Gel Permeation Chromatography of Poly(dimethyl siloxane). I. The Universal Calibration

LUMÍR MANDÍK, *Research Institute for Synthetic Resins and Lacquers, Pardubice, Czechoslovakia,* ALENA FOKSOVÁ, *University of Chemical Technology, Pardubice, Czechoslovakia,** and JOSEF FOLTYN, *East-Bohemian Chemical Works, N.E., Kolín, Czechoslovakia*

Synopsis

The Benoit universal calibration method has been tested for evaluation of GPC data of polydimethylsiloxane (PDMS) in toluene at 60°C. For the conversion of the calibration curve for polystyrene to the PDMS calibration curve, the Mark–Houwink equation for PDMS in toluene at 60°C was derived: $[\eta] = 9.77 \times 10^{-5} M^{0.725}$. The applicability of this universal calibration was proved by the experimental results on five PDMS model samples. For the correct evaluation of the PDMS elution curve, the use of the true calibration is inevitable, because the hydrodynamic volume of PDMS molecular weight unit is somewhat different from the polystyrene one.

INTRODUCTION

The evaluation of data obtained by analytical gel permeation chromatography (GPC) of polymers requires a calibration of the chromatographic equipment for the polymer type of interest. The calibration curve is usually expressed by a straight-line function[1]:

$$\log M = A - BV_e \tag{1}$$

where M is the molecular weight of polymer molecule, V_e is the elution volume, and A and B are constants depending on the conditions of chromatographic separation, the polymer type, and the interaction of polymer molecules with solvent. In an ideal case, the calibration curve may be obtained directly by using of a series of polymer fractions[2] with a low degree of polydispersity, μ, defined as weight-average molecular weight $\overline{M}_w$ divided by number-average molecular weight $\overline{M}_n$ ($\mu < 1,1$).

However, in most cases, standards with $\overline{M}_w/\overline{M}_n < 1.1$ may not be available. Present methods for preparative fractionation of polymers are experimentally complicated and consume too much time. The fractions are rather broad and for decreasing of their polydispersity they must be multirefractionated. Fortunately, the narrow molecular weight distribution standards may be obtained by anionic polymerization of styrene. They have polydispersity about 1.02–1.06 and cover a wide molecular weight range from 600 to 10^6. Thus the calibration problem may be simplified on the transformation of the primary calibration curve for polystyrene to the calibration curve of given polymer by using some universal calibration procedure.

The most reliable universal calibration methods have taken into account the true size of the polymer molecule in solution which is affected by the polymer-

* Present address: 28th August Works, N.E., Partizánské, Czechoslovakia.

0021-8995/79/0024-0395$01.00

solvent interaction and by the structure of the polymer chain. In dilute solution, the polymer molecule can be represented as an equivalent hydrodynamic sphere. Its hydrodynamic dimensions are the acceptable parameters for the universal calibration of the GPC column.

Therefore, the perturbed or unperturbed molecular dimensions, as root-mean-square radius of gyration and root-mean-square end-to-end distance, have been suggested for some universal calibration procedures.[2-10] They were found to be satisfactory only if standard and analyzed polymers had very closed polymer-solvent interactions. The other method, known as Benoit universal calibration,[8] has used a plotting log $[\eta]M$ versus elution volume, which is presupposed to be the same for all polymers regardless of their chemical nature and morphological structure. The product $[\eta]M$ is directly proportional to the hydrodynamic volume V_h of polymer molecule defined by the following equation:

$$V_h = [\eta]M/\gamma N_A \qquad (2)$$

where N_A is Avogadro's number, and γ is the Simha parameter[9]; $[\eta]$ is the intrinsic viscosity.

