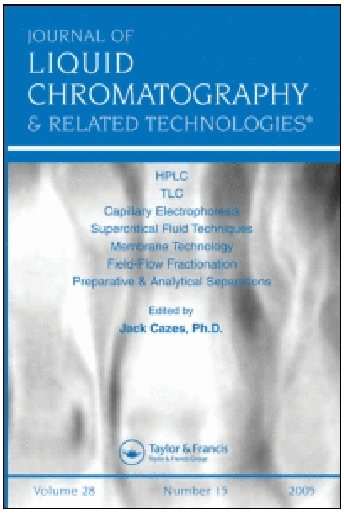

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Molecular Weight Calibration of SEC Using Broad MWD Standards-Application for Poly (P-Methyl Styrene)

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MOLECULAR WEIGHT CALIBRATION OF SEC USING BROAD MWD STANDARDS-APPLICATION FOR POLY (P-METHYL STYRENE)

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ABSTRACT

Broad molecular weight distribution samples of poly (p-methyl styrene) were synthesized using free radical polymerization with thermal initiation over a range of temperatures, 120° - 160°C. The weight-average molecular weights (M_W) of these polymers were measured by low angle laser light scattering photometry (LALLSP) to provide broad MWD standards. Two broad MWD standards were then used to determine the molecular weight calibration curve for poly (p-methyl styrene) using the universal molecular weight calibration curve found using narrow MWD polystyrene standards. SEC was then used to measure the M_W values for the remaining poly (p-methyl styrene) samples. The M_W values by LALLSP and SEC were in excellent agreement confirming the validity of the broad MWD standards calibration method.

INTRODUCTION

Methods of molecular weight calibration using broad MWD standards are of three basic types. Those which employ a broad MWD standard with known molecular weight distribution [1-5]. Those which employ one or more broad MWD standards with known M_N, M_W or $[\eta]$ and assume a linear molecular weight calibration curve [6-9] and finally those which employ one or more broad MWD standards and use the universal molecular weight calibration curve obtained with narrow MWD polystyrene standards [10,11].

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The present investigation makes use of two broad MWD standards and the universal molecular weight calibration curve based on narrow MWD polystyrenes.

THEORY

Let the molecular weight calibration curve for polystyrene be given by

$$M_s = \phi(v) \tag{1}$$

where M_s is the molecular weight of polystyrene and $\phi(v)$ is some arbitrary function of retention volume, v. The universal molecular weight calibration curve can now be given by

$$[\eta]M = K_s\,\phi(v)^{1+a_s} \tag{2}$$

where $[\eta]$ is the intrinsic viscosity, M molecular weight, K_s and a_s are Mark-Houwink constants for polystyrene. The molecular weight calibration curve for a second polymer such as poly (p-methyl styrene) may be expressed as

$$M_x = A\phi^{\beta}(v) \tag{3}$$

where M_x is the molecular weight of the second polymer and

$$A = (K_s/K_x)^{1/(1+a_x)} \tag{4}$$

$$\beta = (1+a_s)/(1+a_x) \tag{5}$$

where K_x and a_x are Mark-Houwink constants for the second polymer.

We now consider a mass concentration detector and assume that either correction for peak broadening is negligible or that the normalized detector response, F(v) has been suitably corrected for broadening. The weight- average molecular weights of 2 broad MWD standards of the second polymer measured by SEC are given by

$$M_{w_1} = A\int_0^\infty F_1(v)\,\phi^{\beta}(v)\,dv \tag{6}$$

$$M_{w_2} = A\int_0^\infty F_2(v)\,\phi^{\beta}(v)\,dv \tag{7}$$

Setting M_{w_1} and M_{w_2} equal to those values already measured by light scattering, we now have 2 equations for the 2 unknowns, A and β. Dividing equation (6) by equation (7) gives

$$M_{w_1}/M_{w_2} = \int_0^\infty F_1(v)\,\phi^\beta(v)\,dv \Big/ \int_0^\infty F_2(v)\,\phi^\beta(v)\,dv \tag{8}$$

A single-variable search will provide β and then a direct calculation using either equation (6) or (7) provides A and thus the calibration curve for the second polymer via equation (3). It should be pointed out that the validity of the molecular weight calibration curve for the second polymer does not depend on the validity of the Mark-Houwink constants for polystyrene. However, the validity of the Mark-Houwink constants for the second polymer (found using equations (4) and (5)) does depend on the validity of the polystyrene Mark-Houwink constants. This is inherent in all previous methods of broad MWD standard calibration [11].

