

Gel Permeation Chromatography of Polyethylene. I. Calibration

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Synopsis

An accurate GPC calibration is essential if computer techniques are to be utilized in obtaining the molecular weight distribution and degree of long-chain branching from an intrinsic viscosity and GPC trace of a polymer. The use of the National Bureau of Standards Linear Polyethylene Standard Reference Material, SRM 1475, to calibrate GPC is described. Employing this calibration, the Mark-Houwink relationship for linear polyethylene in 1,2,4-trichlorobenzene was established utilizing narrow molecular weight fractions derived through fractionation of SRM 1475 and other polymers. This Mark-Houwink equation was subsequently employed for the evaluation of high molecular weight fractions which were then used to extend the GPC calibration to the high molecular weight region not covered by SRM 1475. An iterative technique was used to obtain coincidence of the measured intrinsic viscosity and the viscosity calculated from the GPC data. The accuracy of the GPC calibration was demonstrated by obtaining coincidence of the measured and calculated viscosity of high and low molecular weight polymers of both narrow and broad polydispersity.

INTRODUCTION

Gel permeation chromatography (GPC) is probably the most powerful single analytical tool for polymer evaluation available to the polymer chemist. The description of the molecular weight distribution (MWD) derived through the GPC technique for a wide range of polymer types has given valuable insight into the nature of the polymerization process, influence of production variables, and control of end-use properties. The increasing routine use of GPC for resin analysis has borne many fruits, particularly through more sophisticated methods of data handling.^{1,2} However, the GPC process itself only provides a separation of the various molecular species according to their size, and then it is necessary to calibrate each system to provide MWD data. The inability, in practice, to provide consistent and reliable MWD data from instrument to instrument and from time to time is a source of increasing frustration as more detailed use of data is undertaken.

Over the past decade, we have applied the GPC method to analysis of all types of polyethylene products.³⁻⁶ A major part of the effort in developing the technique has been directed toward establishing an effective calibration procedure. An approach has evolved which it is believed will yield the needed consistent and reliable MWD data from any instrument or system of columns providing good molecular separation over the range of molecular weight of interest. The method

involves an initial detailed calibration using the National Bureau of Standards Linear Polyethylene Standard Reference Material, SRM 1475, to cover the low to medium molecular weight region (10^3 to 7×10^5), with high molecular weight fractionated samples to extend the calibration into the higher molecular weight region. A broad-MWD secondary standard is then established and used in routine calibration experiments. Details of the method are given below.

EXPERIMENTAL

Materials

In addition to the NBS material, two other linear polymers were also employed in the calibration procedure. From past experience, the latter were known to have broad polydispersities and exhibited a complete absence of long-chain branching.

Two low molecular weight hydrocarbons, dotriacontane ($C_{32}H_{66}$) and tetra-tetracontane ($C_{44}H_{90}$), having molecular weights of 450 and 618, respectively, were purchased as pure compounds from CHEM SAMP CO (4692 Kenny Road, Columbus, Ohio 43220).

The solvent used throughout all the measurements described in this paper was distilled 1,2,4-trichlorobenzene (TCB). For both convenience and economy, all the TCB solvent is recycled by distilling it under vacuum.

Solution Viscosity

Solution viscosities were measured at 140°C in modified Ubbelohde viscometers; automatic timing devices accurate to 0.01 sec were used to measure the solvent and solution flow times. The polymer was dissolved in TCB, a 0.1% solution being employed to determine the inherent viscosity. It was found, for the linear polyethylene fractions, that below 1.2 dl/g inherent and intrinsic viscosity values are indistinguishable. Above this value, Martin's single point determination technique⁷ was employed to calculate the intrinsic viscosity. It was determined that the constant to be used in Martin's method applied to linear polyethylene in TCB at 140°C is 0.294.

Fractionation

The three linear polymers were fractionated using both the gradient elution column technique³ and the preparative GPC procedure.⁸ In utilizing the gradient elution method, polymer (10 g) was loaded on the Chromosorb-P column packing by cooling from hot xylene solution. A continuous exponential solvent gradient was employed at 115°C with 70:30 and 20:80 mixtures of xylene and ethylene glycol monoethyl ether as solvent and nonsolvent, respectively. Aliquots, 400 ml each, of the column effluent were collected and the polymer was precipitated in acetone, filtered, and dried.