The universal calibration curve is usually a straight line expressed by eq. (3):

$$\log[\eta]M = C - DV_e \qquad (3)$$

The physical meaning of the constants C and D is evident from the eqs. (4) and (5):

$$C = \log K + (a + 1)A \qquad (4)$$

$$D = (a + 1)B \qquad (5)$$

where A and B are the constants in eq. (1), and K and a are constants in the Mark-Houwink equation:

$$[\eta] = KM^a \qquad (6)$$

The constants of the Mark-Houwink equations for some polymers may likewise be found in the literature.[10-12]

The calibration curve for an analyzed polymer can be obtained from the calibration curve of polystyrene by making use of the constants K and a of polystyrene and a given polymer under the conditions of chromatographic separation. The conversion can be carried out with the following equation:

$$\log M_P = \frac{1}{1 + a_P} \log \frac{K_S}{K_P} + \frac{1 + a_S}{1 + a_P} \log M_S \qquad (7)$$

where subscript P refers to the polymer requiring analysis, and subscript S to the standard polymer.

Recently, it was showed that eq. (7) may be also used for transformation of calibration curve for polystyrene to the calibration curve of polydimethylsiloxane. Dawkins[5,13] examined various universal calibration procedures for polydimethylsiloxane fractions and compared the calibration curves of polystyrene and polydimethylsiloxane obtained under the different operational conditions. The experimental polydimethylsiloxane molecular weight–elution volume semilogarithmic plot for chloroform at 30°C was in a close accordance with the same kind of calibration curve for polystyrene. However, the calibration curves

of the two polymers for o-dichlorobenzene at 87 and 138°C were particularly different in the high-molecular-weight range. This may be interpreted by the difference in their hydrodynamic volumes due to unlike flexibilities of the silicone backbone and the basic polystyrene chain and due to different interactions of two polymers with the chromatographic solvents. Therefore, the calibration curve of polystyrene is not acceptable for the evaluation of gel permeation chromatograms of polydimethylsiloxanes.

The most frequently used solvent for GPC analysis of polydimethylsiloxane samples is toluene which is a good solvent for both polystyrene and polydimethylsiloxane. In this article, we report GPC calibration studies made by using the product $[\eta]M$ as the universal calibration parameter and carried out in toluene at 60°C.

EXPERIMENTAL

Materials

Polydimethylsiloxane samples were prepared by anionic polymerization of octamethylcyclotetrasiloxane at temperature about 110°C. For the regulation of molecular weight of a reaction product, the calculated amount of water was added to the reactor at the end step of technological process. The samples were then dissolved in a pure toluene to obtain 10% (w/v) solution from which the polymer was precipitated by addition of 10-times greater volume of methanol. The isolated polymer was dried in vacuum at 60°C.

Polystyrene standards for GPC calibration were supplied by Waters Associates.

Gel Permeation Chromatography

Chromatographic measurements were performed on a Waters Associates Model 200 gel permeation chromatograph with using a set of five Styragel columns designated 7×10^5–5×10^6, 5×10^4–1.5×10^5, 5×10^3–1.5×10^4, 700–2000, and 100 Å. The elution solvent was toluene at 60°C. The flow rate was maintained on 1 cm³/min. A very sensitive differential refractometer was used to indicate polymer concentration in eluate.

The polydimethylsiloxane samples were injected 2 min as a 1% (w/v) solutions in toluene. The polystyrene standard solutions had concentration 0.2% (w/v). They were also injected into the GPC apparatus for 2 min. Elution volume was calculated from the initial point of injection to the appearance of the peak height maximum of the elution curve.

The calculation of number-, weight-, and z-averages of molecular weights, and polydispersities of polydimethylsiloxane samples from the GPC curves was carried out on the IBM 360-40 computer regardless of a zone broadening.

Solution Viscosity

Viscosity measurements were carried out in toluene at 25 and 60°C with Ubbelohde-type viscometers. They were inserted into a 100-liter water bath where the temperature might be kept with the better accuracy than ±0.01°C. Data

at four concentrations (up to 1 g/dl) were extrapolated linearly by the Huggins plot to find intrinsic viscosity. The intrinsic viscosity in toluene at 25–C was used for the determination of the viscosity-average molecular weight $\overline{M}_v$ which was calculated with the relation given by Barry[14]:

$$[\eta] = 2.0 \times 10^{-4}\, \overline{M}_v^{0.66} \tag{8}$$

Membrane Osmometry

The determination of the number-average molecular weights $\overline{M}_n$ of polydimethylsiloxane samples was made on Hewlett-Packard Model 502 high speed membrane osmometer with a membrane of approximately 15,000 molecular weight diffusion limit. Measurements were carried out in toluene at 37°C.

