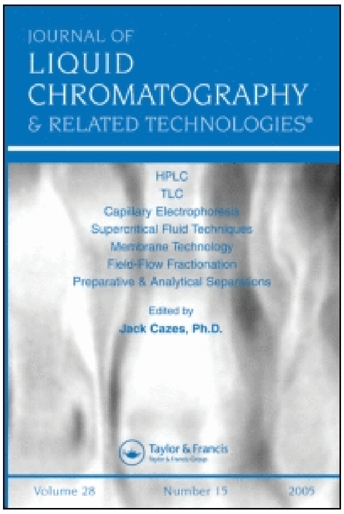

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article De Kok, A. C. and Oomens, A. C.(1982) 'Calibration in High Temperature Gel Permeation Chromatography of Linear Polyethylenes', Journal of Liquid Chromatography & Related Technologies, 5: 5, 807 — 817
To link to this Article: DOI: 10.1080/01483918208060614
URL: http://dx.doi.org/10.1080/01483918208060614

JOURNAL OF LIQUID CHROMATOGRAPHY, 5(5), 807-817 (1982)

CALIBRATION IN HIGH TEMPERATURE GEL PERMEATION CHROMATOGRAPHY OF LINEAR POLYETHYLENES

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ABSTRACT

The mathematical relationship between the gel permeation chromatography calibration curves of polystyrene and linear polyethylene has been determined in 1,2,4-trichlorobenzene at 130, 135 and 140°C. The experimentally determined relationship is in good agreement with that predicted from application of the principles of the universal calibration technique and published Mark-Houwink coefficients. Definition of this relationship enables the use of polystyrene as a secondary standard for gel permeation chromatographic determination of linear polyethylene molecular weight determinations.

INTRODUCTION

In Gel Permeation Chromatography (GPC) the separating columns have to be calibrated using standard samples of known molecular weight of the polymer of interest. Conventionally, this is done by chromatographing narrow distribution standard materials. In non-aqueous GPC, use is almost exclusively made of readily available polystyrene standards covering the molecular weight range from 6×10^2 to 2×10^7.

For the analysis of polyethylene, calibration with monodisperse polyethylene standards is to be preferred. However, narrow distribution standards are commercially available with molecular weights up to 150,000 only. We have overcome this disadvantage by establishing a mathematical relation between the molecular weight of polyethylene and the molecular weight of polystyrene, applicable under standardized analytical conditions.

THEORY

In gel permeation chromatography one often uses a polynomial to fit the calibration curve. In its general form the logarithm of the molecular weight and the elution volume V is selected as function and variable respectively :

$$\log M = A_0 + A_1.V + A_2.V^2 + \;....\; + A_n.V^n \qquad (1)$$

where A_0, A_1, A_2 ....A_n are the coefficients of the n-th order polynomial. These coefficients can be obtained using the method of the least squares[1]. The order of the polynomial applied to fit the calibration curve will of course have an influence on the calculated molecular weight data, as will be demonstrated in this paper (section RESULTS).

If calibration curves can be obtained for two different polymers, i.e. polystyrene (PS) and polyethylene (PE), then the following relations hold for the linear parts of these curves:

$$\log M_{PS} = A_0 + A_1 V_{PS} \qquad (2)$$

$$\log M_{PE} = B_0 + B_1 V_{PE} \qquad (3)$$

at $V_{PS} = V_{PE}$:

$$\frac{\log M_{PS} - A_0}{A_1} = \frac{\log M_{PE} - B_0}{B_1} \qquad (4a)$$

or :

$$M_{PE} = 10^{B_0 - A_0 B_1/A_1} \cdot M_{PS}^{\;B_1/A_1} \qquad (4b)$$

where A_0 and A_1 are intercept and slope of the polystyrene calibration curve and B_0 and B_1 are intercept and slope of the polyethylene calibration curve.

This formula of equation 4b allows calibration of the GPC column with polystyrene standards as secondary standards for gel permeation chromatographic analysis of linear polyethylenes (or another polymer).

MATERIALS

Polystyrene standards for calibration were purchased from Pressure Chemical Co. (Pittsburg, Pa, USA) and Toyo Soda Co., Ltd. (Tokyo, Japan) with nominal molecular weights of 600, 2100, 2500, 2800, 4000, 10000, 20400, 25000, 107000, 110000, 186000, 200000, 422000, 475000, 498000, 670000, 775000, 1.8×10^6, 3.84×10^6, 5.48×10^6, 6.77×10^6, 8.42×10^6 and 20.6×10^6.