The preparative GPC was equipped with three Waters preparative-scale GPC columns packed with Styragel having porosities of (a) mixed $10^2/10^3$ Å, (b) 10^4 Å, and (c) 10^5 Å. The unit was operated at 105°C using xylene as solvent at a flow rate of 40 ml/min. The maximum sample size was 1 g, i.e., 100 cc of a 1%

solution. Normally, 100-ml aliquots of the column eluent were collected, the polymer precipitated with acetone, and the fractions recovered using a Millipore filter.

GPC analysis of fractions obtained from the two preparative techniques indicated that the gradient elution technique provided the narrower-MWD fractions in the medium-low molecular weight region. Preparative GPC proved more effective in providing narrow-MWD fractions in the high molecular weight region.

Gel Permeation Chromatography

Gel permeation chromatography data were obtained using a modified Waters Model 200 GPC instrument equipped with an automatic sample injection system and digital curve translator. Measurements were made using four Styragel packed columns having porosities of 10^4 Å, 10^4 Å, 10^5 Å, and 10^6 Å arranged in order of increasing porosity. Trichlorobenzene at 140°C was used as the solvent; the flow rate was 1 ml/min.

Two minor modifications were made to the basic GPC unit. In order to improve the baseline stability, i.e., long-term drift, the block holding the two photodetector cells was cooled with thermostated water and maintained at a constant 55°C temperature. This also reduced the baseline noise.

The second modification was made to improve the temperature control of the siphon oven. Measurements had shown a 40°C temperature differential existed between the top and bottom of the siphon oven at 135°C ; therefore, a recirculating fan was installed. It was calculated, and shown by experiment, that a 5°C change in siphon temperature would cause a 1% change in retention volume. Consequently, the heating system was changed so that the temperature was controlled through a thermistor detector. This resulted in a marked improvement in elution volume reproducibility.

Derivation of Mark-Houwink Relationships

The linear polyethylene SRM 1475 was fractionated by both the gradient elution technique and preparative GPC in order to provide well-defined, sharp fractions. The solution viscosity of the fractions was measured as described above; the solution was then withdrawn from the viscometer and injected into the GPC. The GPC data for the fractions were analyzed using a calibration based on the MWD provided with SRM 1475 as outlined below. The weight-average molecular weight of each fraction was plotted as a function of intrinsic viscosity. Using these data, the Mark-Houwink coefficients were determined and substituted in the GPC computer program. The data for the fractions were subsequently recomputed to give the viscosity-average molecular weights using the summation

$$M_v = \left(\sum_{i=1}^{\infty} w_i M_i^\alpha \right)^{1/\alpha}$$

and

$$[\eta] = KM_v^\alpha$$

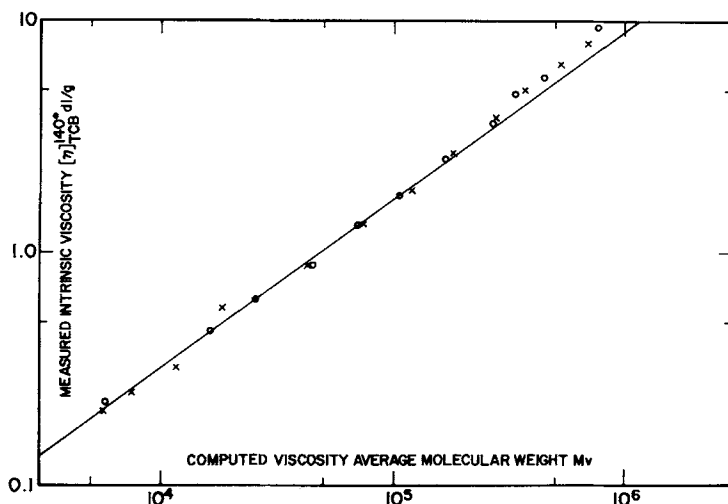


Fig. 1. Mark-Houwink relationship for polyethylene in TCB at 140°C. Also divergence shown by high molecular weight fractions caused by incorrect extrapolation of the initial GPC calibration: (—) Mark-Houwink equation; (O) polymer A; (X) polymer B.

