

Determination of Mark–Houwink–Sakurada Constants for Measurements of the Molecular Weights by Gel Permeation Chromatography I. On the Generalization of Mathematical Procedure

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ABSTRACT: Fourteen equations in terms of molecular weights and intrinsic viscosity are shown to determine Mark–Houwink–Sakurada (MHS) constants on the basis of gel permeation chromatography (GPC), six equations being for determination from one sample, four from two samples, and four by the method of least squares. These equations are examined, using the data obtained for poly(methyl methacrylate). It is pointed out that the determination of MHS constants from one sample is very sensitive to the measured condition of GPC, and thus we should get good GPC data. Using two samples, the reasonable MHS constants are obtained when the weight- and viscosity-average molecular weights are known. Using more than two samples, the MHS constants are determined by the method of least squares. It is shown that the MHS equation obtained previously under a given condition is transferred to a MHS equation under another condition by GPC where the viscosity-average molecular weights calculated by the former equation are used. Further, using the GPC data obtained under good conditions, good MHS constants can be determined when the number- and weight-average molecular weights are known.

KEY WORDS Molecular Weights / Intrinsic Viscosity / Mark–Houwink–Sakurada Constants / Gel Permeation Chromatography / Calibration Curve / Polystyrene / Poly(methyl methacrylate) / Method of Least Squares /

In polymer science, measurement of the molecular weight of a polymer is very important. It has been carried out by the osmotic method, the light scattering method, gel permeation chromatography (GPC), etc. Recently, GPC is the most popular method. To calculate the molecular weights by GPC, we have to make a calibration curve using several standard polymer samples whose molecular weight distributions are narrow. However, their preparations are difficult except for several kinds of polymers such as polystyrene, ethylene oxide, etc. Therefore, many workers have proposed modifications of a calibration curve made by the standard

polymer to apply it to other polymers. Almost all the modifications are based on the suggestion¹ that the hydrodynamic volume of polymer can be used to establish a universal calibration curve in GPC, because all polymers have the same hydrodynamic volume at a given elution volume on the assumption that Φ in the Flory–Fox equation is invariable.² That is, the modifications are based on an equation:

$$[\eta]_s M_s = [\eta] M \quad (1)$$

Using the Mark–Houwink–Sakurada (MHS) equation:

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

Equation 1 is written as:

$$K_s M_s^{1+a_s} = K M^{1+a} \quad (3)$$

The modification of the calibration curve has been carried out by eq 3. Thus, we have to determine a and K as MHS constants. In the past, the MHS constants have been determined when the number- and weight-average molecular weights and the intrinsic viscosities of one sample or two samples were known.³⁻⁸ However, the viscosity-average molecular weights have not been used. Probably, using a MHS equation obtained previously when the molecular weight distribution was narrow, we may calculate the precise viscosity-average molecular weights. Then, the MHS constants (a_s , K_s) in such an equation under the previous condition may be transferred to new MHS constants (a , K) under the other condition. On the above, using eq 3, we can make ten more methods in terms of the number-, weight-, and/or viscosity-average molecular weights and/or the intrinsic viscosities, three methods being determinations from one sample, three from two samples, and four from by the method of least squares. That is, we have fourteen methods to determine the MHS constants by GPC. However, on comparison of all fourteen methods, the applicability has not been examined. Therefore, the aim of this article is to examine such applicability. Then, all fourteen methods are presented. Every method is examined, using the data obtained for poly(methyl methacrylate) (PMMA).

THEORY

The number-, weight-, and viscosity-average molecular weights and the intrinsic viscosity of a polydisperse polymer are given by:

$$M_n = \sum_{i=1}^{\infty} N_i M_i / \sum N_i \quad (4)$$

$$M_w = \sum N_i M_i^2 / \sum N_i M_i \quad (5)$$

$$M_v = (\sum N_i M_i^{1+a_v} / \sum N_i M_i)^{1/a_v} \quad (6)$$

$$[\eta] = K (\sum N_i M_i^{1+a_v} / \sum N_i M_i)^{a/a_v} \quad (7)$$

Using eq 3, the molecular weight of i -th species in a polymer is given by:

$$M_i = [(K_s/K)^{1/(1+a)}] [M_{is}^{(1+a_s)/(1+a)}] \quad (8)$$

The weight fraction of i -th species is given by:

$$w_i = N_i M_i / \sum N_i M_i \quad (9)$$

Using eq 8 and 9, eq 4—6 and eq 7 become:

$$M_n = [(K_s/K)^{1/(1+a)}] / [\sum w_i / M_{is}^{(1+a_s)/(1+a)}] \quad (10)$$

$$M_w = [(K_s/K)^{1/(1+a)}] / [\sum w_i M_{is}^{(1+a_s)/(1+a)}] \quad (11)$$

$$M_v = [(K_s/K)^{1/(1+a)}] / [\sum w_i M_{is}^{a_v(1+a_s)/(1+a)}]^{1/a_v} \quad (12)$$

$$[\eta] = [K_s^{a/(1+a)} K^{1/(1+a)}] / [\sum w_i M_{is}^{a(1+a_s)/(1+a)}] \quad (13)$$

Here, the K -value is calculated by:

$$K = K_s [\sum w_i / M_{is}^{(1+a_s)/(1+a)} / M_n]^{(1+a)} \quad (14)$$

$$K = K_s [\sum w_i M_{is}^{(1+a_s)/(1+a)} / M_w]^{(1+a)} \quad (15)$$

$$K = K_s [(\sum w_i M_{is}^{(1+a_s)/(1+a)})^{1/a_v} / M_v]^{(1+a)} \quad (16)$$

$$K = [\eta] / K_s^a [\sum w_i M_{is}^{a(1+a_s)/(1+a)}]^{(1+a)} \quad (17)$$

Determination of a from One Sample

When M_n , M_w , and $[\eta]$ are known, the following three equations can be obtained from eq 10 and 11, eq 10 and 13, and eq 11 and 13, to determine a .³⁻⁷

$$M_w/M_n = [\sum w_i M_{is}^{a(1+a_s)/(1+a)}] / [\sum w_i / M_{is}^{(1+a_s)/(1+a)}] \quad (18)$$

$$[\eta] M_n / K_s = [\sum w_i M_{is}^{a(1+a_s)/(1+a)}] / [\sum w_i / M_{is}^{(1+a_s)/(1+a)}] \quad (19)$$

$$[\eta] M_w / K_s = [\sum w_i M_{is}^{a(1+a_s)/(1+a)}] / [\sum w_i M_{is}^{(1+a_s)/(1+a)}] \quad (20)$$

Further, in order to determine a , we can make the following three equations, combining two of eq 10—13.

$$[\eta]M_v/K_s = [\sum w_i M_{is}^{a(1+a_s)/(1+a)}][\sum w_i M_{is}^{a_v(1+a_v)/(1+a)}]^{1/a_v} \quad (21)$$

$$M_v/M_n = [\sum w_i M_{is}^{a_v(1+a_s)/(1+a)}]^{1/a_v} [\sum w_i/M_{is}^{(1+a_s)/(1+a)}] \quad (22)$$

$$M_w/M_v = [\sum w_i M_{is}^{(1+a_s)/(1+a)}] / [\sum w_i M_{is}^{a_v(1+a_s)/(1+a)}]^{1/a_v} \quad (23)$$

After determining the a -value, the K -value can be calculated from eq 14–17.

Determination of a from Two Samples

When the intrinsic viscosities of two samples are known, the a -value can be calculated by:^{3,7,8}

$$[\eta]_1/[\eta]_2 = [\sum w_{i1} N_{is}^{a(1+a_s)/(1+a)}] / [\sum w_{i2} M_{is}^{a(1+a_s)/(1+a)}] \quad (24)$$

Further, to determine a , the following three equations are obtained from eq 10–12.

$$M_{n1}/M_{n2} = [\sum w_{i2}/M_{is}^{(1+a_s)/(1+a)}] / [\sum w_{i1}/M_{is}^{(1+a_s)/(1+a)}] \quad (25)$$

$$M_{w1}/M_{w2} = [(\sum w_{i1} M_{is}^{(1+a_s)/(1+a)}) / (\sum w_{i2} M_{is}^{(1+a_s)/(1+a)})] \quad (26)$$

$$M_{v1}/M_{v2} = [(\sum w_{i1} M_{is}^{a_v(1+a_s)/(1+a)}) / (\sum w_{i2} M_{is}^{a_v(1+a_s)/(1+a)})]^{1/a_v} \quad (27)$$

The K -value can be calculated from eq 14–17.

$$F_j = (\partial f / \partial K) dK_{j+1} + (\partial f / \partial a) da_{j+1} + d_j \quad (28)$$

where f denotes one function of eq 10–13.

