Modification of calibration curve for measurement of molecular weight of small polymers by gel permeation chromatography

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(Received 26 September 1986; revised 22 December 1986; accepted 12 February 1987)

When the molecular weight of a polymer is so small ($M < 10\,000$) that the Mark–Houwink–Sakurada (MHS) constants depend on M, the use of the MHS equation is not appropriate to modify a calibration curve made from standard polymer samples into curves to measure molecular weights of the respective polymers by gel permeation chromatography. Here, such a modification is tried by the Dondos–Benoit (BD) equation: $1/[\eta] = -A_2 + A_1/M^{1/2}$ ($[\eta]$ = intrinsic viscosity; A_1, A_2 = constants), with polystyrene and polybutadiene used as the polymer samples. It is shown that the modification is adoptable for $M < 50\,000$ for polystyrene and for $M < 23\,600$ for polybutadiene. It is also shown that, using the MHS equation when M is high and the BD equation when M is low, a calibration curve made from standard polymer samples can be modified into curves to measure molecular weights of the respective polymers over the whole range of molecular weight.

(Keywords: gel permeation chromatography; small polymer; modification of calibration curve; molecular weight; polystyrene; polybutadiene)

INTRODUCTION

The Mark–Houwink–Sakurada (MHS) expression

$$[\eta] = KM^a \tag{1}$$

is useful for estimating the molecular weights of polymers which are larger than about 10^4, where K and a are invariable.

On the assumption that K and a are independent of M, we reported on 14 methods for the determination of MHS constants by gel permeation chromatography (g.p.c.) in more detail[1] than methods reported on previously[2-4]. However, with decreasing $M < 10^4$, K increases and a decreases; $a \rightarrow 0.5$ at $M \rightarrow 0$.[5] The corresponding experimental data are compiled in reference 6. In reference 1, it was reported that a curve of $[\eta]M$ against elution volume (v) based on equation (1) deviated from the plot for universal calibration for $M < 10^4$ and the deviation was discussed with regard to the dependences of K and a on M. Therefore, it is not appropriate to use equation (1) for the modification of a calibration curve.

To treat the relationship between K, a and M, Dondos and Benoit[7,8] proposed the following equation:

$$1/[\eta] = -A_2 + A_1/M^{1/2} \tag{2}$$

In the present paper, we report that values of A_1 and A_2 for polymer samples can be determined by g.p.c., where the values of A_{1s} and A_{2s} for the standard polymers are used. To examine the validity of the A_1 and A_2 values determined, the $[\eta]M$ against v curve calculated using their values is compared with the plot for universal calibration made from standard polymer samples.

THEORY

On the assumption that all polymers have the same hydrodynamic volume at a given elution volume, we can use[9]:

$$[\eta]_s M_s = [\eta] M \tag{3}$$

Equations (2) and (3) give:

$$M_i^{3/2}/(A_1 - A_2 M_i^{1/2}) = M_{is}^{3/2}/(A_{1s} - A_{2s} M_{is}^{1/2}) \quad (= J_i) \tag{4}$$

Equation (4) can be rewritten as:

$$x_i^3 + J_i A_2 x_i - J_i A_1 = 0 \tag{5}$$

where

$$M_i = x_i^2 \tag{6}$$

A solution of equation (5) is:

$$\begin{aligned} x_i = {} & [J_i A_1/2 + (J_i^2 A_1^2/4 + J_i^3 A_2^3/27)^{1/2}]^{1/3} \\ & + [J_i A_1/2 - (J_i^2 A_1^2/4 + J_i^3 A_2^3/27)^{1/2}]^{1/3} \end{aligned} \tag{7}$$

The number- and weight-average molecular weights are:

$$\bar{M}_n = \sum_{i=1}^{\infty} M_i N_i / \sum N_i \tag{8}$$

$$\bar{M}_w = \sum M_i^2 N_i / \sum M_i N_i \tag{9}$$

Equations (6) and (10) can be formulated equally as equations (11) and (12), in which w_i denotes the weight fraction of species i:

$$w_i = N_i M_i / \sum N_i M_i \tag{10}$$

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0032–3861/87/091589–04$03.00
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Table 1 Elution volume[a] and intrinsic viscosity of PSt