These molecular weights (M_v) were then plotted against the measured viscosities in order to obtain a better estimate of the Mark-Houwink coefficients. This procedure was repeated until no further change occurred in the coefficients, at which time there was also good agreement between the measured and calculated viscosities. The final equation, illustrated in Figure 1, was determined as

$$[\eta] = 3.95 \times 10^{-4} M_v^{0.726}$$

This is in excellent agreement with the relationship of Wagner et al.⁹ for polyethylene in TCB at 135°C, which was determined as part of the derivation of the MWD for SRM 1475. The coefficients of the Mark-Houwink equation established by Otocka¹⁰ and Whitehouse¹¹ in TCB at 135° and 130°C, respectively (Table I), also are in good agreement with the above equation.

CALIBRATION PROCEDURES

A gel permeation chromatograph may be calibrated utilizing either a well-characterized whole polymer having a broad molecular weight distribution or a series of equally well-characterized sharp fractions. In our opinion, the former is preferred since it provides a continuous calibration which may be rapidly ap-

TABLE I
Mark-Houwink Coefficients Determined for Linear Polyethylene
in 1,2,4-Trichlorobenzene^a

Reference	$K \times 10^4$	α
Wagner ⁹	3.92	0.725
Otocka ¹⁰	5.1	0.706
Whitehouse ¹¹	4.95	0.715
This work	3.95	0.726

^a $[\eta]$ Expressed in dl/g.

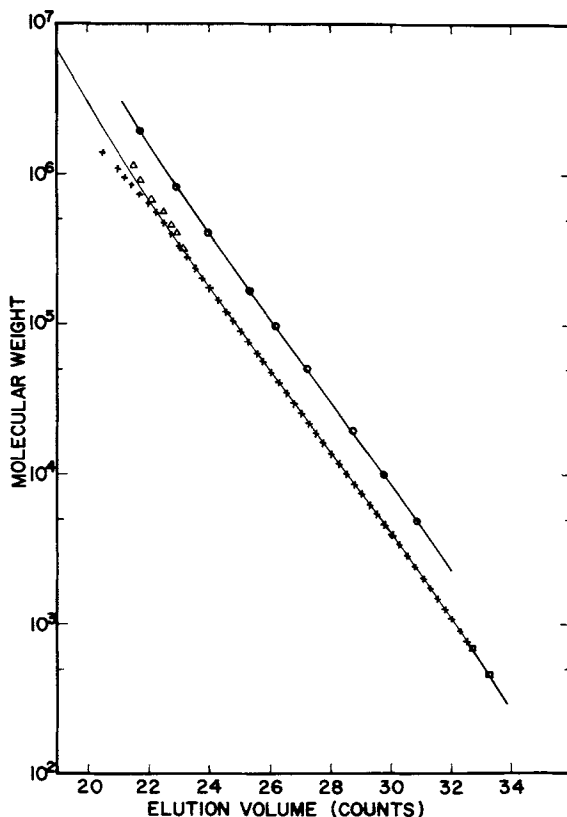


Fig. 2. Molecular weight calibration curves for polystyrene and polyethylene indicating discrepancies which may occur through incorrect extrapolation of the PE curve: (□) low molecular weight compounds; (×) NBS calibration points; (Δ) high molecular weight fractions (M_v); (—) corrected curve (polyethylene); (○) polystyrene standards.

plied and minimizes effects due to axial dispersion and band broadening. Unfortunately, such a broad-MWD standard is not available for polyethylene, and we have combined both methods to obtain a satisfactory calibration utilizing SRM 1475 at the lower molecular weights and fractions at the higher ranges.