Determination of a and K by the Method of Least Squares

When we have more samples than two, we can use the method of least squares.⁹ In the present case, F_j is set as the difference between the value measured for M_n , M_w , M_v , or $[\eta]$ and the respective value calculated using a_j and K_j at j -th computations. Then, F_j is given by:

The values of dK_{j+1} ($=K_{j+1}-K_j$) and da_{j+1} ($=a_{j+1}-a_j$) can be calculated under the

condition that $\sum_{n=1}^m (d_j)_n^2$ is minimized. Thus,

we show the pair of respective partial differential equations as $\partial f / \partial K$ and $\partial f / \partial a$ in the following.

When the number-average molecular weights are known, the pair is given by:

$$\partial M_n / \partial K = -[(K_s/K)^{1/(1+a)}] / [(1+a)K \sum w_i / M_{is}^{(1+a_s)/(1+a)}] \quad (29a)$$

$$\begin{aligned} \partial M_n / \partial a = - \{ & [(K_s/K)^{1/(1+a)}] / [(1+a)^2 \sum w_i / M_{is}^{(1+a_s)/(1+a)}]^2 \} \{ [\ln(K_s/K)] [\sum w_i / M_{is}^{(1+a_s)/(1+a)}] \\ & + (1+a_s) [\sum w_i (\ln M_{is}) / M_{is}^{(1+a_s)/(1+a)}] \} \end{aligned} \quad (29b)$$

When the weight-average molecular weights are known, the pair is:

$$\partial M_w / \partial K = -[(K_s/K)^{1/(1+a)}] [\sum w_i M_{is}^{(1+a_s)/(1+a)}] / [K(1+a)] \quad (30a)$$

$$\begin{aligned} \partial M_w / \partial a = -[(K_s/K)^{1/(1+a)}] / (1+a)^2 \{ & [\ln(K_s/K)] [\sum w_i M_{is}^{(1+a_s)/(1+a)}] \\ & + (1+a_s) [\sum (\ln M_{is}) w_i M_{is}^{(1+a_s)/(1+a)}] \} \end{aligned} \quad (30b)$$

When the viscosity-average molecular weights are known, we use:

$$\partial M_v/\partial K = [(K_s/K)^{1/(1+a)}][\sum w_i M_{is}^{a_v(1+a_s)/(1+a)}]^{1/a_v} \quad (31a)$$

$$\begin{aligned} \partial M_v/\partial a = & [(K_s/K)^{1/(1+a)}][\sum w_i M_{is}^{a_v(1+a_s)/(1+a)}]^{1/a_v} \{ \ln(K_s/K) \\ & + (1+a_s)[\sum (\ln M_{is}) w_i M_{is}^{a_v(1+a_s)/(1+a)}] / [\sum w_i M_{is}^{a_v(1+a_s)/(1+a)}] \} \end{aligned} \quad (31b)$$

When the intrinsic-viscosities are known, the pair is:

$$\partial[\eta]/\partial K = -[(K_s/K)^{a/(1+a)}][\sum w_i M_{is}^{a(1+a_s)/(1+a)}] \quad (32a)$$

$$\begin{aligned} \partial[\eta]/\partial a = & [K_s^{a/(1+a)} K^{1/(1+a)} / (1+a)^2] \{ [\ln(K_s/K)][\sum w_i M_{is}^{a(1+a_s)/(1+a)}] \\ & + (1+a_s)[\sum (\ln M_{is}) w_i M_{is}^{a(1+a_s)/(1+a)}] \} \end{aligned} \quad (32b)$$

Using the pair of differential equations, we obtain the numerical values of dK_{j+1} and da_{j+1} , then more probable values than K_j and a_j are calculated to be $K_{j+1} = K_j + dK_{j+1}$ and $a_{j+1} = a_j + da_{j+1}$. Here, the values of K_{j+1} and a_{j+1} , obtained when $|K_{j+1}/K_j - 1| < 0.005$ and $|a_{j+1}/a_j - 1| < 0.005$, are presented as the most probable MHS constants.