M	v	$[\eta]$ (dl g^{-1})
106[b]	42.2	
196[c]	41.2	0.0153
800	38.5	0.0300
2 200	36.7	0.0490
4 000	36.3	0.0660
17 500	33.8	0.138
50 000	31.7	0.301
233 000	28.3	1.061
422 000	27.1	1.395
600 000	26.3	1.804

[a] At given molecular weight of standard PSt and elution rate 1 ml min^{-1}
[b] Ethylbenzene
[c] Diphenylpropane

$$\bar{M}_n[=1/\sum(w_i/M_i)]=1/\sum(w_i/x_i^2) \quad (11)$$

$$\bar{M}_w[=\sum(w_iM_i)]=\sum(w_ix_i^2) \quad (12)$$

To determine the values of A_1 and A_2, we can use the method of least squares[10]. Here, F_j is set as the difference between the value measured for $\bar{M}_n$ or $\bar{M}_w$ and the respective value calculated using $A_{1,j}$ and $A_{2,j}$ at the jth computation. Then F_j is given by:

$$F_j=(\partial f/\partial A_1)\mathrm{d}A_{1,j+1}+(\partial f/\partial A_2)\mathrm{d}A_{2,j+1}+d_j \quad (13)$$

where f denotes a function of equations (8) and (9). The values of $\mathrm{d}A_{k,j+1}$ $(=A_{k,j+1}-A_{k,j})$ $(k=1$ for A_1 and $k=2$ for $A_2)$ are calculated under the condition that $\sum_{n=1}^{m}(d_j)_n^2$ is minimized. Thus we show the partial differential equations as:

$$\partial\bar{M}_n/\partial A_k=2\left[\sum(w_i/x_i^3)(\partial x_i/\partial A_k)\right]\Big/\left[\sum(w_i/x_i^2)\right]^2 \quad (14)$$

$$\partial\bar{M}_w/\partial A_k=2\sum[w_ix_i(\partial x_i/\partial A_k)] \quad (15)$$

where:

$$\frac{\partial x_i}{\partial A_1}=\frac{2J_i+J_i^2A_1/(J_i^2A_1^2/4+J_i^3A_2^3/27)^{1/2}}{12[J_iA_1/2+(J_i^2A_1^2/4+J_i^3A_2^3/27)^{1/2}]^{2/3}}+\frac{2J_i-J_i^2A_1/(J_i^2A_1^2/4+J_i^3A_2^3/27)^{1/2}}{12[J_iA_1/2-(J_i^2A_1^2/4+J_i^3A_2^3/27)^{1/2}]^{2/3}} \quad (16a)$$

$$\frac{\partial x_i}{\partial A_2}=\frac{J_i^3A_2^2}{54(J_i^2A_1^2+J_i^3A_2^3)^{1/2}}\{[J_iA_1/2+(J_i^2A_1^2/4+J_i^3A_2^3/27)^{1/2}]^{-2/3}-[J_iA_1/2-(J_i^2A_1^2/4+J_i^3A_2^3/27)^{1/2}]^{-2/3}\} \quad (16b)$$

Using the above equations, we obtain numerical values of $\mathrm{d}A_{k,j+1}$. Then more probable values than $A_{k,j}$ are calculated to be $A_{k,j+1}=A_{k,j}+\mathrm{d}A_{k,j+1}$. Here, the values of $A_{k,j+1}$ obtained when $|A_{k,j+1}/A_{k,j}-1|<0.005$ are presented as the most probable values of A_k.

EXPERIMENTAL

Two standard calibration curves at 38±1°C were made between elution volume and molecular weight for standard polystyrene (PSt, *Table 1*), purchased from Toyo Soda Ltd Company and General Science Corporation, and for polybutadiene (PBD, *Table 2*), purchased from Scientific Polymer Products Inc. (*Figure 1*). To supplement these curves, commercial ethylbenzene ($M=106$), diphenylpropane (196), 1,4-octadiene (110) and 1,7-octadiene (110) were used as models for low molecular weight polymers. A Toyo Soda GPC HLC-802A with TSK gel GMH columns was used to make the curves, with tetrahydrofuran (THF) as eluent. Six samples of PSt were prepared by radical polymerization. Their molecular weights were measured by g.p.c. using the calibration curve made for PSt (*Table 3*). Intrinsic viscosities of the polymers shown in *Tables 1* and *2* were measured at 38.0±0.05°C in THF.