Initial Calibration

The initial calibration of the GPC was achieved using the linear polyethylene SRM 1475 which is of known MWD. This was accomplished in the following manner. At least six samples of the polymer, 0.25% concentration, were injected into the GPC and the output was tabulated in the form of elution volume, i.e., count number (C), versus integrated weight percent (I_x). A reading of the differential refractive index (polymer solution concentration, i.e., GPC trace) was taken at every 0.2 counts. The integration was performed using the Schulz-Dinglinger equation

$$I_x = \sum h_n + \frac{1}{2} h_{n+1}$$

Since there were slight variations in the integrated weight at each reading, the averages of the readings were tabulated at each count interval. The information

A combination of the two techniques was finally adopted which, in essence, provides continuous coverage of the extension of the calibration curve with multiple checks of the accuracy. This is accomplished by calculating the viscosity-average molecular weight for each fraction from the intrinsic viscosity and computing it from the GPC data. The calibration curve is then adjusted to obtain coincidence of the two values for all the fractions. The method is described in detail in the following.

The preparative GPC was employed to fractionate two different linear homopolymers, designated A and B, which contain a significant amount of high molecular weight material; that is, more than 10% of the material has a molecular weight $>10^6$. Each resin was fractionated once only, and the fractions were precipitated, dried, and weighed. The integral viscosity distribution curves showed that both fractionations were successful. A number of high molecular weight fractions were obtained in each case. The same solutions at 0.1% concentration, used for the viscosity measurements, were subsequently analyzed by GPC, and the computed viscosity-average molecular weight of the fractions was plotted as a function of the measured intrinsic viscosity (Fig. 1).

It can be seen that, as the molecular weights of the fractions increase, the points diverge from the Mark-Houwink relationship, exhibiting lower molecular weight values. All the lower molecular weight fractions ($<300,000$) have GPC curves which fall within the limits of the NBS standard calibration. As the portion of the GPC curve which is covered by the extrapolated region of the calibration curve increases, the deviation from the Mark-Houwink relationship also increases, showing that the extrapolated calibration curve is in error and underestimates the molecular weight of the samples. This assumes that the linear Mark-Houwink relationship as derived above is realistic.

The calibration was therefore corrected in the following manner. The viscosity-average molecular weight of the fraction was calculated from its intrinsic viscosity using the Mark-Houwink equation. The viscosity-average count number was determined from the GPC data for the fractions. The C_v-M_v points for all the high molecular weight fractions were then calculated from the initial calibration curve (Fig. 2). Utilizing these points to extend the calibration curve

TABLE III
Molecular Weight Data for Fractions of Linear Polymer B

Fraction	M_n $\times 10^{-4}$	M_w $\times 10^{-4}$	R	M_v $\times 10^{-4}$	Viscosity, dl/g	
					Calcd.	Measured
9	48.9	93.3	1.91	86.7	8.05	8.07
13	34.0	67.5	1.98	62.1	6.33	6.48
14	22.0	45.2	2.06	41.6	4.73	5.02
16	17.1	32.5	1.90	29.9	3.72	3.79
18	10.8	20.7	1.92	18.8	2.66	2.71
20	7.4	13.4	1.81	12.2	1.94	1.86
22	4.8	8.0	1.69	7.4	1.35	1.33
24	2.8	4.6	1.64	4.3	0.91	0.87
30	0.73	1.29	1.77	1.18	0.36	0.32
32	0.46	0.83	1.83	0.76	0.26	0.25
Whole polymer	1.84	14.83	8.07	11.09	1.81	1.70

provided by NBS, i.e., integral weight per cent (I_x) versus molecular weight (M), was then employed to obtain the initial elution volume (C)-versus-molecular weight (M) calibration for the GPC. The large number of points thus obtained are used to compute an equation for the calibration curve. In general, a third-degree polynomial has been found to give the best fit, i.e.,

$$\log M = A_0 + A_1C + A_2C^2 + A_3C^3$$

where M = molecular weight; A_0 , A_1 , A_2 , and A_3 are constants; and C is count number. Since the NBS material has a narrow polydispersity, the calibration covers only the 700 to 10^6 molecular weight range (Fig. 2); and, in our opinion, due to uncertainty about the extremes, only the 10^3 to 7×10^5 range is usable. Although too narrow for most commercial polymers, the calibration spans a sufficient breadth of molecular weight to enable us to derive the Mark-Houwink equation as described above and provides an excellent starting point for an extended calibration.