RESULTS AND DISCUSSION

The elution curves of five precipitated samples of polydimethylsiloxane are shown in Figure 1. The number- and viscosity-average molecular weights of these samples are given in Table I. There are also the intrinsic viscosities there obtained from viscosity measurements in toluene at 25 and 60°C. The linear extrapolations of viscosimetric data are shown in Figures 2 and 3.
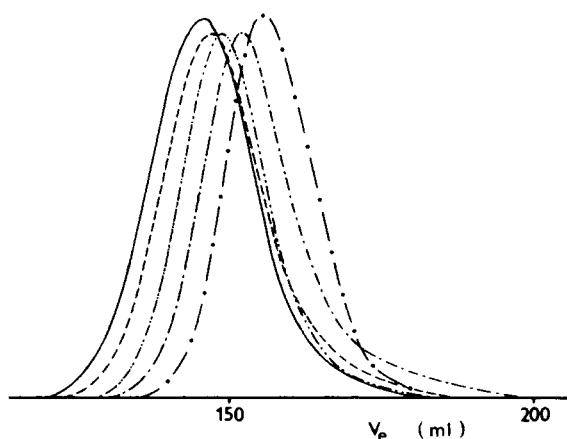

Fig. 1. Elution curves of precipitated samples of polydimethylsiloxane: PDMS-1 (—), PDMS-2 (- - -), PDMS-3 (—-—), PDMS-4 (- . . - . . -), PMDS-5 (— ·).

TABLE I
Experimental Characteristics of Polydimethylsiloxanes

Sample	$[\eta]_{25°C}$ (dl/g)	$\overline{M}_v{}^a$	$\overline{M}_n{}^b$	$[\eta]_{60°C}$ (dl/g)
PDMS-1	0.577	174,850	88,000	0.616
PDMS-2	0.470	128,150	71,000	0.496
PDMS-3	0.382	93,600	54,000	0.390
PDMS-4	0.289	61,330	41,000	0.293
PDMS-5	0.197	34,320	27,600	0.188

[a] Calculated from $[\eta]_{25°C}$ using eq. (8).
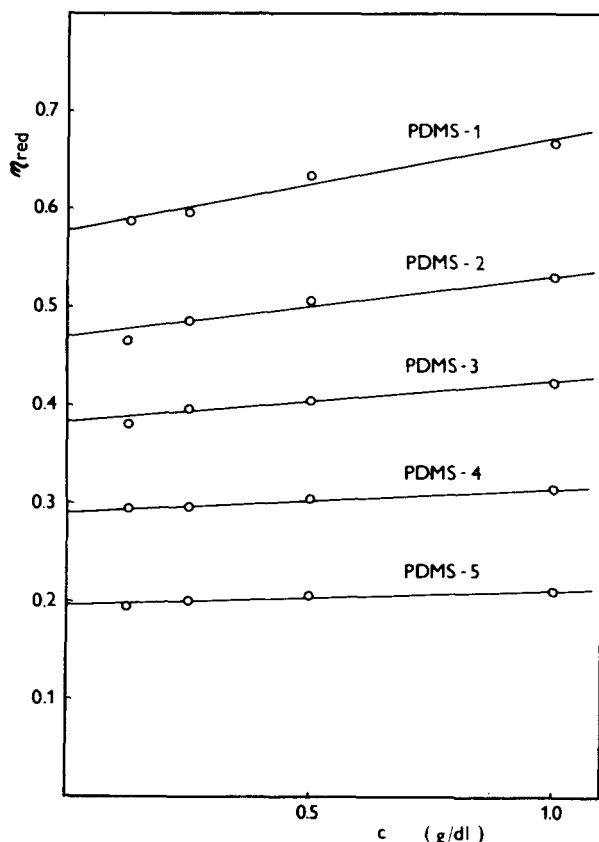[b] Determined by membrane osmometry.

