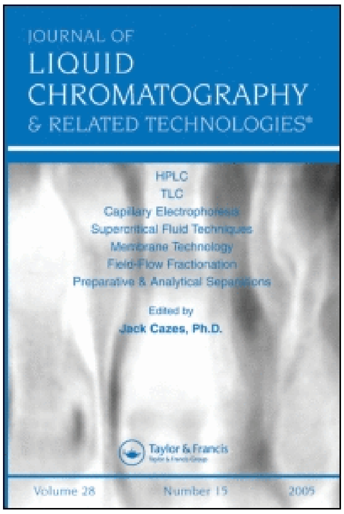

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Conversion Factors for Polystyrene Molecular Weight into Molecular Weights of Polymethacrylates in Size Exclusion Chromatography

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CONVERSION FACTORS FOR POLYSTYRENE MOLECULAR WEIGHT INTO MOLECULAR WEIGHTS OF POLYMETHACRYLATES IN SIZE EXCLUSION CHROMATOGRAPHY

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ABSTRACT

Relationships of molecular weights between polystyrene (PS) and several polymethacrylates, poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(butyl methacrylate) (PBMA), poly(isobutyl methacrylate) (PIBMA), and poly(lauryl methacrylate) (PLMA), were examined. A conversion equation,

$$M_{\mathrm{polymethacrylate}} = sM_{\mathrm{PS}}^{t}$$

was first defined, where s and t are constants, and M_{ps} and $M_{\mathrm{polymethacrylate}}$ are molecular weights of these polymers at the same retention volume. Conversion factors s and t for these polymethacrylates were estimated by using a PS calibration curve and corresponding polymethacrylates having broad molecular weight distributions. Pairs of s and t are as follows: 0.362 and 1.107 for PMMA; 0.2078 and 1.153 for PEMA; 0.01859 and 1.348 for PBMA; 1.727 and 0.978 for PIBMA; 21.64 and 0.746 for PLMA. These conversion factors are effective in the mobile phase of tetrahydrofuran at room temperature. By knowing these conversion factors and a PS calibration curve, molecular weight averages for these polymethacrylates can be calculated. Calibration curves for these polymers are demonstrated.

INTRODUCTION

The determination of molecular weight averages by size exclusion chromatography (SEC) usually requires the construction of a calibration curve using relatively monodisperse polymers such as a series of polystyrene (PS). Calculation of the molecular weight averages for any polymer species other than the PS standards used for the construction of a calibration curve of a SEC column system requires the transformation of molecular weight in the calibration to that for the specified polymer.

The so-called universal calibration method [1] and the "Q" factor method [2] have been proposed as the transformation techniques. The universal calibration method has wide applicability, however, it requires accurate values of the Mark-Houwink parameters for both the sample and the standard used for the calibration, and also, the sencondary effects between the sample and the gel should not exist when the universal calibration method is applied for [3]. The "Q" factor method has many shortcomings and it should be used with caution. It is recommended that the "Q" factor is determined experimentally in advance [4], and the method can provide fairly accurate results when the Mark-Houwink exponents for both the sample and the standard are identical [5].

Many attempts have been undertaken to construct a calibration curve for each polymer species besides these two techniques. These attempts employ a known set of molecular weight averages of broad molecular weight distribution polymers concerned without any PS standards. Some of the methods used assumed a calibration curve to be linear [6] and others were applied to the third-order polynomial [7]. A method reported by some workers required the use of a calibration curve for the PS standards, the Mark-Houwink parameters for PS, and intrinsic viscosity and average molecular weights for the sample polymer [8,9].

The author has presented a method for preparing a calibration curve for a sample polymer where only broad molecular weight distribution samples were available [10]. The method requires only a calibration curve of retention volume vs log molecular weight for the PS standards and does not need any universal calibration concepts. Therefore, the method can be applied to a system where some secondary effects are observed [3].

In the present report, the method has been applied to poly (methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly (butyl methacrylate) (PBMA), poly (isobutyl methacrylate) (PIBMA), and poly(lauryl methacrylate) (PLMA), and calibration curves for these polymers were constructed. Conversion factors of molecular weights from PS to these polymers have been estimated.

EXPERIMENTAL

Apparatus.