Extension of Calibration

The sample SRM 1475 covers only a narrow range of molecular weights and is therefore limited in its usefulness. In the low molecular weight region, the calibration is readily improved through use of the linear hydrocarbons dotriacontane and tetratetracontane. The main problem is extending the calibration at the high molecular weight end while continuing to maintain the accuracy of the initial calibration over the whole molecular weight range. A purely mathematical extension of the calibration equation is not desirable since it is heavily influenced by any slight discrepancy in the high molecular weight data points of the initial calibration and uncertainty as to the shape of the curve.

The use of sharp high molecular weight fractions to provide count versus molecular weight again places a great deal of reliance on single points. It also demands independent methods of measuring the molecular weight of the fractions, e.g., osmometry and/or light scattering with all their attendant problems.

TABLE II
Molecular Weight Data for Linear Polymer A Fractions

Fraction	M_n $\times 10^{-4}$	M_w $\times 10^{-4}$	R	M_v $\times 10^{-4}$	Viscosity, dl/g	
					Calcd.	Measured
8	54.1	105.1	1.95	97.8	8.79	9.51
10	28.7	54.8	1.91	50.7	5.46	5.76
11	21.5	40.4	1.88	37.2	4.36	4.84
12	18.1	31.1	1.72	28.9	3.63	3.64
14	10.7	18.5	1.73	17.1	2.48	2.59
16	6.93	11.6	1.67	10.7	1.76	1.76
18	4.61	7.52	1.63	6.93	1.29	1.30
20	3.01	4.79	1.59	4.44	0.93	0.87
22	1.72	2.67	1.55	2.50	0.61	0.61
24	1.07	1.76	1.64	1.62	0.45	0.45
28	0.32	0.63	1.94	0.57	0.21	0.24
Whole polymer	1.58	11.79	7.45	8.97	1.55	1.53

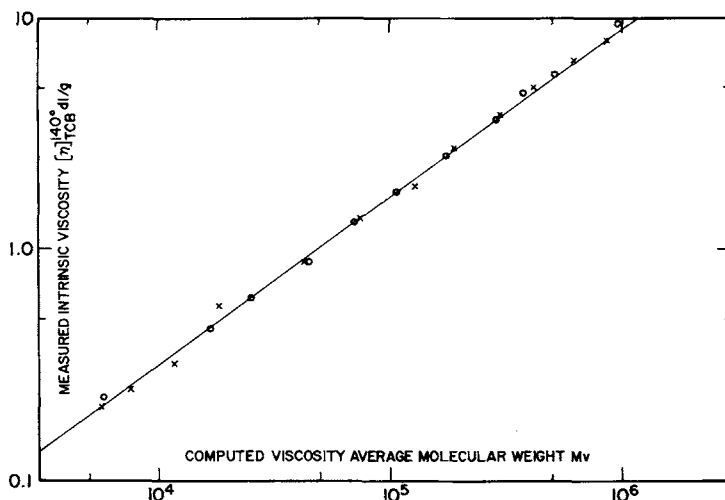


Fig. 3. Mark-Houwink relationship for polyethylene showing coincidence obtained for high molecular weight fractions using the correct extrapolation of the GPC calibration curve: (—) Mark-Houwink equation; (O) polymer A; (X) polymer B.

resulted in an overestimation of the molecular weight of the fractions. In order to counterbalance this tendency, the calibration curve was recalculated including the molecular weights derived using the original calibration curve which corresponded to the viscosity-average count numbers. This procedure was repeated three or four times until no further improvement in the measured and calculated data was obtained. The calibration curve thus derived by the computer is shown in Figure 2. This calibration was checked by analyzing the fractions obtained from linear polymers A and B and comparing the Mark-Houwink relationship thus obtained with that obtained using the NBS fractions. The final results are shown in Tables II and III and plotted in Figure 3.

It can be seen that, with the exception of the very highest molecular weight fraction, the measured and calculated viscosity values for the fractions and whole polymers are within acceptable limits. The changes in the molecular weight averages calculated for the NBS standard caused by the modification of the upper part of the calibration curve are insignificant and within experimental error (Table IV).

