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A Direct GPC Calibration for Low Molecular Weight Polybutadiene, Employing Dual Detectors*

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Summary

The calibration of gel permeation chromatograph (GPC) for a given polymer type is usually done by running well-characterized polymer samples of the same type. The available polystyrene and polyglycol standards with molecular weights below 5000 do not give parallel calibration curves, and the points for polystyrene are not on an extension of the higher-molecular-weight portion of the curve. In order to check the calibration in this low molecular-weight region and to establish an independent curve for polybutadiene, a polybutadiene sample prepared by α-methylstyrene tetramer-Na_2 initiation was chromatographed. In doing this, dual detection was used, consisting of a differential refractometer, and an ultraviolet absorption spectrophotometer.

The UV signal from the spectrophotometer was assumed to represent the tetramer portion of the polymer, and its percentage was calculated at each volume increment, using externally determined response factors. This percentage and the tetramer molecular weight gives the molecular weight of the polymer eluting at each volume increment. After correction for the aromatic portion of the polymer, these data and the points obtained with the polybutadiene standards were found to give a reasonable calibration curve for the entire range. The present paper describes the application of this technique to the examination of low molecular-weight polybutadiene.

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DISCUSSION

The most commonly used standards for calibrating GPC columns are the anionic polystyrenes distributed by Pressure Chemical Company which have been described repeatedly in the literature. While prior work in this laboratory has been largely with polystyrene in the molecular weight range of 100,000 to 2 million, polybutadiene and its copolymers became of interest, particularly material in the lower molecular-weight range from monomer to 20,000.

Figure 1 shows the usual log molecular weight versus elution volume calibration curves. In the higher range of molecular weight the polystyrene (PS) standards and the few polybutadiene (PBD) standards available from Phillips Petroleum Company give smooth, parallel calibration curves separated by about 1½ counts. This relationship would be predicted from the fact that tetrahydrofuran is a good solvent for both polymers.

As there were no polybutadiene standards available below molecular weight 17,000, consideration was given to extending the polybutadiene curve parallel to polystyrene. Low molecular-weight standards are available for the latter polymer. However, when GPC data for these were plotted using their nominal weights, the points made a sharp and unexplainable deviation from the rest of the calibration curve. The question arose as to the advisability of using this wandering curve for polystyrene much less for polybutadiene. That polyglycol standards which are available gave a smooth curve through this region suggested that something was wrong.

Dual detectors for styrene–butadiene copolymers had been used for some time when a sample labeled polybutadiene was received which gave a response at 260 mμ in the UV (Fig. 2). On investigation, it was found that this sample was one of the α-methylstyrene tetramer-Na_2 initiated polymers described by Dennis (*1*). This meant that each molecule contained one tetramer unit besides the butadiene chains of varying length. At low molecular weight, the aromatic portion becomes greater in spite of the decreasing total signal.

It was evident that with the proper calibration, this sample would provide a continuous polybutadiene molecular-weight calibration for the GPC columns. Such a calibration is seen in Fig. 3. The sample solution consisted of equal weights of a polybutadiene, a polystyrene, and the α-methylstyrene tetramer (AMST).

Two relative response factors are needed in this application: (a)