RESULTS AND DISCUSSION

The relationship between $[\eta]$ and M for the PSt samples in *Table 1* is given in *Figure 2*. A curve based on equation

Table 2 Elution volume[a] and intrinsic viscosity of PBD

$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	v	$[\eta]$ (dl g^{-1})
110[b]	1	41.3	
110[c]	1	41.2	
439	1.05	39.0	0.0338
960	1.07	37.9	0.0535
2980	1.08	36.2	0.107
23 600	1.07	38.3	0.473
170 000	1.26	28.3	2.11
423 000	1.48	26.4	3.79

[a] At given molecular weight of standard PBD and elution rate 1 ml min^{-1}
[b] 1,4-octadiene
[c] 1,7-octadiene

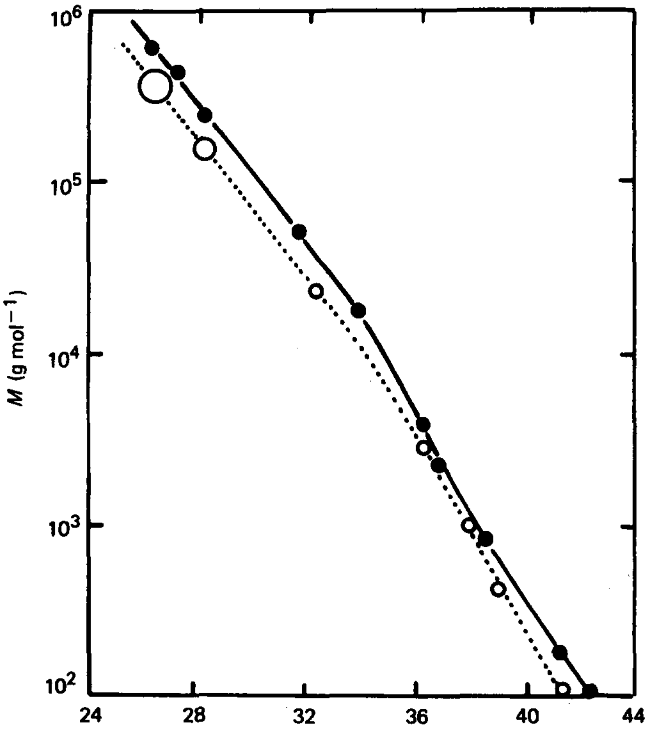

Figure 1 Calibration curves for PSt (●) and PBD (○)

Table 3 Molecular weights of PSt prepared by radical polymerization

$\bar{M}_n$	$\bar{M}_w$	v (peak)	$\bar{M}_w/\bar{M}_n$
500	580	39.4	1.16
633	807	38.8	1.27
850	1 257	38.1	1.48
1475	2 885	37.1	1.96
4360	10 370	35.0	2.38
6030	15 490	34.2	2.57