Polyethylene standards were purchased from Societé Nationale Elf Aquitaine (Lacq, France), National Bureau of Standards (Washington DC, USA) and Polymer Laboratories Ltd (Church Stretton, UK) with nominal molecular weights of 700, 1000, 2000, 13600, 16200, 32100, 33100, 63600, 96000, 119600 and 161000.

The polyethylene used as a test sample was a linear polyethylene, NBS 1475, obtained from the National Bureau of Standards (Washington DC, USA) with a certified weight average molecular weight (Mw) of 53070 and a number average molecular weight (Mn) of 18310.

Analyses were performed on a M 150C gel permeation chromatograph (Waters Associates, Milford, USA) operating at elevated temperatures (130-140°C); 1,2,4-Trichlorobenzene (TCB, J.T. Baker Chemicals Co, Phillipsburg, NJ, USA) was used as the mobile phase. This mobile phase is spiked with 100 mg/kg 2,6-di-tertiary-butyl-1-hydroxy-4-methylbenzene (Merck, Darmstadt, Germany) as an antioxidant.

The columns were purchased from Toyo Soda Ltd. A series arrangement of two TSK-GEL GMH6 mixed-bed porosities columns was used (120 cm x 3/8").

Data acquisition and calculations were done on-line by means of a 3354 C data system (Hewlett-Packard Corp., Avondale, Pa, USA). A Philips PM 8151 digital plotter (Philips, Eindhoven, the Netherlands) was used for on-line plotting of molecular weight distributions and calibration curves.

METHOD

Polystyrene standards are dissolved at ambient temperature in 1,2,4-trichlorobenzene (0.016 wt %). The solutions are heated to the GPC operating temperature (130-140°C) and 200 µl of each solution is injected onto the columns and the peak retention times are measured. Polyethylene standards are dissolved in 1,2,4-trichlorobenzene at operating temperature (130-140°C) and injected as 0.02 wt % solutions.

RESULTS

Twenty-three monodisperse polystyrene standards were used to characterize the relation between log M and elution volume V on the TSK-GEL GMH6 columns. The data points are illustrated in Figure 1 together with the elution curves of some of the monodisperse polystyrene standards.

Good linearity of the calibration curve was observed in the range from 10^4 to 2×10^6 molecular weight. First to fifth order polynomials were established to fit the data in Figure 1. Precision of the polynomials calculated is listed in Table 1 and evidently the third order polynomial is to be preferred for the applied set of columns as this fit exhibits the best correlation coefficient.

TABLE 1

Curve fit of different polynomials to log M versus V for PS standards on TSK-GEL GMH6

Order	Mean square of residual	Correlation coefficient
1	6.68×10^{-3}	.9848
2	6.61×10^{-3}	.9849
3	1.09×10^{-3}	.9938
4	6.65×10^{-3}	.9848
5	6.67×10^{-3}	.9848