Another approach involving broad MWD standards for calibration is to use 2 broad MWD standards with known intrinsic viscosities. The intrinsic viscosities of 2 broad MWD standards measured by SEC are given by

$$[\eta]_1 = K_x \int_0^\infty F_1(v) M_x^{a_x} dv = A^{a_x} K_x \int_0^\infty F_1(v)\phi^{\beta a_x}(v)dv \tag{9}$$

$$[\eta]_2 = A^{a_x} K_x \int_0^\infty F_2(v)\phi^{\beta a_x}(v)dv \tag{10}$$

Given $[\eta]_1$ and $[\eta]_2$ one can solve for $A^{a_x}K_x$ and βa_x. In this case, where whole polymer intrinsic viscosities are used, the validity of the molecular weight calibration curve does depend on the validity of the polystyrene Mark-Houwink constants. The use of this approach to find Mark-Houwink constants K_x and a_x has the same limitations. A procedure which gives both valid molecular weight calibration curve and Mark-Houwink constants for a polymer follows. For this method, 2 broad MWD standards with known M_w are required to find M_x, the molecular weight calibration curve. A knowledge of $[\eta]$ for these two standards or for any other 2 broad MWD standards would then permit one to find valid K_x and a_x using equations (9) and (10). For this method valid Mark- Houwink constants for polystyrene are not required.

In this investigation, the broad MWD standards method involving two M_w, is thoroughly investigated and then applied in the search for the molecular weight calibration curve for poly (p-methyl styrene). The sensitivity of the method was investigated using theoretical distributions and a linear molecular weight calibration curve for polystyrene. This calibration curve for polystyrene is given by

$$M_s = 2.15*10^{10} \exp(-0.357\ v) \tag{11}$$

Using Mark-Houwink constants ($K_s = 1.11*10^{-2}$ and $a_s = 0.723$) for polystyrene provided the following universal molecular weight calibration curve

$$\ell n([\eta]M) = 36.492 - 0.6151\, v \tag{12}$$

The two broad MWD standards were assumed to have most probable distributions of the form

$$W(M) = M/M^2_N \exp(-M/M_N) \tag{13}$$

Use of the identity

$$W(M)dM = - W(v)dv \tag{14}$$

one can transform this distribution into a SEC mass concentration detector response as follows

$$W(v) = D^2{}_1 D_2 \exp(-2\, D_2 v) \exp(-(D_1/M_N)\exp(-D_2 v))/M^2_N \tag{15}$$

where

$$M(v) = D_1 \exp(-D_2 v) \tag{16}$$

is the molecular weight calibration curve for the second polymer. After choosing Mark-Houwink constants for the second polymer, one can evaluate D_1 and D_2 using equation (12). To investigate the sensitivity of the method, various Mark-Houwink constants and M_N values were used for the second polymer. It should be noted that $M_w = 2M_N$ for polymers having the most probable distribution. In the computer simulation of sensitivity of the method, two detector responses of the form given by equation (15) were used.

RESULTS AND DISCUSSION

The results of the investigation of sensitivity using computer simulation are shown in Tables 1 and 2.

Figures 1-3 show the chromatograms or detector responses for the cases investigated in Table 1. The recoveries of the Mark-Houwink constants, K_x and a_x for the two methods using pairs of M_w or $[\eta]$ are equivalent and satisfactory when the chromatograms for the standards are not near to overlapping. For the Mw pairs, ($4.0*10^{-5}$, $5.4*10^5$) and ($4.0*10^5$, $4.4*10^5$), the exponent a_x recovered is satisfactory, however, the pre-exponential factor K_x is significantly larger than the true value which is $1.54*10^{-2}$. Errors in the measured detector responses and in M_w and $[\eta]$

TABLE 1

Sensitivity of two broad MWD standards method of calibration found by computer simulation

$K_x = 1.540*10^{-2}$ and $a_x = 0.650$

M_{w_1}	$[\eta]_1$	M_{w_2}	$[\eta]_2$	K_x	a_x
$3.2*10^5$	55.2	$6.8*10^5$	90.1		
X		X		$1.581*10^{-2}$	0.649
	X		X	$1.514*10^{-2}$	0.651
$1.2*10^5$	29.2	$1.20*10^6$	130.0		
X		X		$1.576*10^{-2}$	0.649
	X		X	$1.547*10^{-2}$	0.649
$4.0*10^5$		$5.4*10^5$		$1.614*10^{-2}$	0.647
$4.0*10^5$		$4.4*10^5$		$1.624*10^{-2}$	0.647