The number of samples and the molecular weights and/or the intrinsic viscosities, which are necessary to use the above equations, are shown in Table I.

EXPERIMENTAL

Two standard calibration curves were made between elution volume (count number) and the molecular weight of polystyrene purchased from Toyo Soda Ltd Company and General Science Corporation ($M = 800$ to 2.06×10^7) (Table II and Figure 1). To supplement these curves, commercial ethylbenzene ($M = 106$) and diphenylpropane (196) were used. A Toyo Soda GPC HLC-802A with TSK gel GMH as columns was used at $25 \pm 1^\circ\text{C}$ and $38 \pm 1^\circ\text{C}$, where tetrahydrofuran (THF) was used as the solvent.

The samples of PMMA, whose number- and weight-average molecular weights are known, were purchased from General Science Corporation. Using these, determinations of MHS constants from one sample and two samples were carried out. For determination by the method of least squares, PMMA was formed by radical polymerization. Its weight-average molecular weight was measured by the light scattering method, using a Toyo Soda LS8 and GPC HLC-802A. The number-average molecular weight was calculated, using a calibration curve for PMMA modified by the MHS equation obtained previously at $25 \pm 1^\circ\text{C}$ in THF.¹⁰ Intrinsic viscosities were measured at $25.0 \pm 0.05^\circ\text{C}$ in THF and acetone and at $38.0 \pm 0.05^\circ\text{C}$ in THF. The molecular weights and intrinsic viscosities of the above PMMA are shown in Table III. The viscosity-average molecular weights were calculated using the MHS equa-

Table I. Equations to determine MHS constants

Equations		Number of samples		MW ^a and/or $[\eta]$
<i>a</i>	<i>K</i>	<i>m</i>		
18	14, 15	1		M_n, M_w
19	14, 17	1		$M_n, [\eta]$
20	15, 17	1		$M_w, [\eta]$
21	16, 17	1		$M_v, [\eta]$
22	14, 16	1		M_n, M_v
23	15, 16	1		M_w, M_v
24	17	2		$[\eta]$
25	14	2		M_n
26	15	2		M_w
27	16	2		M_v
29a, b		$m \geq 3$		M_n
30a, b		$m \geq 3$		M_w
31a, b		$m \geq 3$		M_v
32a, b		$m \geq 3$		$[\eta]$

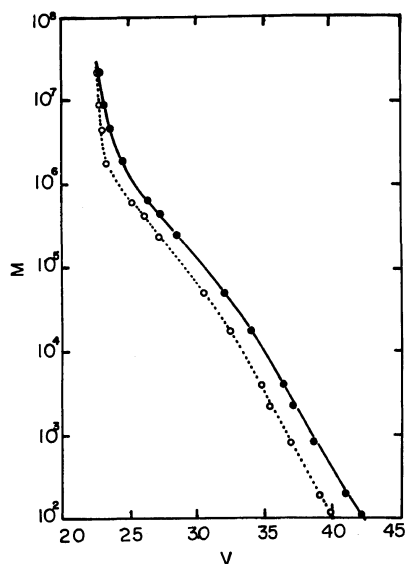
^a MW, molecular weight.

Table II. The elution volume at given molecular weight of standard polystyrene when elution volume rate is 1 ml min⁻¹

<i>M</i>	<i>v</i>	
	25°C	38°C
106 ^a	40.0	42.2
196 ^b	39.1	41.2
800	36.9	38.8
2200	35.4	37.2
4000	34.8	36.5
17500	32.5	34.0
50000	30.5	32.2
233000	27.2	28.6
422000	26.2	27.3
600000	25.2	26.3
1800000	23.3	24.5
4480000	23.0	23.6
8420000	22.8	23.2
20600000	22.6	22.7

^a Ethylbenzene.

^b Diphenylpropane.