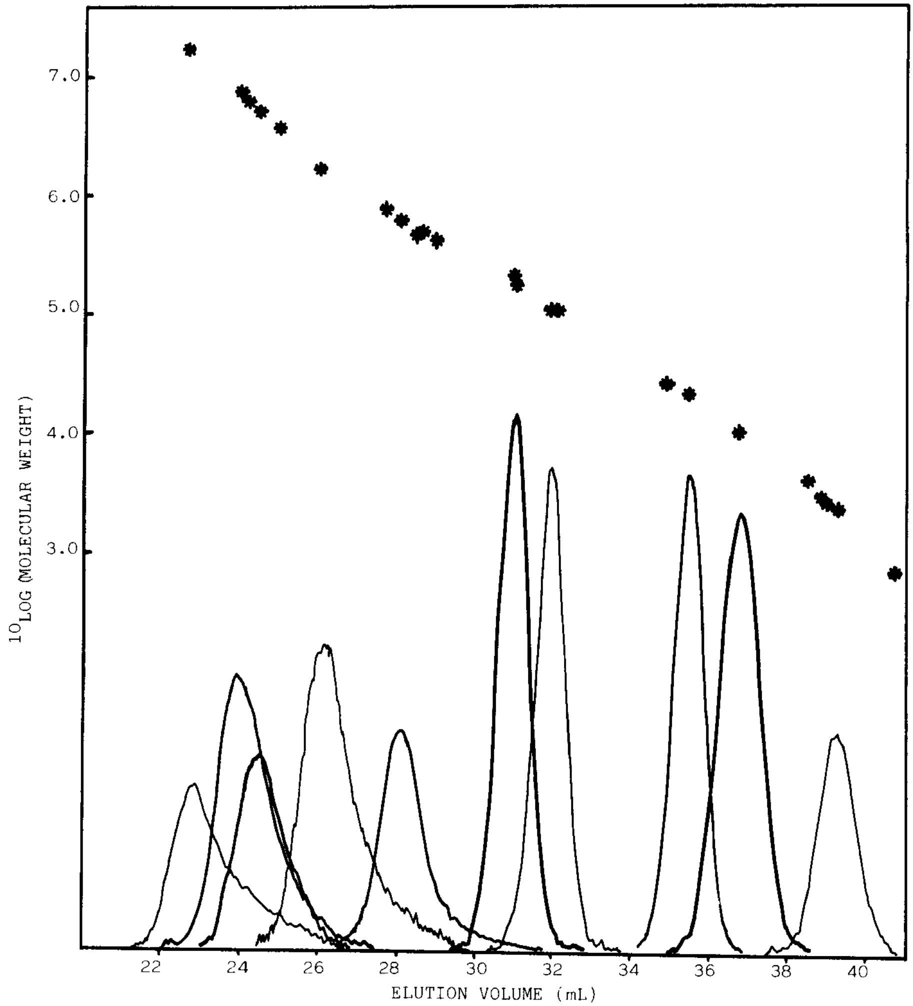

Figure 1 : Elution behaviour of narrow distribution polystyrene standards on TSK-GEL GMH6 columns at 135°C.

The columns were also calibrated with monodisperse polyethylene standards. See Figure 2.

The linear parts of both polystyrene calibration curve (ranging from 10^4 to 2×10^6 Mw) and polyethylene calibration

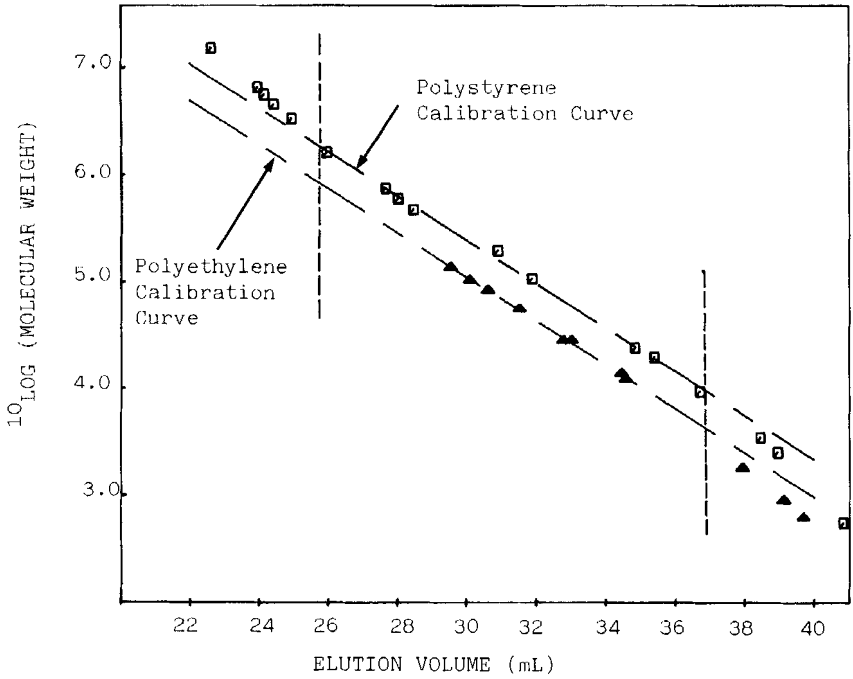

Figure 2 : Calibration curves of PS and PE on TSK-GEL GMH6 columns at 135°C.
PS curve : slope - 0.205746, intercept 11.5838, correlation coefficient 0.994233;
PE curve : slope - 0.206297, intercept 11.2672, correlation coefficient 0.996639.