Fig. 2. Concentration dependence of η_{sp}/c of polydimethylsiloxane samples. The determination of the intrinsic viscosities in toluene at 25°C.

The viscosity average molecular weights of polydimethylsiloxanes are calculated with using the eq. (8). This equation was derived empirically from intrinsic viscosities of 13 fractions of polydimethylsiloxane of which molecular weights were determined by membrane osmometry. Therefore, the calculated molecular weights of our samples are lower than values of $\overline{M}_v$ calculated using the other intrinsic viscosity–molecular weight relationships (see Table II). It is quite comprehensible, because eq. (9)

$$[\eta] = 8.28 \times 10^{-5} \, \overline{M}_w^{0.72} \tag{9}$$

was obtained from molecular weights of fractions determined by ultracentrifuge,[15] and eq. (10)

$$[\eta] = 1.87 \times 10^{-4} \, \overline{M}_w^{0.658} \tag{10}$$

was derived from molecular weight data determined by light scattering and sedimentation analysis.[16] However, the use of $\overline{M}_v$ calculated with the Barry relation [eq. (8)] gives the GPC calibration function which makes it possible to obtain $\overline{M}_n$ from the GPC elution curve close enough to the experimental value of $\overline{M}_n$.

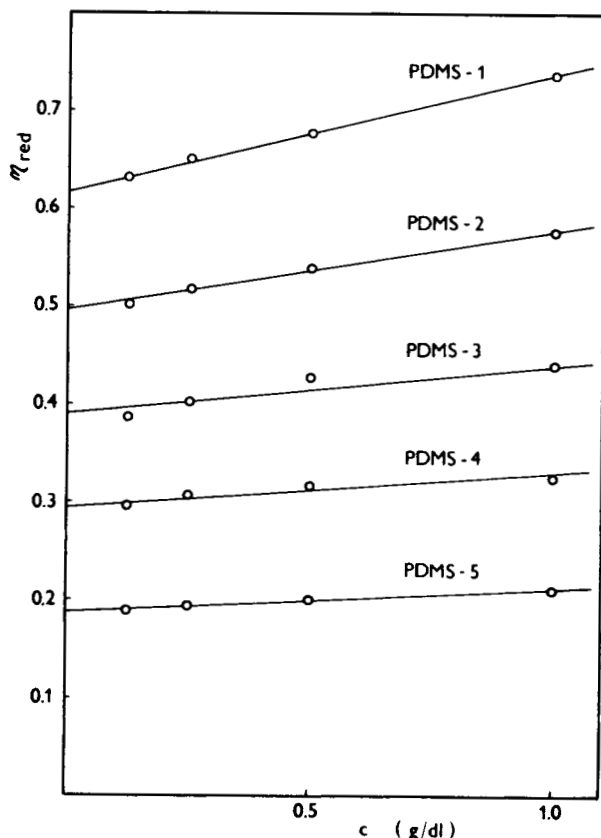The calibration of a column system was carried out with using the Waters

Fig. 3. Concentration dependence of η_{sp}/c of polydimethylsiloxane samples. The determination of the intrinsic viscosities in toluene at 60°C.

TABLE II
Comparison of Values of $\overline{M}_v$ Calculated Using Different Mark-Houwink Equations

Sample	$\overline{M}_v$		
	eq. (8)	eq. (9)	eq. (10)
PDMS-1	174,850	217,650	200,900
PDMS-2	128,150	163,700	147,100
PDMS-3	93,600	122,730	107,340
PDMS-4	61,330	83,300	70,240
PDMS-5	34,320	48,920	39,230

Associates polystyrene standards. Their characterization data are summarized in Table III. The values of intrinsic viscosities in toluene at 60°C were calculated from M_{peak} with the following equation[17] (PS, toluene, 60°C):

$$[\eta] = 7.97 \times 10^{-5} M^{0.75} \tag{11}$$

The calibration curve of polystyrene is shown in Figure 4.