Figure 1. The calibration curves for polystyrene at 25°C (○) and 38°C (●).

tions with (a_v , K_v) obtained when the samples of the molecular weight distribution being narrow were used.¹¹⁻¹⁴

Table III. The molecular weights and intrinsic viscosities of PMMA to determine MHS constants

M_n	M_w	$[\eta]_{\text{THF}}$		$[\eta]_{\text{acetone}}$
		25°C	38°C	25°C
13700 ^c	33300 ^c	0.160	0.162	0.125
46400 ^c	93300 ^c	0.320	0.330	0.235
119200 ^c	490200 ^c	1.030	1.025	0.675
113200 ^{a,d}	175600 ^{b,d}	0.520	0.530	0.360
126500 ^{a,d}	218800 ^{b,d}	0.610	0.624	0.420

^a Calculated by GPC.

^b Measured by the light scattering method.

^c Purchased from General Science Corporation.

^d Formed by radical polymerization.

RESULTS AND DISCUSSION

A MHS equation for polystyrene in THF is:¹⁵

$$[\eta] = 1.60 \times 10^{-4} M^{0.706} \text{ at } 25^\circ\text{C} \quad (33)$$

At 38°C, eq 34 is obtained as:

$$[\eta] = 1.247 \times 10^{-4} M^{0.720} \text{ at } 38^\circ\text{C} \quad (34)$$

As shown in Figure 1, the calibration curve at 38°C is better than that at 25°C, because the former can be used over a wider range of the elution volume or count number and, especially, when $v \leq 24$, dM/dv at 38°C is not steeper than that at 25°C. The MHS constants for PMMA at 38°C may be nearly equal to those at 25°C, because $[\eta]_{38}$ is approximated to $[\eta]_{25}$ as shown in Table III.

Determination of a and K from One Sample

Estimation of the a -value was tried using eq 18–23, the K -value calculated if the a -value was obtained. The a -value at 25°C, which is in 1/2 to 1,² could not be obtained from $[\eta]M_n/K_s$, $[\eta]M_w/K_s$, $[\eta]M_v/K_s$, and M_w/M_v , except M_w/M_n and M_v/M_n (Table IV). The determination by M_w/M_n may be better than that by M_v/M_n , because the MHS constants were obtained from all three samples by the former, but they were obtained from only two by the later. Generally, a increases and K de-

Table IV. The values of MHS constants obtained from one sample^a

M_n	M_w	M_w/M_n^b		M_v/M_n^b		$[\eta]M_n^c$		$[\eta]M_w^c$	
		a	$10^4 K$	a	$10^4 K$	a	$10^4 K$	a	$10^4 K$
13700	33300	0.840	0.490	0.600	3.94	—	—	—	—
46400	93300	0.700	1.72	0.551	7.84	0.681	1.40	—	—
119200	490200	0.600	7.84	—	—	0.571	5.13	0.840	0.200

^a M_v , calculated by MHS equation in ref 11.

^b At 25°C.

^c At 38°C.

creases with increasing M .^{2,16} However, as shown in Table IV, the present value of a decreases and the value of K increases with increasing M_n , M_w , and M_v . That is, the present MHS constants obtained from one sample are not consistent with the Flory theory² and the previous experimental results.¹⁶

In the past, MHS constants were obtained from $[\eta]M_n/K_s$ and $[\eta]M_w/K_s$.³⁻⁶ Here, using the better calibration curve at 38°C, MHS constants were also obtained from eq 19 and 20 (Table IV). Therefore, we may state that we should be very careful to measure GPC under good conditions when eq 19 and 20 are used.

Determination of a and K from Two Samples

The values calculated as MHS constants are shown in Table V. Here, they were not obtained using eq 25 (M_{n1} , M_{n2})=(13700, 46400) and (46400, 119200) and eq 26 (M_{w1} , M_{w2})=(33300, 93300). Dobbin *et al.*⁷ stated that the determination by eq 24 was quite good. However, with decreasing $[\eta]$ (accordingly M), the present value of a increases from 0.818 to 0.865 and the value of K decreases from 0.269×10^{-4} to 0.169×10^{-4} . As stated in Determination from One Sample, this is unreasonable. Thus, the use of eq 24 is not better. On the other hand, the MHS constants obtained by eq 26 (M_w) and 27 (M_v) are reasonable, because a increases and K decreases with increasing M . It is recommended to determine the MHS constant by eq 26 and 27 on the use of two samples.