curve (Mw above 5 x 10^3) were used to establish a molecular weight relationship according to equation 4. This procedure was followed for operating conditions 130°C, 135°C and 140°C with the results indicated in equations 5, 6 and 7 :

at 130°C : $$M_{PE} = 0.42198\ M_{PS}^{1.0091} \tag{5}$$

at 135°C : $$M_{PE} = 0.44914\ M_{PS}^{1.0027} \tag{6}$$

at 140°C : $$M_{PE} = 0.45334\ M_{PS}^{1.0028} \tag{7}$$

It is evident that no significant differences are obtained. However, it is remarked that these equations are only valid for the temperature indicated and when 1,2,4-trichlorobenzene is used as mobile phase. For verification of equation 6 the following experiment has been performed.

Eighteen narrow distribution polystyrene standards ranging from Mw 600 to Mw 20.6 x 10^6 were used for calibration of the columns. These polystyrenes were chosen to cover a molecular weight range which extends the linear part as indicated in Figure 2. The M_{PS} data were converted into M_{PE} data using equation 6 and a third order polynomial was calculated.

Figure 3 shows how close this calculated PE calibration curve matches with the experimental elution data obtained on

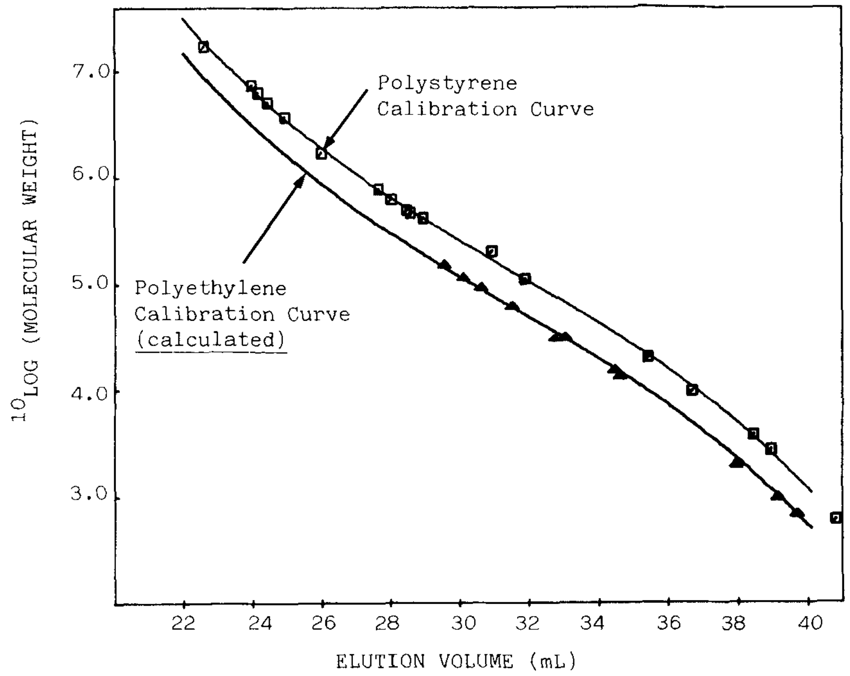

Figure 3 : Fit of narrow distribution PE standards on calculated third-order polynomial PE calibration curve.
□ Monodisperse PS standards elution data
▲ Monodisperse PE standards elution data

TABLE 2

Influence of curve fit technique and derived M_{PS} - M_{PE} relation on calculated Mw values of PE standards

	Mw	Mw	Mw	Mw	Mw
Linear fit	184,800	112,000	66,900	32,500	920
Third order fit	161,500	102,600	64,800	33,900	760
Suppliers' value	161,000	96,000	63,600	33,100	700

TABLE 3

Repeatability and accuracy of NBS 1475 linear PE polymer

Sample	NBS 1475			
Analysis	Mn	Mw	Mz	D
1	18,600	57,300	145,500	3.07
2	19,700	59,000	157,900	2.98
3	17,700	54,000	145,400	3.05
4	18,500	56,400	166,500	3.05
5	18,500	58,100	163,700	3.14
6	18,500	57,100	153,600	3.09
7	18,500	56,700	150,100	3.07
8	17,700	55,900	161,400	3.15
9	18,400	56,100	148,700	3.05
10	18,700	56,900	155,100	3.04
Average	18,500	56,800	154,800	3.07
SD	560	1,340	7,500	0.05
RSD (%)	3.05	2.36	4.84	1.63
CV	18,310	53,070	138,000	2.90

Notes : SD = Standard Deviation, RSD = Relative Standard Deviation
CV = Certified value, D = Dispersivity = Mw/Mn

narrow distribution polyethylene standards, even in the lower molecular weight part of the curve.