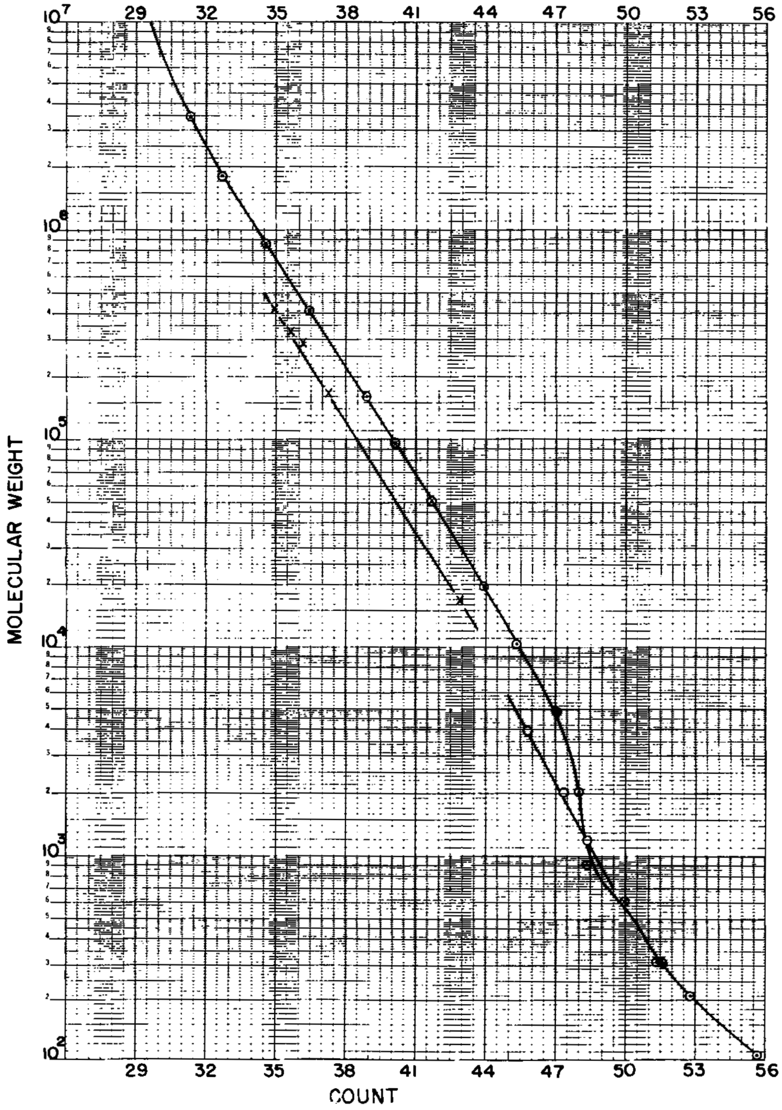

FIG. 1. GPC calibration curves from commercially available standards. ⊙, Pressure Chemical polystyrenes; ×, Phillips Petroleum polybutadienes; ○, polyglycols. Columns used were 5×10^6 Å, 10^6 Å, mixed gel, 5×10^4 Å, 5×10^4 Å, and 300 Å. The points at 104, 208, and 312, are styrene monomer, dimer, and trimer, respectively.

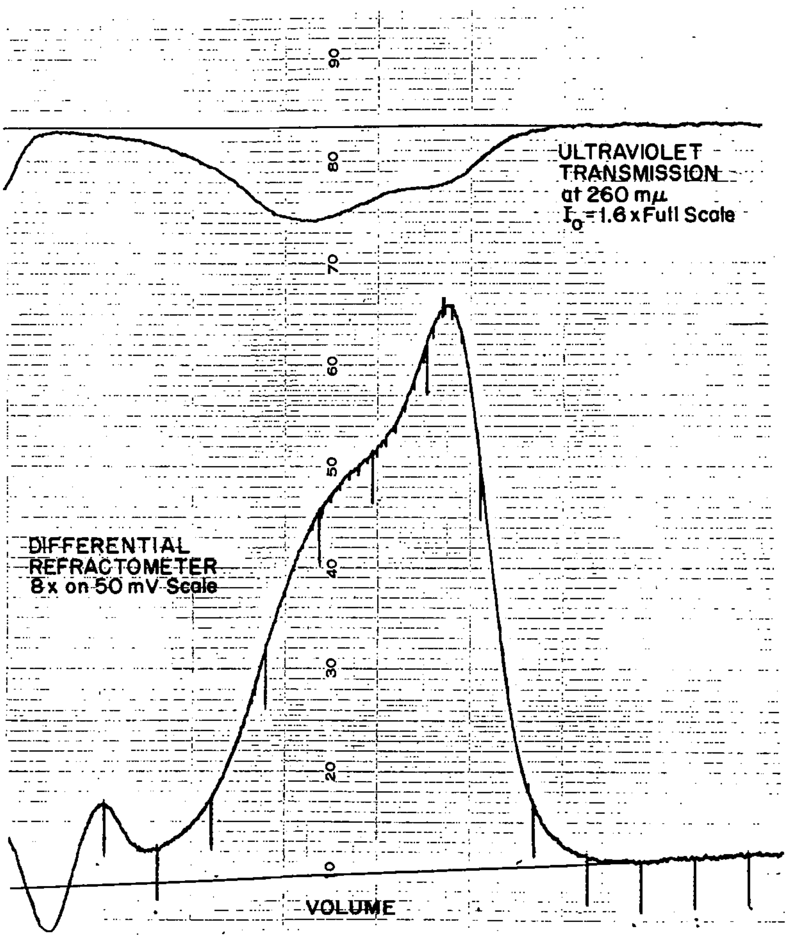

FIG. 2. Dual detector GPC trace of α-methylstyrene tetramer-Na_2 initiated polybutadiene. In the upper trace the pen is offset to correct for volume between detectors. The scale of the abscissa is 2½ min per division. Marks on the chromatogram are 5 ml counts.

the differential refractometer response to the tetramer as compared to polybutadiene; and (b) for the tetramer alone, the amount of signal to be expected in the refractometer for a given optical density (OD). Comparison of the integrals of the GPC curves has been shown to be a reliable way to obtain these response factors (*2*). Table 1 summarizes the average values used in the present calculations. The