Table V. The values of a and K obtained from two samples at 25°C

M_{n1}	M_{n2}	a	$10^4 K$
13700	46400	—	—
13700	119200	0.756	1.11
46400	119200	—	—

M_{w1}	M_{w2}	a	$10^4 K$
33300	93300	—	—
33300	490200	0.564	6.10
93300	490200	0.626	2.62

$[\eta]_1$	$[\eta]_2$	a	$10^4 K$
0.160	0.320	0.865	0.169
0.160	1.030	0.833	0.236
0.320	1.030	0.818	0.290

M_{n1}	M_{v2} (a_v , $10^4 K_v$, ref) ^a	a	$10^4 K$
40200	99000 (0.70, 0.75, 11)	0.660	1.40
40200	447000	0.692	0.991
99000	447000	0.709	0.790
39800	96800 (0.71, 0.676, 12)	0.684	1.11
39800	428000	0.716	0.786
96800	428000	0.734	0.619
41700	99100 (0.73, 0.53, 13)	0.729	0.636
41700	421000	0.763	0.439
99100	421000	0.781	0.343
32600	81400 (0.69, 0.96, 14)	0.635	2.57
32600	375000	0.667	1.80
81400	375000	0.687	1.41

^a (a_v , K_v), at 25°C in acetone.

Determination of a and K by the Method of Least Squares

The values obtained for MHS constants at 25 and 38°C are shown in Table VI. All eq 29—32 at 38°C yielded the MHS constants, but eq 29 (M_n) and 32 ($[\eta]$) at 25°C did not yield. This dif-

Table VI. The values of a and K obtained from five samples

Method	25°C		38°C	
	a	$10^4 K$	a	$10^4 K$
M_n	—	—	0.555	6.89
M_w	0.724	1.29	0.641	2.89
$[\eta]$	—	—	0.753	0.559
M_v				
$(a_v, 10^4 K_v, \text{ref})^a$				
(0.70, 0.75, 11)	0.653	2.50	0.688	1.33
(0.71, 0.676, 12)	0.676	2.00	0.713	1.03
(0.73, 0.53, 13)	0.725	1.09	0.767	0.532
(0.69, 0.96, 14)	0.631	4.47	0.663	2.46

^a (a_v, K_v), at 25°C in acetone.

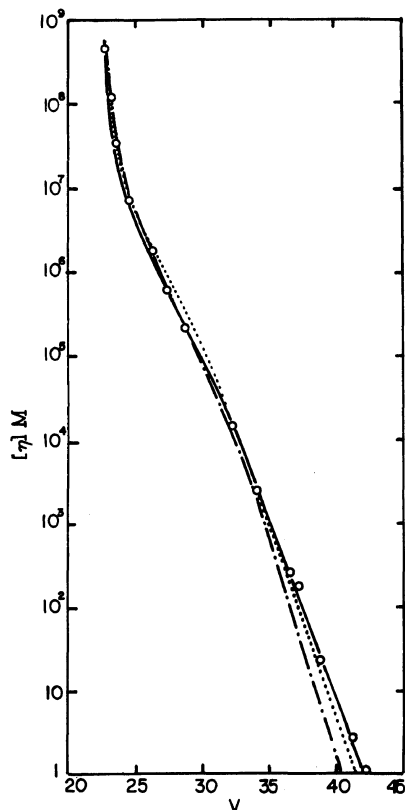


Figure 2. Relationships between $[\eta]M$ and v at 38°C for polystyrene (○) and MMA by M_n (—); by M_w (-----); by $[\eta]$ (-·-·-).