TABLE 2

Sensitivity of two broad MWD standards method of calibration found by computer simulation

$K_x = 0.800*10^{-2}$ and $a_x = 0.740$

M_{w_1}	M_{w_2}	K_x	a_x
$3.20*10^5$	$6.80*10^5$	$0.801*10^{-2}$	0.740
$4.0*10^5$	$4.4*10^5$	$0.825*10^{-2}$	0.738
$1.20*10^5$	$1.20*10^6$	$0.799*10^{-2}$	0.740

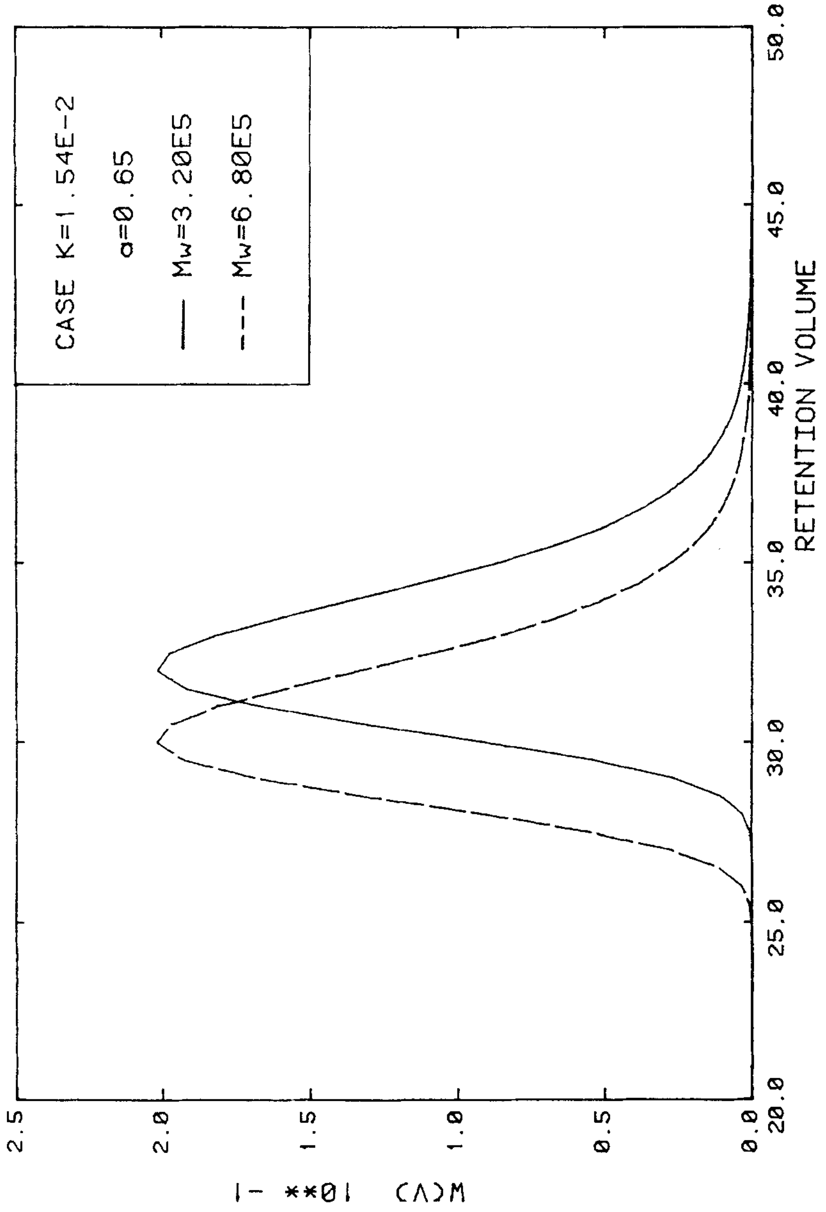
CASE K=1.54E-2
a=0.65
Mw=3.20E5
Mw=6.80E5
W(V) 10** -1
RETENTION VOLUME
2.5
2.0
1.5
1.0
0.5
0.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0

