimate Mark-Houwink-Sakurada constants. Two samples with different molecular weights are needed. The ratio of the intrinsic viscosities of these two samples in the GPC solvent and other solvents can be combined with the information in the GPC chromatogram to estimate the MHS constants for the particular polymer type in these solvents. This procedure is much less tedious than the usual techniques which require fractionation of the polymeric species. The accuracy of the GPC method is limited by the reliability of the intrinsic viscosity and GPC analyses. On the whole, it is probably at least as reliable, for the molecular weight range of the samples used, as the older procedures.

This work was supported by the Natural Sciences and Engineering Research Council of Canada. One of us (A.R.) gratefully acknowledges the grant of a fellowship from the Lady Davis Fellowship Trust.

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Received July 7, 1981

Accepted September 28, 1981