The product $[\eta]M$ was used as a universal calibration parameter to obtain a general molecular weight calibration for any polymer from the calibration data of polystyrene standards. The universal calibration curve is shown in Figure

TABLE III
Some Characteristics of Polystyrene Standards

Standard	$\overline{M}_n$[a]	$\overline{M}_w$[a]	μ	M_{peak}[a]	Elution volume (cm^3)	$[\eta]_{60°C}$ (dl/g)
PS-1	4,600	5,000	1.09	4,800	177.5	0.038
PS-2	19,650	19,850	1.01	19,750	162.0	0.135
PS-3	49,000	51,000	1.04	50,000	153.0	0.283
PS-4	96,200	98,200	1.02	97,200	148.0	0.427
PS-5	164,000	173,000	1.05	171,000	143.5	0.618
PS-6	392,000	411,000	1.05	402,000	134.5	1.293

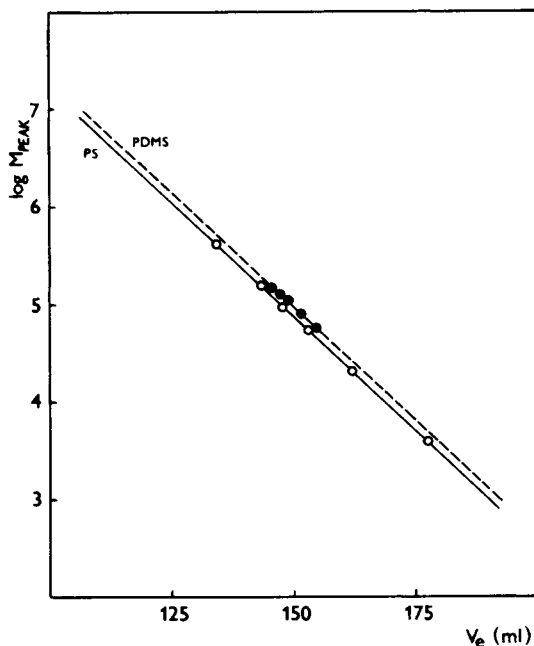[a] Data from Waters Associates designation of samples.

Fig. 4. Calibration curves for polystyrene (O) and polydimethylsiloxane (●).

5. In this curve, there are also the points obtained by plotting the elution volumes of polydimethylsiloxane samples versus $\log[\eta]M$ calculated from experimental values of $[\eta]_{60°C}$ and M_{peak} given in Tables I and V.   It is evident that this universal calibration procedure is excellently valid and may be used for conversion of the polystyrene calibration curve to the calibration curve of polydimethylsiloxane.

For the above mentioned conversion of calibration data, the Mark-Houwink equation for polydimethylsiloxane in toluene at 60°C was derived from $\overline{M}_v$ and $[\eta]_{60°C}$ listed in Table I.   It is given by the following relationship (PDMS, toluene, 60°C):

$$[\eta] = 9.77 \times 10^{-5} M^{0.725} \tag{12}$$

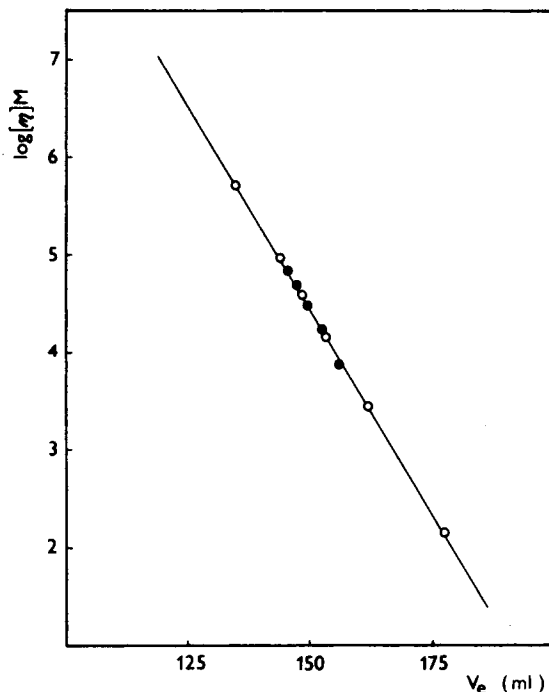The constants from eqs. (11) and (12) were employed in eq. (7) to calculate