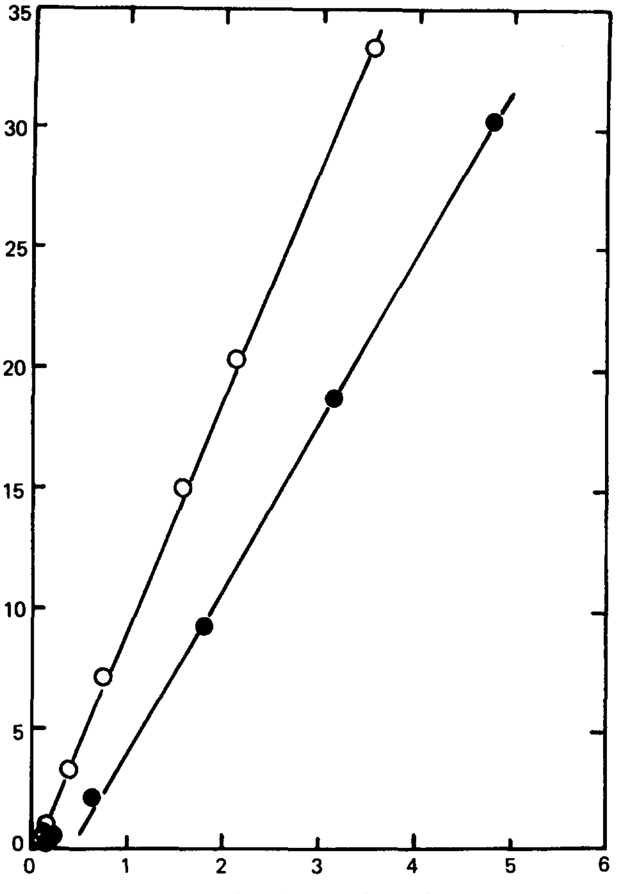

Figure 2 Relationship between $[\eta]$ and M for PSt (●) in *Table 1* and for PBD (○) in *Table 2*

(2) is shown for all the samples ($800 \leq M \leq 600\,000$). Then we obtain $(A_{1s}, A_{2s})_{\mathrm{PSt}} = (990, 0.800)$. The relationship between $[\eta]$ and M for PBD (*Table 2*) is also shown in *Figure 2*. Here, a curve based on equation (2) is shown for four samples of $M < 23\,600$. The data for $M > 17\,000$ deviated from such a curve. The value of $[\eta]$ for PBD is larger than that for PSt at the same molecular weight. Thus the range of molecular weights for which equation (2) is adoptable depends on $[\eta]$. We obtain $(A_{1s}, A_{2s})_{\mathrm{PBD}} = (700, 3.40)$ from the curve in *Figure 2*.

When PBD is used as a standard polymer ($(A_{1s}, A_{2s})_{\mathrm{PBD}} = (700, 3.40)$), the method of least squares is applied to all the data for PSt in *Table 3*. The values of (A_1, A_2) are calculated to be (1057, 5.52) from $\bar{M}_n$ and (872, 2.19) from $\bar{M}_w$ where A_1 is expressed in g$^{3/2}$ dl^{-1} mol$^{-1/2}$ and A_2 in g dl^{-1}. To examine the validity of these values by equation (3), two curves of $[\eta]M$ against v were made and are shown in *Figure 3*. The curve obtained from $\bar{M}_n$ fits the plot for universal calibration made for M between 10 000 ($v = 35.0$) and 196 (41.2), using the standard polymer samples. The curve obtained from $\bar{M}_w$ fits the plot for M between 50 000 (32.0) and 196 (41.2). Therefore, the values obtained from $\bar{M}_w$ are better than those from $\bar{M}_n$.

When PSt is used as a standard polymer ($(A_{1s}, A_{2s})_{\mathrm{PSt}} = (990, 0.800)$), the method of least squares is applied to the data for PBD in *Table 2*, using $\bar{M}_w$. The values of A_1 and A_2 are calculated to be (892, 3.22) from the data on the four samples with $\bar{M}_w < 23\,600$, where they satisfy equation (2) (*Figure 2*). From the data on the five samples with $\bar{M}_w < 170\,000$, we obtain $(A_1, A_2) = (444, 0.345)$. Further, we obtain (393, 0.225) from the data on the six samples with $\bar{M}_w < 423\,000$. It is apparent that (A_1, A_2) decrease with increasing M. This shows that the values of (A_1, A_2) become smaller in order to fit equation (2) in the data on the polymer samples with higher