SEC measurements were performed on a high-performance liquid chromatograph Model TRIROTAR (Japan Spectroscopic Co., Ltd., Hatioji, Tokyo 192, Japan) with a differential refractometer Model SE-51 (Showa Denko Co., Ltd., Minato-ku, Tokyo 105, Japan). The columns used in this experiment were two Gelpak GL-A100M SEC columns (50 cm x 8 mm i.d.) (Hitachi Chemical Co., Hitachi, 317, Japan) packed with PS gels used for polymer fractionation. Columns were thermostated at 30 ^{o}C in an air oven Model TU-100 (Japan Spectroscopic).

Samples.

The primary calibration curve was constructed by determining the peak retention volume of PS standards (Polymer A) obtained from Pressure Chemical Co., Pittsburgh, PA. The characterized polymethacrylates (Polymer B), used in this work and listed in Table 1, were purchased from Arro Laboratories, Inc., Joliet, IL. These samples were polydisperse polymers. Relatively monodisperse

TABLE 1
Molecular Weight Averages of Polymethacrylates having Broad Molecular Weight Distribution

Sample	Molecular weight	
	Weight average	Number average
PMMA	60,600	33,200
PEMA	395,000	144,000
PBMA	320,000	73,500
PIBMA	300,000	140,000
PLMA	113,000	77,000

PMMA samples were purchased from Polymer Laboratories (England) through Showa Denko Co.

Elution.

Tetrahydrofuran (THF) was used as the mobile phase and the flow rate was 1.0 ml/min. Sample concentrations were 0.1%(w/v) for PS standards and relatively monodisperse PMMA, and 0.3% for polymethacrylates having a broad molecular weight distribution (MWD) except PLMA which was dissolved in THF in 0.5% concentration. The injection volume for these sample solutions was 0.2 ml.

Calculation.

The molecular weight $(M_B)_i$ of a molecule of a polymer B eluted at retention volume i is related to the molecular weight $(M_A)_i$ of a molecule of a polymer A eluting at the same retention volume i by the expression

$$(M_B)_i = s(M_A)_i^t \qquad (1)$$

where s and t represent constants and are defined as conversion factors. Here, a polymer A is PS and molecular weight $(M_A)_i$ of a polymer A at retention volume i is obtained from a PS calibration curve. Molecular weight averages of a polymer B are calculated from the chromatogram of the polymer B by assuming t as follows:

$$(\bar{M}_w)_c = \Sigma(h_i s(M_A)_i^{\,t})/\Sigma h_i$$
$$= s\{\Sigma(h_i(M_A)_i^{\,t})/\Sigma h_i\} \qquad (2)$$

$$(\bar{M}_n)_c = \Sigma h_i/\Sigma(h_i/s(M_A)_i^{\,t})$$
$$= s\{\Sigma h_i/\Sigma(h_i/s(M_A)_i^{\,t})\} \qquad (3)$$

where h_i is the height of the chromatogram at retention volume i.

Then the molecular weight averages of the polymer B are obtained as

$$(\bar{M}_w)_c = s\{\text{numerical value 1}\} \qquad (4)$$
$$(\bar{M}_n)_c = s\{\text{numerical value 2}\} \qquad (5)$$

By comparing $(\bar{M}_w)_c$ and $(\bar{M}_n)_c$ with molecular weight averages in Table 1, we obtain two values of s, which may not be equal in most cases. The calculation process is repeated with other values of t until the value of s of eq 4 becomes nearly equal to the value of s of eq 5. A calibration curve for the polymer B can be constructed from eq 1, a final set of t and s, and a PS calibration curve.

RESULTS AND DISCUSSION

The constants t and s in eq 1, calculated from several polymethacrylates, are shown in Table 2. The values of t increased and those of s decreased with increasing the carbon number of an ester group for PMMA, PEMA, and PBMA, and these relations are reverse among PBMA, PIBMA, and PLMA. Conversion factors for PMMA (narrow) were calculated by constructing a calibration curve using several PMMA (narrow) standards and by plotting several sets of data for log molecular weight of PMMA against log molecular weight of PS at the same retention volume.