The calibration curve thus established covered the molecular weight range of 2×10^2 to 10^7 , i.e., the range of most interest in the polyethylene area. As a

TABLE IV
Effect of Correcting GPC Calibration at High Molecular Weight
End on Molecular Weight Data of NBS Standard SRM 1475

Original calibration			Corrected calibration		
M_n $\times 10^{-4}$	M_w $\times 10^{-4}$	R	M_n $\times 10^{-4}$	M_w $\times 10^{-4}$	R
1.72	5.43	3.16	1.73	5.47	3.16
1.74	5.26	3.02	1.75	5.28	3.01
1.73	5.46	3.15	1.74	5.49	3.15

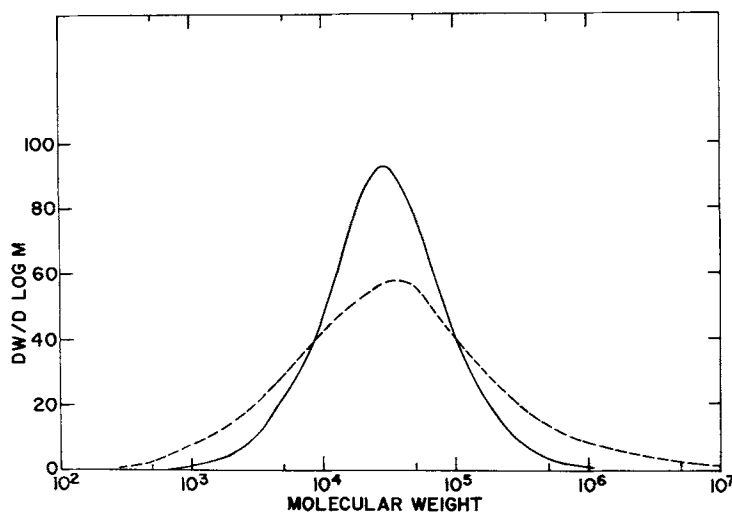


Fig. 4. Comparison of MWD curves for SRM 1475 (—) and Marlex 6009 (- - -).

further check on the accuracy of the calibration, six whole polymers of linear polyethylene varying in molecular weight and polydispersity were examined through solution viscosity and GPC measurements. The results, Table V, showing the excellent agreement between the measured and calculated solution viscosities, confirmed the accuracy of both the calibration and the experimental technique.

Secondary Standard

The calibration curve, which covers a wide molecular weight range, was utilized to establish a secondary calibration standard. The secondary standard enables the calibration to be rapidly checked over the whole molecular weight range on a routine basis and provides a means for calibrating new column systems. The criteria for selecting this polymer were that it was a linear polyethylene, had a broad MWD, i.e., covers the minimum and maximum elution volumes observed for high pressure polyethylenes, and preferably has a symmetric MWD. The polymer Marlex 6009 fulfills these requirements, as is shown in Figure 4 where the MWD curve is compared with that for SRM 1475. To establish Marlex 6009 as the secondary standard, it was subjected to GPC analysis at least six times,

TABLE V
Comparison of Calculated and Measured Solution Viscosities for Linear Polyethylene

Resin	M_n $\times 10^{-4}$	M_w $\times 10^{-4}$	R	Viscosity, dl/g	
				Calcd.	Measured
R	0.97	3.89	4.01	0.75	0.78
S	1.29	6.58	5.11	1.02	1.01
T	1.52	9.93	6.53	1.33	1.26
U	1.62	13.08	8.07	1.62	1.68
V	1.75	18.92	10.81	2.09	2.05
W	0.89	21.16	23.78	2.23	2.34