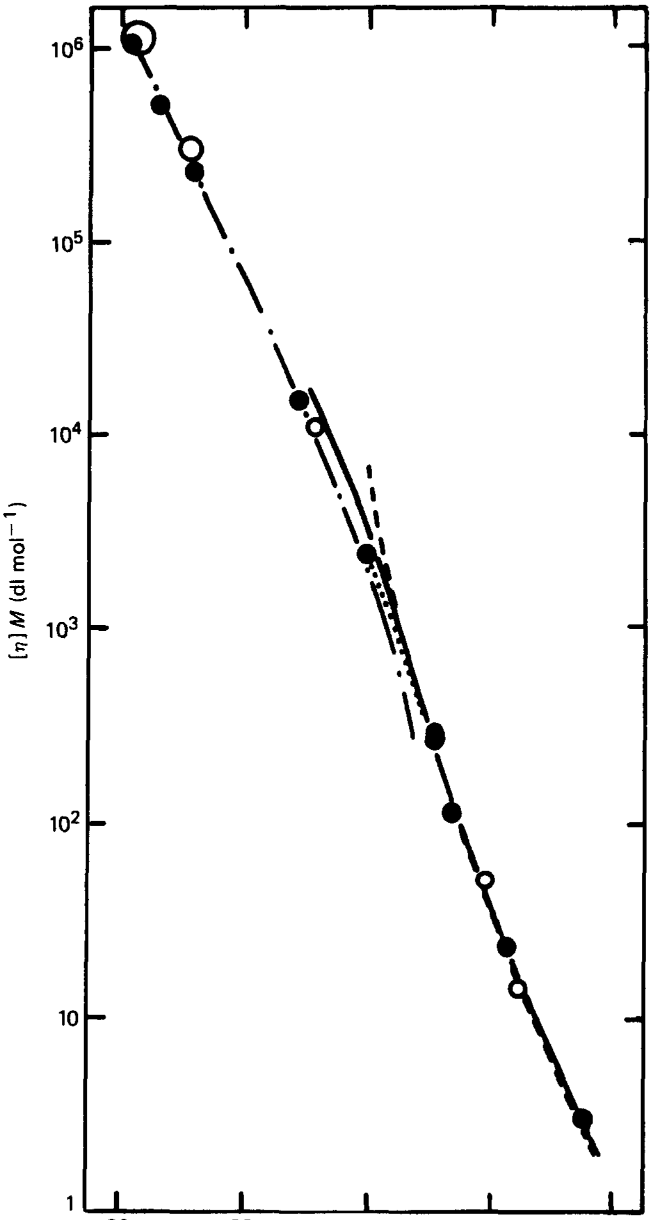

Figure 3 Relationship between $[\eta]M$ and v for PSt: ———, $(A_1, A_2) = (872, 2.19)$; – – –, $(A_1, A_2) = (1057, 5.52)$; –·–·–, $(K, a) = (1.247 \times 10^{-4}$ dl g^{-1}, 0.720); ·····, border curve between the curve made by equation (1) and that by equation (2); ●, universal calibration plot from PSt; ○, universal calibration plot from PBD