The constants obtained from a PMMA sample having a broad molecular weight distribution (MWD) are different from those

TABLE 2
Conversion Factors t and s Obtained from Several Polymethacrylates of Known Melucular Weight Averages

Polymethacrylate	t	s
PMMA (broad)	1.019	0.644
PMMA (narrow)*	1.107	0.362
PEMA	1.153	0.2078
PBMA	1.348	0.01859
PIBMA	0.978	1.727
PLMA	0.746	21.64

* PMMA standards having a narrow MWD.

obtained from PMMA standards having a narrow MWD. Calibration curves of these two sets of the constants are located on the both sides of a PS calibration curve over molecular weight 20000 as shown in Figure 1. Molecular weight relationships between PS and PMMA obtained from a set of Mark-Houwink parameters have been reported as follows [11].

$$M_{PMMA} = 1.410\ M_{PS}^{0.983} \qquad (6)$$

$$1.7\text{x}10^5 < \text{MW range} < 1.3\text{x}10^6$$

or

$$M_{PMMA} = 1.289\ M_{PS}^{1.005} \qquad (7)$$

$$\text{MW range} > 3.1\text{x}10^4$$

and

$$M_{PMMA} = 0.1596\ M_{PS}^{1.213} \qquad (8)$$

$$\text{MW range} < 3.1\text{x}10^4$$

A combination of eqs (7) and (8) has a similar curve to that of PMMA (narrow) standards. The results are also shown in Figure 1. Therefore, the values of s and t obtained from the PMMA

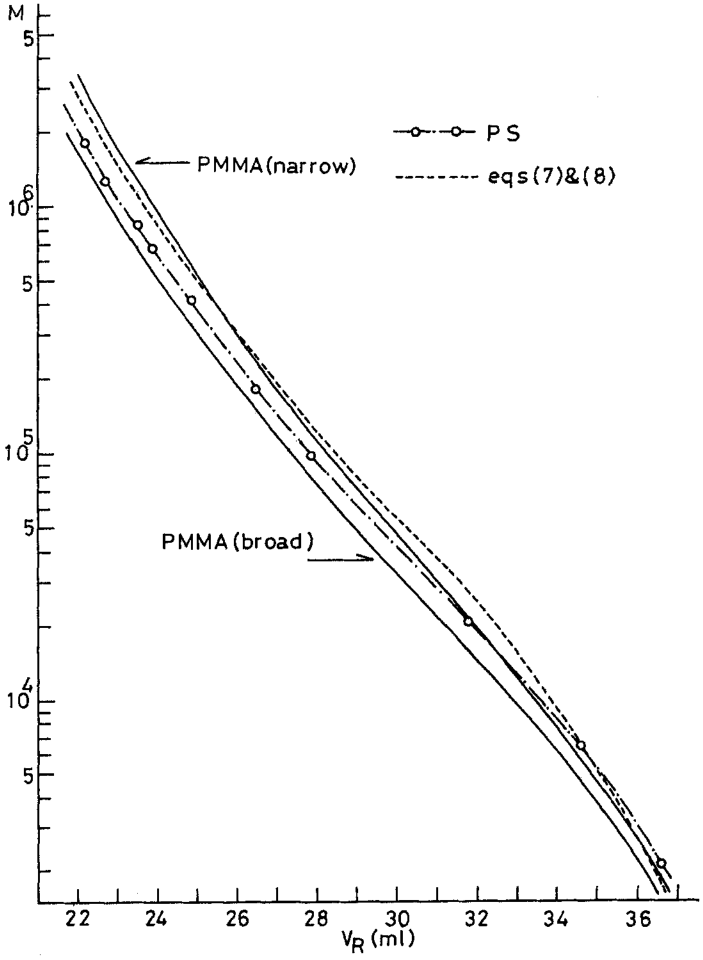

FIGURE 1. Calibration curves for polystyrene, PMMA (broad), PMMA (narrow), and PMMA calculated from eqs (7) and (8).