FIGURE 1

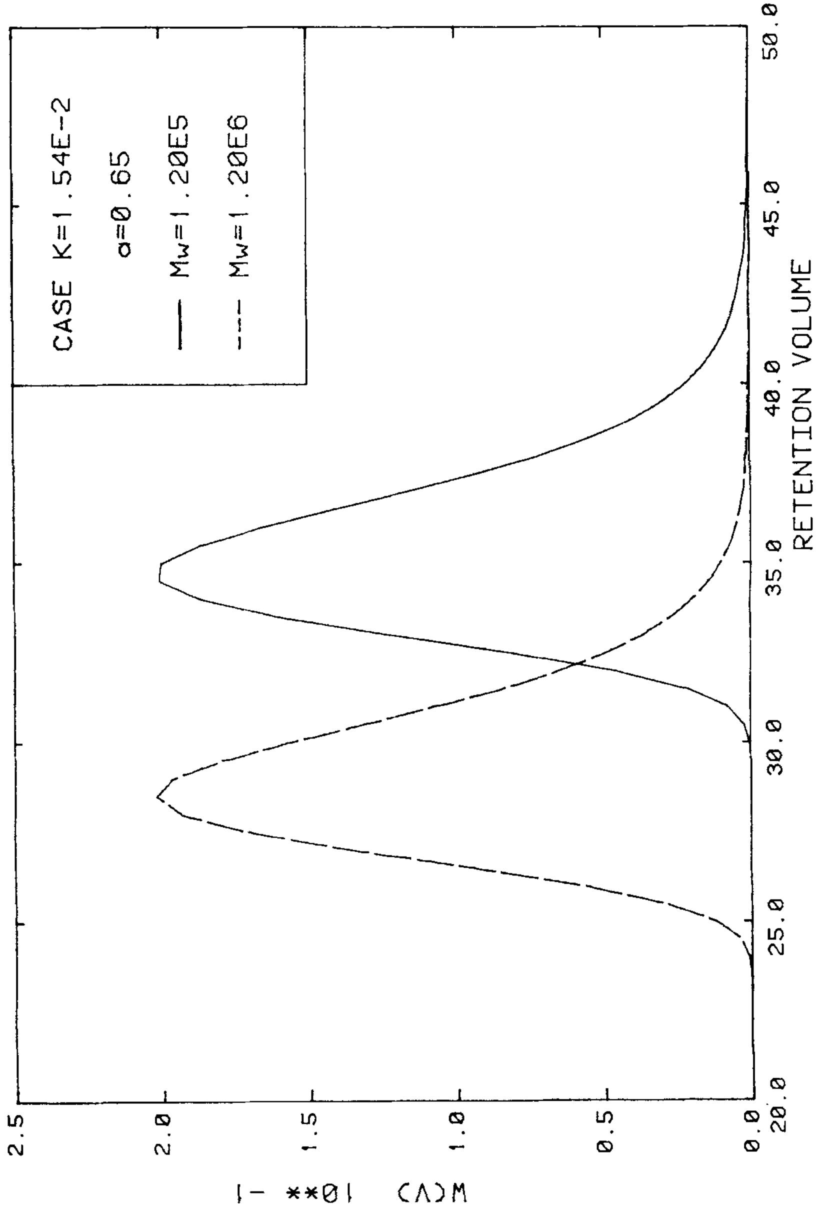
CASE K=1.54E-2
a=0.65
Mw=1.20E5
Mw=1.20E6
RETENTION VOLUME
W(V) 10** -1
0.0
0.5
1.0
1.5
2.0
2.5
20.0
25.0
30.0
35.0
40.0
45.0
50.0