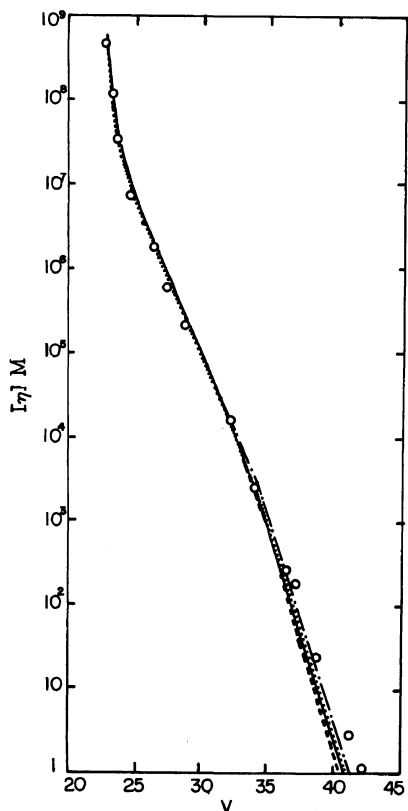


Figure 3. Relationships between $[\eta]M$ and v at 38°C for polystyrene (○) and MMA by $(a, 10^4K) = (0.688, 1.33)$ (-----); $(0.713, 1.03)$ (—); $(0.767, 0.532)$ (-·-·-); $(0.663, 2.46)$ (-·-·-).

ference may be from the fact that the calibration curve at 38°C is better than that at 25°C, as stated previously. It is resulted that the MHS constants (a_v, K_v) obtained previously¹¹⁻¹⁴ can be transferred to new MHS constants (a, K) by GPC. This transability is the same as the determination from two samples. The reason why these results are yielded is discussed in the following. To calculate exact M_n , the reading weight as w_i at lower M or larger v must be precise. Unfortunately, it is more difficult at lower M , because w_i is lower. Further, to calculate exact M_w , the reading w_i at higher M or smaller v must be precise. However, it is also more difficult at higher M , because w_i is also lower. Accordingly, the determinations by both

M_n and M_w are not always good. On the other hand, to calculate exact M_v , it is not necessary to read so precisely w_i at lower or higher M , but near median M or v . In the median, the precise reading w_i is easy, because we can read w_i near the peak on the chromatogram. Thus, the exact M_v can be calculated by GPC and the MHS constants (a_v , K_v) can be transferred to the reasonable MHS constants (a , K).

To examine the MHS constants obtained here on the basis of eq 1, three curves of relationships between $[\eta]M$ and v are made and shown in Figure 2, using the MHS constants obtained at 38°C from M_n , M_w , and $[\eta]$ and those in ref 10 as used in EXPERIMENTAL. The curve obtained from M_n is the best to the plot for universal calibration made from the standard polystyrene when v is larger. The curve obtained from M_w is also a very good fit to the universal plot, except that it slightly deviates when $27 < v < 31$ and $v > 37$. The curve obtained from $[\eta]$ to the universal plot when v is smaller. Four curves made from M_v are shown in Figure 3. Those fit the universal plot except when $v > 36$. Thus, it may be proved that almost all the MHS constants (a_v , K_v) are transferred to the respective good MHS constants (a , K) on the basis of eq 1. However, when v is small except using M_n , the curves deviate from the universal. Experimentally and theoretically, a decreases with decreasing M and approaches $1/2$.^{2,16} Then, use of the MHS constants in eq 33 and 34 are unreasonable when v is so small that $M < 3000$.¹⁵ To obtain such a curve as fit the universal curve, the present methods shown in THEORY and Table I are not better. Thus, the deviation from the universal plot when $M < 3000$ may be reasonable. In the near future, we will try to make the curve which is a fit to the universal curve when M is small.

NOMENCLATURE

Φ = Flory's universal constant

K_s, a_s	= MHS constants for a standard polymer
K, a	= MHS constants for a polymer
K_v, a_v	= MHS constants to calculate the viscosity-average molecular weight
$[\eta]_s$	= intrinsic viscosity for a standard polymer
$[\eta]$	= intrinsic viscosity for a polymer
M_s	= molecular weight for a standard polymer with narrow molecular weight distribution
M	= molecular weight for a polymer with narrow molecular weight distribution
N_i	= number of i -th species in a polymer
M_{si}	= molecular weight of i -th species in a standard polymer
M_i	= molecular weight of i -th species in a polymer
M_n	= number-average molecular weight
M_w	= weight-average molecular weight
M_v	= viscosity-average molecular weight
w_i	= weight fraction of i -th species in a polymer
v	= elution volume or count number
m	= number of samples

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