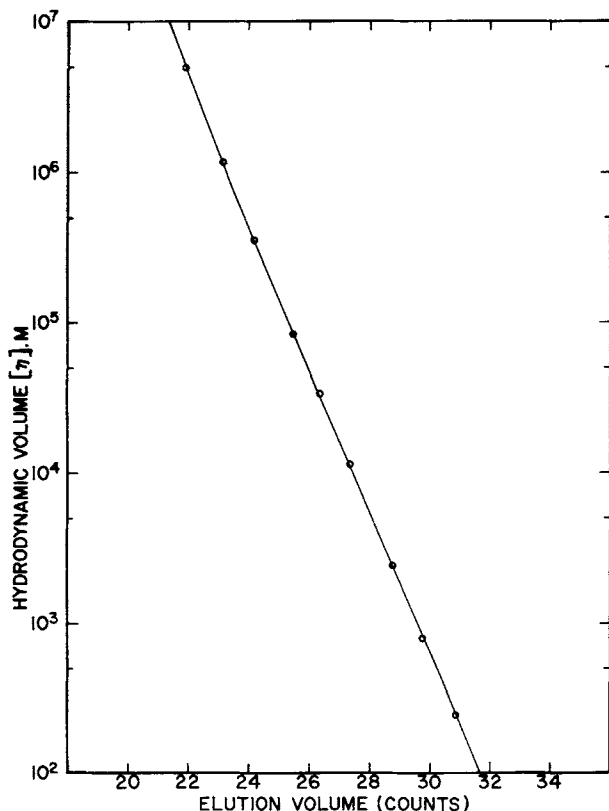


Fig. 5. Universal GPC calibration curve illustrating coincidence of the polyethylene and polystyrene data: calculated universal calibration (PE data) (—); polystyrene data points (O).

and the integral weight (I_x)-versus-molecular weight data were averaged at each elution volume (0.2 count) interval.

Universal Calibration

The universal calibration hypothesis proposed by Benoit¹² has shown itself to be most useful in enabling the GPC calibration established for one polymer to be converted to that for a different polymer system. Its greatest value to us, however, is in enabling one to determine realistic molecular weight data for long-chain branched materials such as low-density polyethylene.⁴⁻⁶ The classical methods of establishing the structural parameters, i.e., molecular weight and long-chain branch index, would inevitably be more time consuming and probably less accurate.

The universal calibration is readily established by combining the Mark-Houwink equation for the polymer-solvent system employed in the GPC with the molecular weight calibration equation of the instrument as shown:
GPC Calibration

$$\log M = A_0 + A_1C + A_2C^2 + A_3C^3$$

Mark-Houwink equation

$$\log [\eta] = \log K + \alpha \log M$$

Universal calibration equation

$$\log [\eta M] = \log K + (1 + \alpha)(A_0 + A_1C + A_2C^2 + A_3C^3)$$

Briefly, the universal calibration hypothesis states that the molecules are separated during GPC on the basis of hydrodynamic volume. As can be seen in Figure 2, the molecular weight calibration curves for polyethylene and polystyrene are quite separate, but coincidence of the hydrodynamic volume ($M\eta$)-versus-elution volume curves for these two polymers (Fig. 5) clearly confirms the accuracy of the concept. The Mark-Houwink coefficients for polystyrene in TCB at 140°C were determined as $K = 1.90 \times 10^{-4}$ and $\alpha = 0.655$, which are in close agreement with Otocka's values.¹⁰

CONCLUSIONS

The data obtained in developing a reliable GPC calibration technique has led to the following conclusions:

(a) The NBS standard reference material SRM 1475 provides a most satisfactory method of calibrating the GPC for the molecular weight range of 10^3 to 7×10^5 .

(b) The calibration may be accurately extended at the high molecular weight end by using suitable fractions and obtaining coincidence of the viscosity-average molecular weights calculated through viscosity measurements and computed from the GPC data for the fractions. This assumes accurate Mark-Houwink coefficients.

(c) A linear polyethylene having a symmetric broad molecular weight distribution provides a useful secondary standard capable of rapidly and routinely verifying the accuracy of a calibration over a wide molecular weight range or calibrating new column sets.

(d) The equations for the GPC calibration and Mark-Houwink relationship are readily combined to provide the universal calibration for the GPC equipment. This allows one to calibrate the GPC for polymers for which it is difficult to obtain standards. Most importantly, it provides a means for analyzing long chain-branched polymers such as low-density polyethylene and obtaining realistic values for the molecular weight averages and long-chain branch index.

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