FIGURE 2

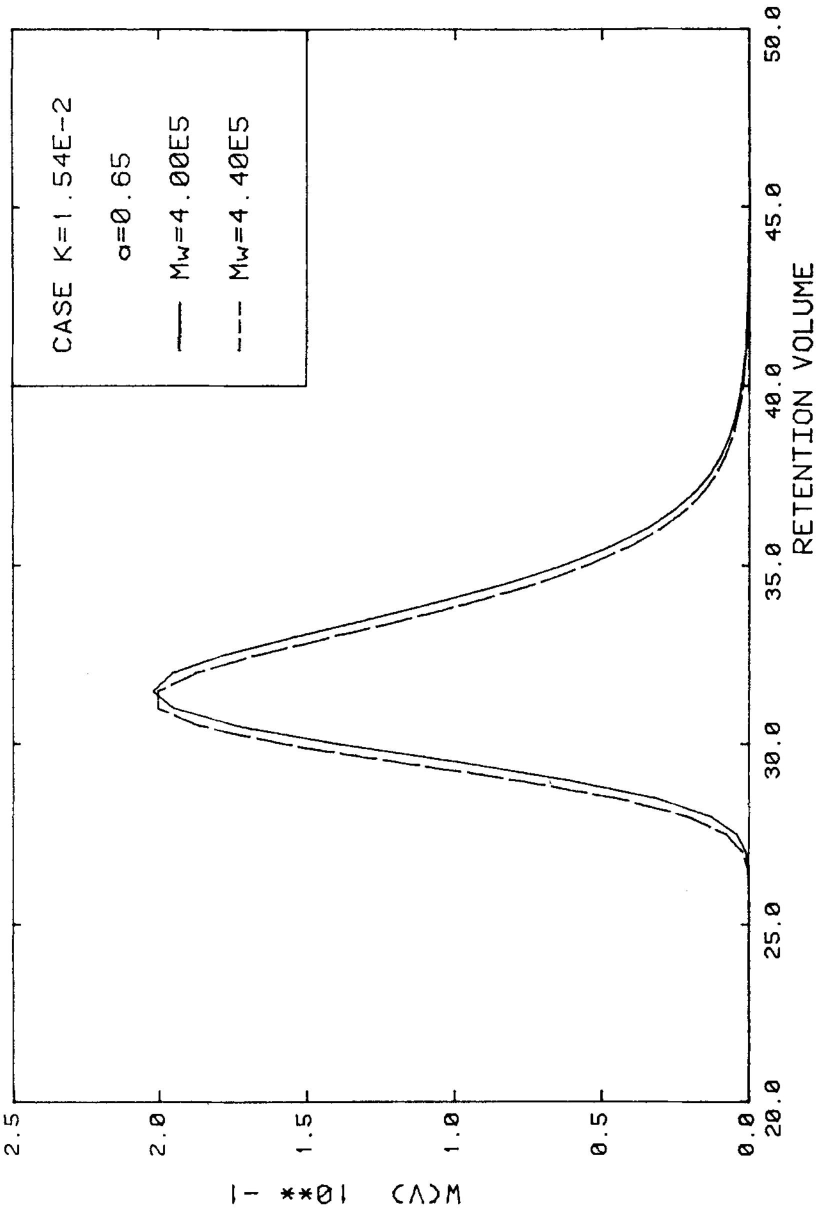
CASE K=1.54E-2
a=0.65
Mw=4.00E5
Mw=4.40E5
RETENTION VOLUME
20.0
25.0
30.0
35.0
40.0
45.0
50.0
W(V) 10** -1
0.0
0.5
1.0
1.5
2.0
2.5