Fig. 5. Universal calibration curve. Experimental points for polystyrene (O) and polydimethylsiloxane (●).

the calibration curve for polydimethylsiloxane. This curve is shown in Figure 4 beside the calibration curve of polystyrene. It is seen that the two calibration curves are almost parallel straight lines very near together. Polystyrene and polydimethylsiloxane have very similar interactions with toluene as may be seen from the values of exponents a in eqs. (11) and (12), and also from the comparison of thermodynamic polymer-solvent interaction parameters in toluene at 25°C:

$$\chi_{PS} = 0.44 \text{ (ref. 18)}$$

$$\chi_{PDMS} = 0.465 \text{ (ref. 19)}$$

In this case, the hydrodynamic dimensions of two polymers in used chromatographic solvent are also very near together[11]:

$$[\langle \overline{L_0^2} \rangle^{1/2}/M^{1/2}] \times 10^3 = 670 \pm 20 \text{ Å (for PDMS)}$$

$$[\langle \overline{L_0^2} \rangle^{1/2}/M^{1/2}] \times 10^3 = 700 \pm 15 \text{ Å (for PS)}$$

The ratio of $\langle \overline{L_0^2} \rangle^{1/2}/M^{1/2}$ is a characteristic constant for a polymer chain independent of molecular weight and is expressed in terms of the root-mean-square end-to-end distance of molecular weight unit.

In spite of all that, it is evident that the polydimethylsiloxane chain in toluene at 25 and 60°C is less expanded than the basic carbon chain of polystyrene. Therefore, the polydimethylsiloxane fractions elute later than polystyrene of the same molecular weight, and the calibration curve of polydimethylsiloxane (Fig. 4) is shifted into the range of higher molecular weights. Then the average

values of molecular weights calculated from GPC data with the polydimethyl-siloxane calibration curve are obviously somewhat higher than these obtained from the polystyrene calibration (Table IV).

As shown in Figure 1, elution curves of polydimethylsiloxanes in toluene are symmetrical and have Gaussian shape. Therefore, it is possible to assume that the elution curves can be approximated by the log-normal molecular weight distribution function defined by the following relationship:

$$w_m = (\sigma \sqrt{2\pi} \, \overline{M}_n)^{-1} \exp \{-[\ln(M_m/\overline{M}_n) + \sigma^2/2]^2/2\sigma^2\} \qquad (13)$$

where w_m is a value of the differential distribution function in the point corresponding to the molecular weight M_m and σ is a characteristic of the polydispersity of the sample

$$\sigma^2 = \ln \mu \qquad (14)$$

Average molecular weights are then given by the eqs. (15)–17:

$$\overline{M}_n = M_{\text{peak}} \exp(-\sigma^2/2) \qquad (15)$$

$$\overline{M}_w = M_{\text{peak}} \exp(\sigma^2/2) \qquad (16)$$

$$\overline{M}_v = M_{\text{peak}} \exp(a\sigma^2/2) \qquad (17)$$

TABLE IV
Comparison of Molecular Weight Averages Calculated with Both Polydimethylsiloxane and Polystyrene Calibration Curves

Sample	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	μ	Calibration
PDMS-1	90,500	167,900	273,200	1.86	PDMS
	86,100	156,100	249,800	1.81	PS
PDMS-2	69,000	134,100	218,800	1.94	PDMS
	66,000	125,100	200,500	1.89	PS
PDMS-3	53,000	109,900	167,900	2.07	PDMS
	51,200	103,000	155,200	2.01	PS
PDMS-4	36,850	75,750	114,650	2.05	PDMS
	35,800	71,550	106,900	2.00	PS
PDMS-5	31,100	54,000	81,200	1.74	PDMS
	30,200	51,300	76,100	1.70	PS

TABLE V
Elution Data and Molecular Weights M_{peak} of Polydimethylsiloxane Samples