Now, the narrow distribution polyethylene standards were treated as samples. Linear and third order polynomial log M_{PE} and V calibration relations were used for the calibration of 5 selected monodisperse PE standard polymers. See Table 2.

The results indicate that serious errors can be introduced when the calibration curve is represented by a linear relationship between log M_{PE} and V.

The accuracy and repeatability were also checked by analyzing ten times the broad molecular weight distribution linear polyethylene standard NBS 1475 (t = 135°C). Results are depicted in Table 3. Our results for both the standards and the reference material are in good agreement with suppliers' and certified values respectively.

DISCUSSION

Using the universal calibration technique[2] together with published Mark-Houwink coefficients for linear polyethylene in TCB, it is possible to calculate relations similar to equations 5, 6 and 7 between the molecular weight of polystyrene and that of polyethylene :

$$M_{PE} = \left[\frac{K_{PS}}{K_{PE}}\right]^{\frac{1}{\alpha_{PE} + 1}} . M_{PS}^{\left[\frac{\alpha_{PS} + 1}{\alpha_{PE} + 1}\right]} \qquad (8)$$

where K_{PE} and α_{PE}, K_{PS} and α_{PS} are the Mark-Houwink coefficients for polymers PE and PS. Substituting the Mark-Houwink coefficients from other references (see Table 4) into equation 8 gives :

for 130°C : $M_{PE} = 0.518\ M_{PS}^{0.992}$ (9)

for 135°C : $M_{PE} = 0.441\ M_{PS}^{0.998}$ (10)

for 140°C : $M_{PE} = 0.654\ M_{PS}^{0.959}$ (11)

TABLE 4

Summary of published Mark-Houwink coefficients in trichlorobenzene

	$K(\times 10^4)$	α	Temperature (°C)
Whitehouse[3]			
Polyethylene	4.95	0.715	130
Polystyrene	1.60	0.702	
Otocka[4]			
Polyethylene	5.10	0.706	135
Polystyrene	1.26	0.702	
Barlow[5]			
Polyethylene	3.95	0.726	140
Polystyrene	1.90	0.655	

Our experimentally determined relation equation 6 matches extremely close with Otocka's result in equation 10. The reason for the difference in scaler and exponent between equations 5 and 9, and between equations 7 and 11 is not known, but is very likely due to the experimental difficulties involved in obtaining K and α values. The influence of differences in scaler and exponent on the final calculated results are illustrated in Table 5. Good agreement is obtained at 130 and 135°C. Considerable deviations occur between equations 7 and 11 (t = 140°C) especially in the higher molecular weight range.

It is shown that the calibration of log M versus V of TSK-GEL GMH6 columns can best be described by means of a third order polynomial relation. This, together with derived equations 5, 6 and 7, makes a reliable determination of the molecular weight averages of linear polyethylene possible using readily available narrow distribution polystyrenes as "secondary standards" for calibration.

TABLE 5

Comparison of data calculated from experimentally obtained M_{PS} - M_{PE} equations and Mark-Houwink derived M_{PS} - M_{PE} equations

Mw (PS)	Calculated Mw (PE)					
	eq. 5	eq. 9	eq. 6	eq. 10	eq. 7	eq. 11
10,000	4,590	4,810	4,600	4,330	4,650	4,480
50,000	23,300	23,750	23,120	21,580	23,400	21,000
100,000	46,900	47,200	46,300	43,100	46,800	40,800
500,000	237,700	233,200	232,700	214,800	235,200	190,900
1,000,000	471,200	463,800	466,200	429,000	468,200	371,200
5,000,000	2,427,900	2,289,300	2,341,200	2,138,000	2,366,750	1,737,400

ACKNOWLEDGEMENTS

The authors are indebted to Steve Martin for his helpful suggestions during preparation of this paper and to Warren Crummett for reviewing of the final manuscript. The Dow Chemical Company is thanked for kind permission to publish this paper.

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