FIGURE 3

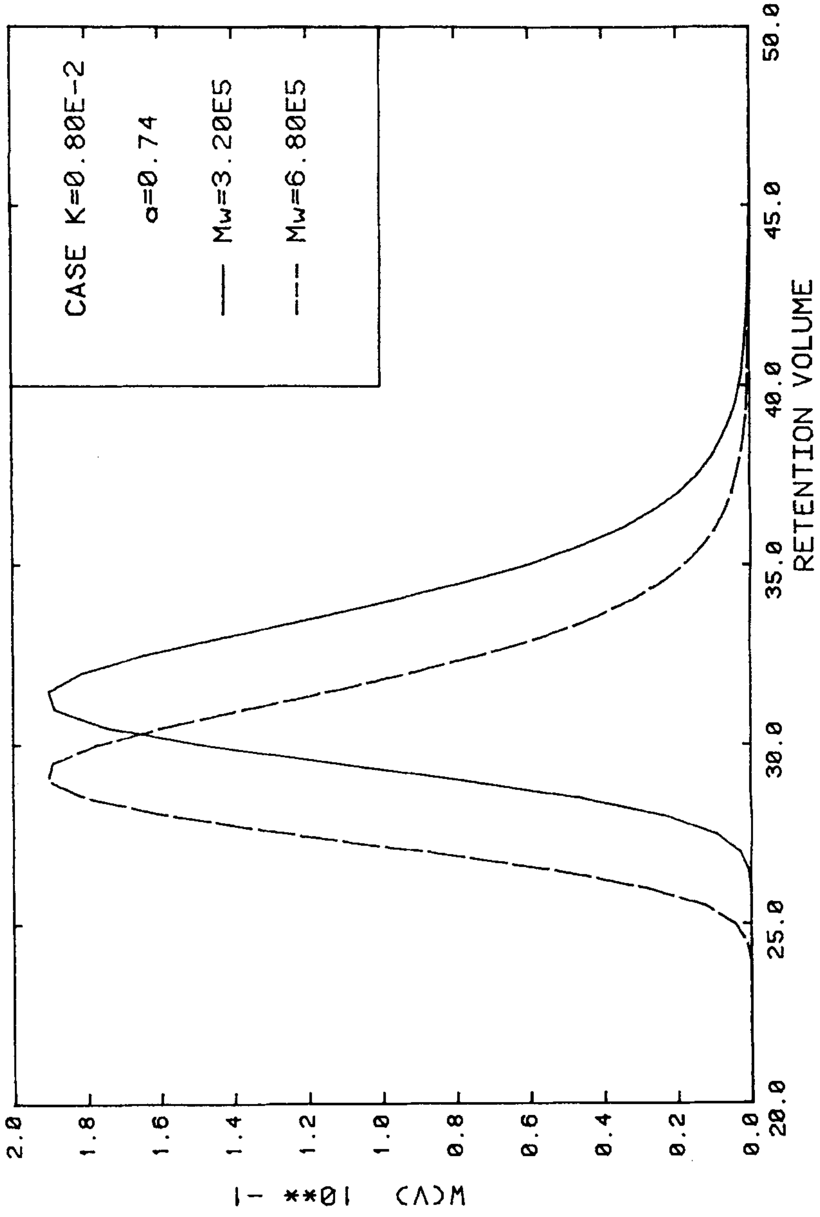
CASE K=0.80E-2
a=0.74
— Mw=3.20E5
--- Mw=6.80E5
W(V) 10** -1
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
RETENTION VOLUME

FIGURE 4

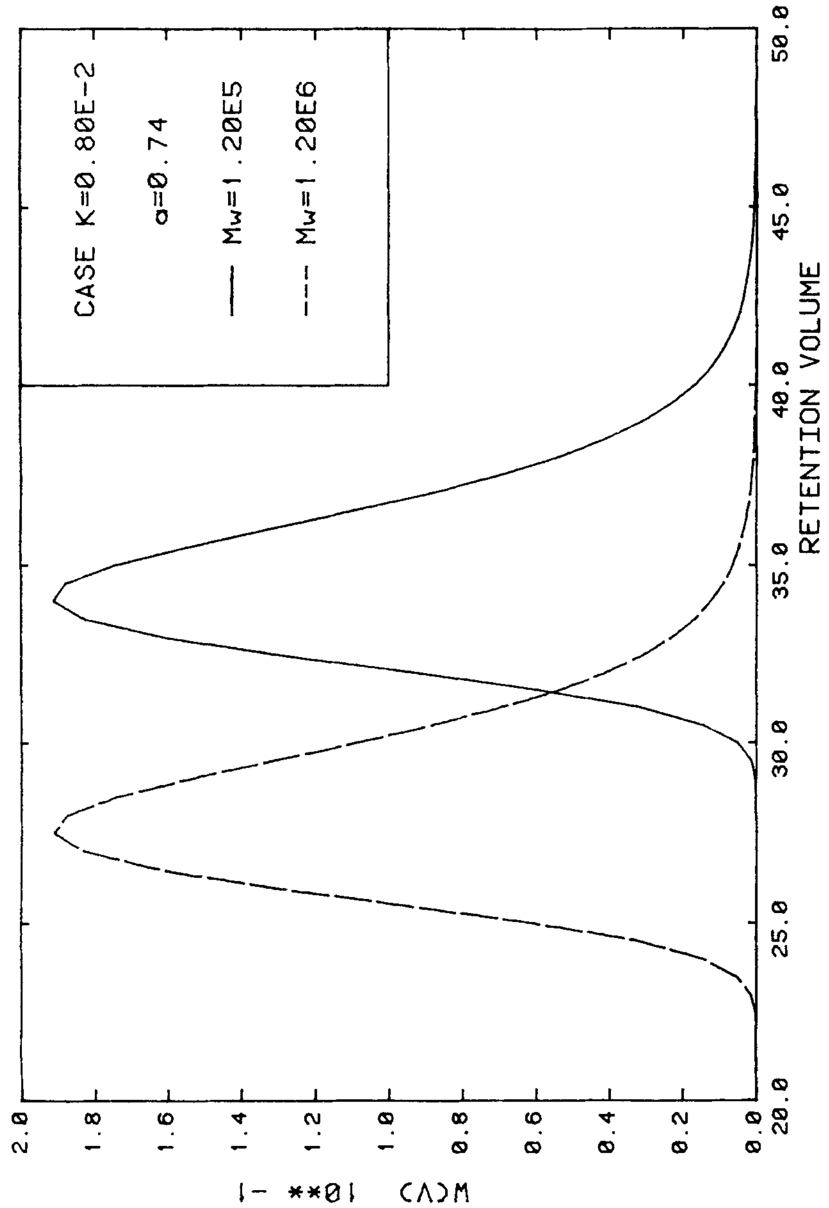
CASE K=0.80E-2
a=0.74
Mw=1.20E5
Mw=1.20E6
W(V) 10** -1
RETENTION VOLUME
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0