Sample	Elution volume (cm^3)	$M_{\text{peak}}^{\text{expt}}$ [a]	$(M_{\text{peak}}^{\text{calc.}})_n$ [b]	$(M_{\text{peak}}^{\text{calc.}})_w$ [c]	$M_{\text{peak}}^{\text{os}}$ [d]
PDMS-1	146.10	123,130	123,420	123,110	120,000
PDMS-2	148.40	96,540	96,110	96,270	98,900
PDMS-3	150.60	76,290	76,260	76,380	77,700
PDMS-4	154.00	53,130	52,760	52,905	58,700
PDMS-5	156.50	40,730	41,020	40,940	36,400

[a] Experimental value from peak elution volume.
[b] Calculated from $\overline{M}_n$ (GPC—Table IV).
[c] Calculated from $\overline{M}_w$ (GPC—Table IV).
[d] Calculated from $\overline{M}_n$ determined by membrane osmometry.

where M_{peak} is determined from the elution volume of the peak of elution curve. These data are summarized in Table V.

The molecular weight M_{peak} can be calculated from $\overline{M}_w$ and $\overline{M}_n$ obtained from chromatographic data, and also from $\overline{M}_n$ determined by high-speed membrane osmometry. These calculations are carried out using eqs. (15) and (16), employing the value of σ obtained from GPC data. In Table V, the calculated M_{peak} are compared with the experimental ones. It is evident that this procedure gives excellent agreement between experimental and calculated values of M_{peak}. As expected from earlier works,[5-7] the assumption of log-normal molecular weight distribution of polydimethylsiloxane is quite right.

The above mentioned results prove applicability of universal calibration with the product $[\eta]M$ for conversion of the polystyrene calibration curve to the calibration curve of polydimethylsiloxane. It is clear that for the correct evaluation of the polydimethylsiloxane toluene elution curve, the use of the true calibration relationship for polydimethylsiloxane is inevitable, because the hydrodynamic volume of molecular weight unit of this polymer is somewhat different from the polystyrene one.

References

1. J. C. Moore, *J. Polym. Sci. A*, **2**, 835 (1964).
2. J. V. Dawkins, *Br. Polym. J.*, **4**, 87 (1972).
3. M. J. R. Cantow, R. S. Porter, and J. F. Johnson, *J. Polym. Sci. A-1*, **5**, 987 (1967).
4. K. A. Boni, F. A. Slimers, and P. B. Stickney, *J. Polym. Sci. A-2*, **6**, 1579 (1968).
5. J. V. Dawkins, J. W. Maddock, and D. Coupe, *J. Polym. Sci., A-2*, **8**, 1803 (1970).
6. J. V. Dawkins, *J. Macromol. Sci. B*, **2**, 623 (1968).
7. J. V. Dawkins, and J. W. Maddock, *Eur. Polym. J.*, **7**, 1537 (1971).
8. Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci. B*, **5**, 753 (1967).
9. R. Simha, *J. Phys. Chem.*, **44**, 25 (1940).
10. M. Kurata, and W. H. Stockmayer, *Fortschr. Hochpolym. Forsch.*, **3**, 196 (1963).
11. J. Brandrup, and E. H. Immergut, *Polymer Handbook*, Vol. IV-7 Wiley, New York, 1966.
12. L. Mandík, *Prog. Org. Coatings*, **5**, 131 (1978).
13. J. V. Dawkins, and M. Hemming, *Makromol. Chem.*, **155**, 75 (1972).
14. A. J. Barry, *J. Appl. Phys.*, **17**, 1020 (1946).
15. A. Haug, and G. Meyerhoff, *Makromol. Chem.*, **53**, 91 (1962).
16. J. Brzezinski, Z. Czlonkowska-Kohutnicka, B. Czarnecka, and A. Kornas-Calka, *Eur. Polym. J.*, **9**, 733 (1973).
17. M. Bohdanecký, private communication.
18. M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **44**, 431 (1943).
19. F. P. Price, S. G. Martin, and J. P. Bianchi, *J. Polym. Sci.*, **22**, 49 (1956).