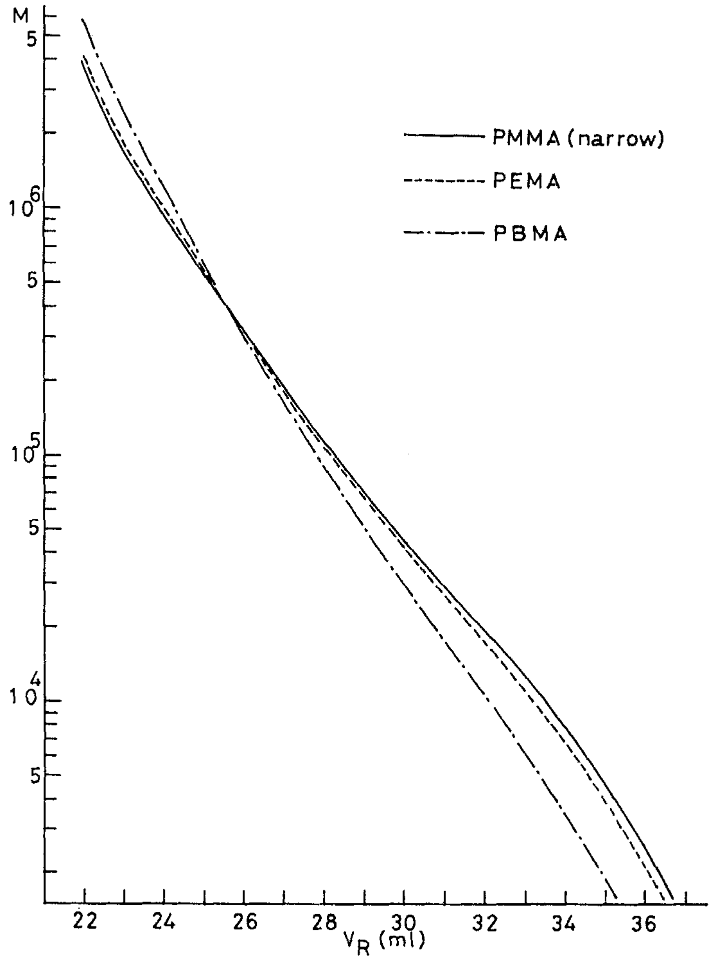

FIGURE 2. Calibration curves for PMMA (narrow), PEMA, and PBMA.

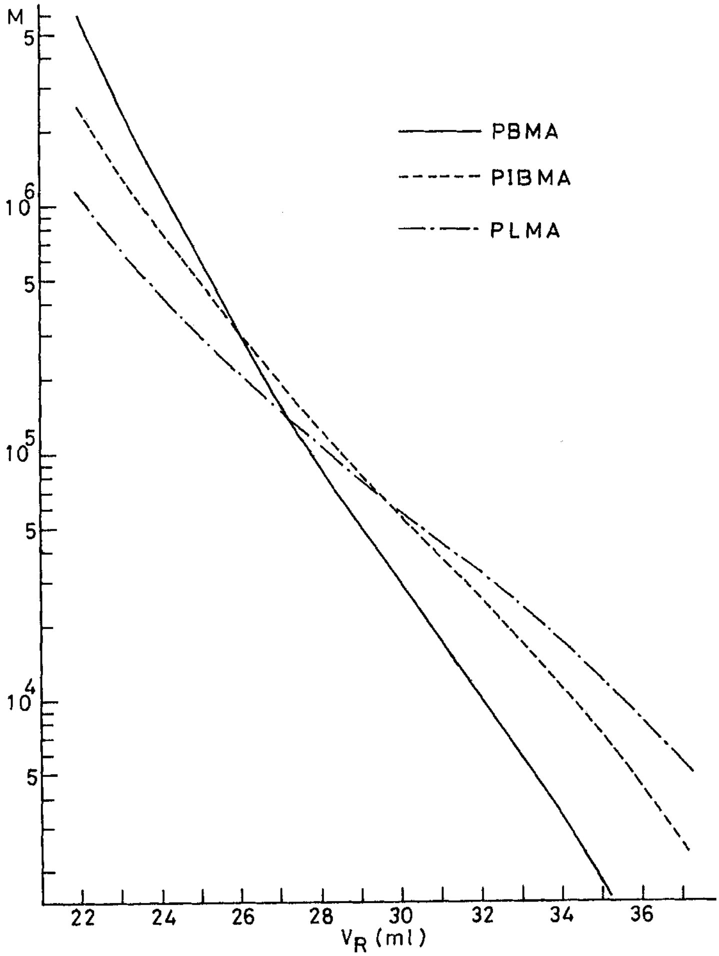

FIGURE 3. Calibration curves for PBMA, PIBMA, and PLMA.

(broad) sample are **shown** as to be incorrect. This is probably due to the incorrect molecular weight averages reported by the manufacturer.

Calibration curves for PMMA (narrow), PEMA, and PBMA are shown in Figure 2. Calibration curves for PMMA (narrow) and PEMA are similar each other. The slope of the calibration curve for PBMA is steeper than others.

Calibration curves for PBMA, PIBMA, and PLMA are shown in Figure 3.

In conclusion, molecular weight averages of PMMA, PEMA, PBMA, PIBMA, and PLMA can be calculated by using eq (1), a PS calibration curve, and corresponding conversion factors in Table 2.

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