FIGURE 5

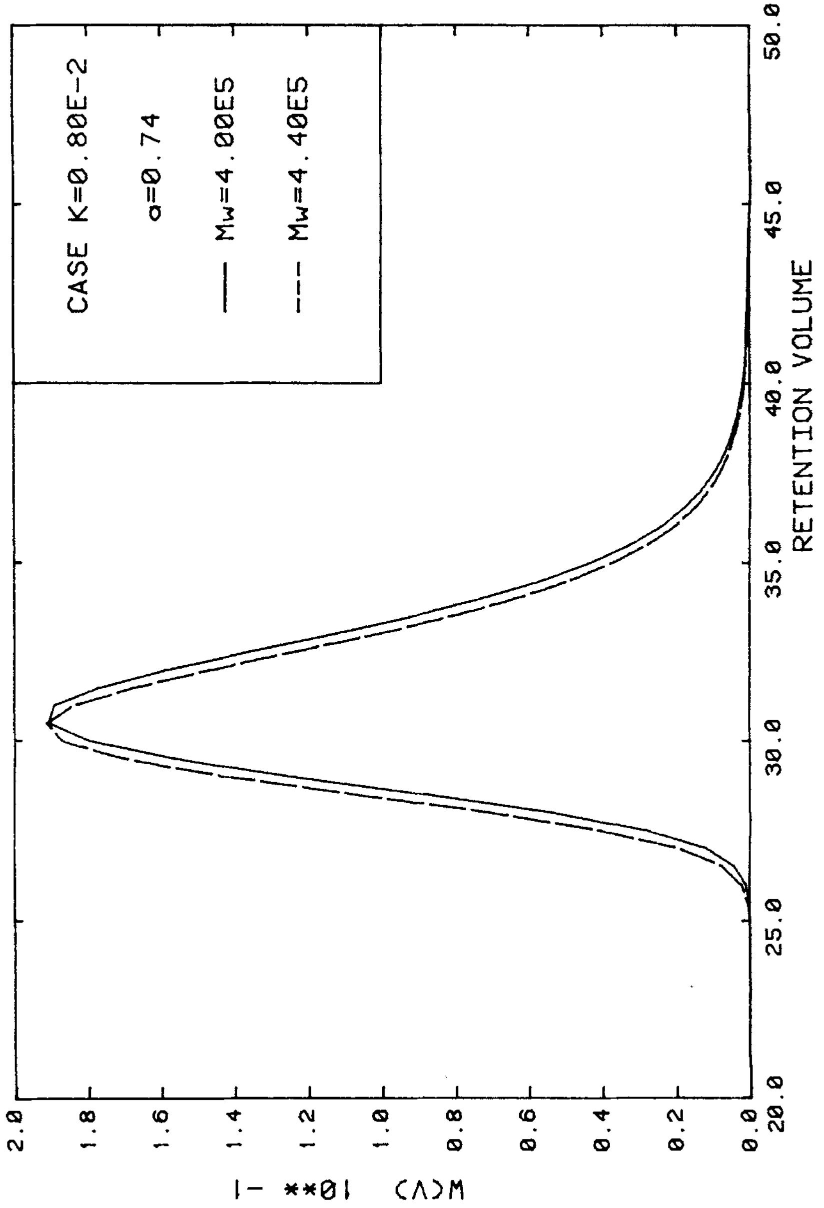
CASE K=0.80E-2
a=0.74
Mw=4.00E5
Mw=4.40E5
RETENTION VOLUME
20.0
25.0
30.0
35.0
40.0
45.0
50.0
W(V) 10** -1
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

FIGURE 6

TABLE 3

Sensitivity of two broad MWD standards method of calibration to peak broadening found by computer simulation - same corrections to both M_w (M_{w_1} = 3.2*10^5, M_{w_2} = 6.8*10^5).