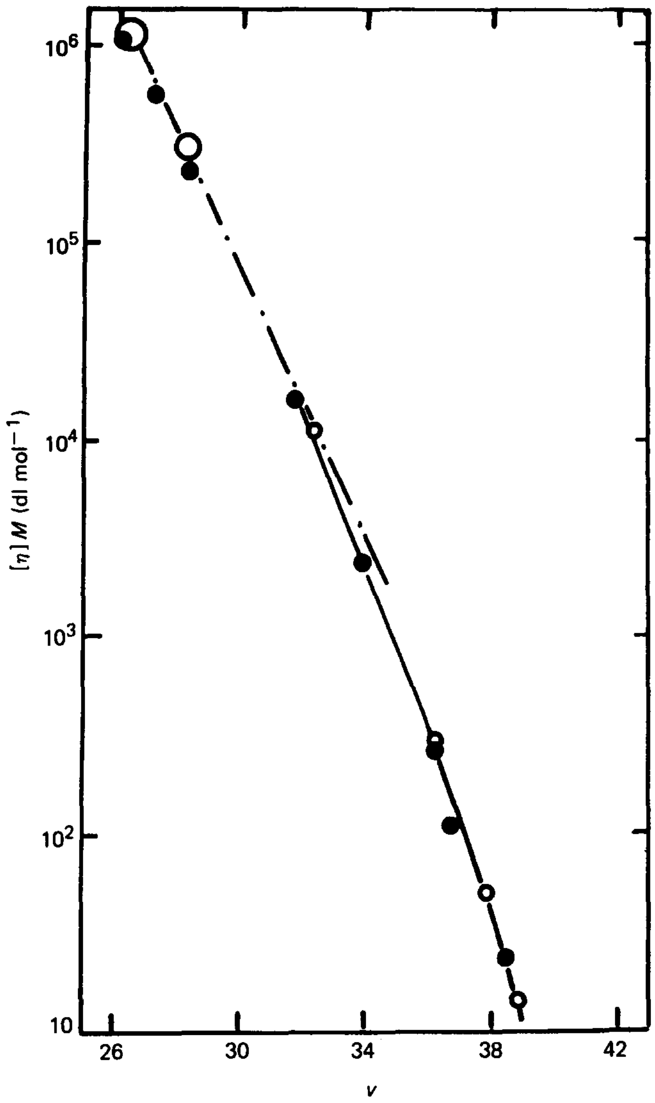

Figure 4 Relationship between $[\eta]M$ and v for PBD: ———, $(A_1, A_2)=(892, 3.22)$; —·—·—, $(K, a)=(1.012\times10^{-3}\,\mathrm{dl\,g^{-1}}, 0.621)$; ●, universal calibration plot from PSt; ○, universal calibration plot from PBD

molecular weights, and is consistent with the result that the curve with $(A_{1s}, A_{2s})_{\mathrm{PBD}} = (700, 3.40)$ deviates from the data on $\bar{M}_w > 170\,000$. Essentially, equation (2) is an empirical formula relating $[\eta]$ to M and the correlation is better when M is lower. It can be understood that (A_1, A_2) are calculated to be the mean values of (A_1, A_2) between the upper and lower limits of the molecular weights of the samples used. Then it is better that the molecular weight of the polymer measured is between the upper and lower limits of the molecular weights of the samples used to determine the values of (A_1, A_2). In the present case, we wish to measure molecular weight below 10 000. Thus we choose $(A_1, A_2) = (892, 3.22)$, which are obtained from the four samples with $\bar{M}_w < 23\,600$. It is shown in *Figure 4* that a $[\eta]M$ against v curve calculated using (892, 3.22) fits the universal calibration plot for $M_w < 23\,600$.

It is concluded that, even if M is so low that K and a depend on M, using equation (2) a calibration curve made from the data on standard polymer samples can be modified into curves to measure molecular weights of the respective polymers. Now we can state that, over the whole range of molecular weight, a calibration curve made from standard polymer samples can be modified into curves to measure molecular weights of the respective polymers by the method of least squares, using equation (1) when M is so large that K and a are invariable and equation (2) when M is so small that they are variable. Two examples are shown in *Figures 3* and *4*: for PSt equation (1) with $(K, a) = 1.247\times10^{-4}\,\mathrm{dl\,g^{-1}}, 0.720)^1$ and equation (2) with $(A_1, A_2) = (872, 2.19)$ are used; for PBD equation (2) with $(A_1, A_2) = (892, 3.22)$ and equation (1) with $(K, a) = (10.12\times10^{-4}\,\mathrm{dl\,g^{-1}}, 0.621)$, calculated from three samples with $\bar{M}_w > 23\,600$ in *Table 2* by the preceding method[1], are used. Both the $[\eta]M$ against v curves obtained fit the universal calibration plot over the whole range of molecular weight.

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NOMENCLATURE

K, a	MHS constants
A_1, A_2	Constants for a polymer
A_{1s}, A_{2s}	Constants for a standard polymer
$[\eta]$	Intrinsic viscosity of a polymer
M	Molecular weight for a polymer with narrow molecular weight distribution
v	Elution volume
N_i	Number of ith species in a polymer
M_i	Molecular weight of ith species in a polymer
M_{si}	Molecular weight of ith species in a standard polymer
w_i	Weight fraction of ith species in a polymer
$\bar{M}_n$	Number-average molecular weight
$\bar{M}_w$	Weight-average molecular weight
m	Number of samples