K_x = 1.540*10^{-2} and a_x = 0.650

Peak Broadening Correction (% M_w)	K_x	a_x
0	1.581*10^{-2}	0.649
2	1.640*10^{-2}	0.649
4	1.754*10^{-2}	0.649
10	2.652*10^{-2}	0.649

TABLE 4

Sensitivity of two broad MWD standards method of calibration to peak broadening found by computer somulation - different corrections for each M_w (M_{w_1} = 3.2*10^5, M_{w_2} = 6.8*10^5) 2% correction for M_{w_2})

K_x = 1.540*10^{-2} and a_x = 0.650

Peak Broadening Correction (% M_{w_1})	K_x	a_x
2	1.640*10^{-2}	0.649
4	5.568*10^{-2}	0.559
10	11.70*10^{-2}	0.168

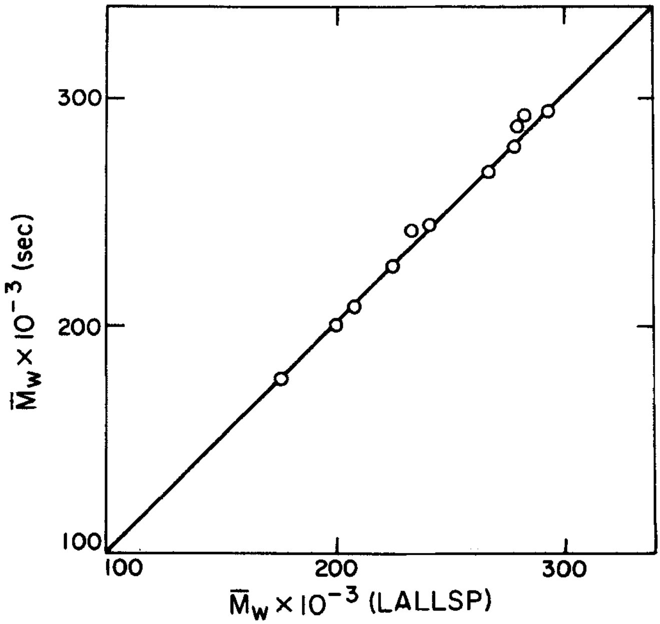

FIGURE 7

values would also be greatly magnified when the two standards are near to overlapping.

In Table 2, results are shown for a polymer whose Mark-Houwink constants are close to those for polystyrene. These results are about the same as those for a polymer whose K_x and a_x are significantly different than those for polystyrene and the same conclusions can be drawn. The chromatograms for these cases are shown in Figures 4-6.

The effect of peak broadening on the recovered Mark-Houwink constants K_x and a_x has also been investigated and the results are given in Tables 3 and 4.

The results in Tables 3 and 4 clearly show the significant effect on recovered K_x and a_x of small corrections for peak broadening. A correction of only 4% to M_w has a large effect on K_x and if the corrections to both M_w are small but different (2% to M_{w_2} and 4% to M_{w_1}) the errors in K_x and a_x are greatly magnified. It is clear that broad MWD standards calibration is very sensitive to peak broadening and if the method is to be effective careful steps should be taken to minimize peak broadening experimentally or to properly correct detector responses for broadening.

To show that the two broad MWD standards method involving an M_w pair is valid, M_w values for eleven poly (p-methyl styrene) samples synthesized thermally at low conversions were measured by low angle laser light scattering photometry (LALLSP) and by SEC. The molecular weight calibration curve for poly (p-methyl styrene) was found using two of the polymer samples as broad MWD standards with known M_{w_1} and M_{w_2}. This molecular weight calibration curve was then used to measure M_w by SEC for the remaining poly (p-methyl styrene) samples. The M_w values found by SEC and LALLSP are compared in Figure 7. The agreement is excellent confirming the validity of the broad MWD standards calibration method.

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