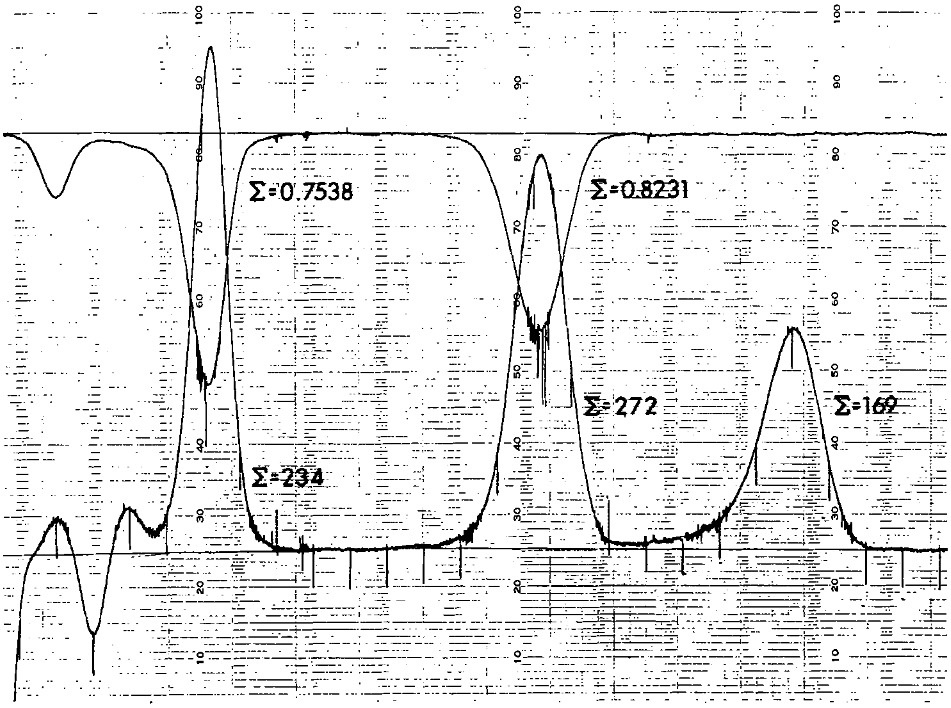

FIG. 3. Dual detector GPC calibration. The axes, etc. are the same as in Fig. 2. The sample was 0.8 ml of a solution containing equal weights of a polybutadiene (MW 423,000), a polystyrene (MW 51,000), and the α-methylstyrene tetramer (hydrogen terminated, MW 474); 0.64 mg of each polymer was injected. The areas of the refractometer peaks at 8× were 169, 272, and 234 "mV ml"; the areas of the UV transmission curves for the polystyrene and the tetramer after conversion to optical density were 0.8231 and 0.7538 "O.D. ml," respectively.

TABLE 1

Relative Responses on Differential Refractometer	
PS/PBD	1.40
PS/PAMS	1.0
AMST/PBD	1.47
Relative "Areas:" ΣΔ Refractive Index/Σ Optical Densities	
PS	320 mV/OD
PAMS	440 mV/OD
AMST	310 mV/OD

polystyrene data is included for general interest. The single sample of poly-α-methylstyrene (PAMS) available at the time gave about the same refractometer response as polystyrene, but considerably less UV absorption. Because the tetramer presumably retains its identity in the center of the polybutadiene molecule, the tetramer response factors were used rather than the poly-α-methylstyrene factors.

In order to calculate the true molecular weight, one must first determine the weight fraction of tetramer. The OD at a given volume increment, multiplied by the appropriate response factor, gives the portion of the refractometer signal that is due to the tetramer:

$$\text{tetramer} = \text{OD} \times 310$$

The rest of the refractometer signal (RI) is due to polybutadiene, but must be multiplied by the relative response of tetramer to obtain a comparable weight number:

$$\text{PBD} = (\text{RI} - \text{tetramer}) \times 1.47$$

The "molecular weight" of the tetramer itself divided by its weight fraction gives the total molecular weight:

$$\text{MW} = 472 \div \frac{\text{tetramer}}{\text{PBD} + \text{tetramer}}$$

At these low weights, the size of the tetramer portion becomes significant, so some correction must be made for it. The correction used here is the same as was used for the styrene–butadiene calculation (*2*), which assumes that a polystyrene molecule has twice the weight for a given size that a polybutadiene molecule has. This

TABLE 2

Low Molecular-Weight Polybutadiene Calibration via Composition Analysis of AMST-Na_2-Initiated Polybutadiene. Data Taken from Fig. 2

Volume	ΔRI[a]	OD	Wt fraction tetramer	Calc butadiene MW	Cor butadiene MW
45.16	4.26	.0029	0.154	3065	2793
46.02	20.16	.01035	0.1141	4136	3864
47.06	24.98	.01702	0.1542	3061	2789
48.10	20.10	.02115	0.2479	1904	1632
49.13	16.92	.02556	0.3744	1261	989
50.00	9.64	.01919	0.5233	902	630

[a] Units = mV at 8 × sensitivity.

may be a somewhat doubtful assumption, but the error will not change the conclusions. Table 2 shows the actual readings and calculations for the part of the distribution curve where the optical density was great enough to be reliable.

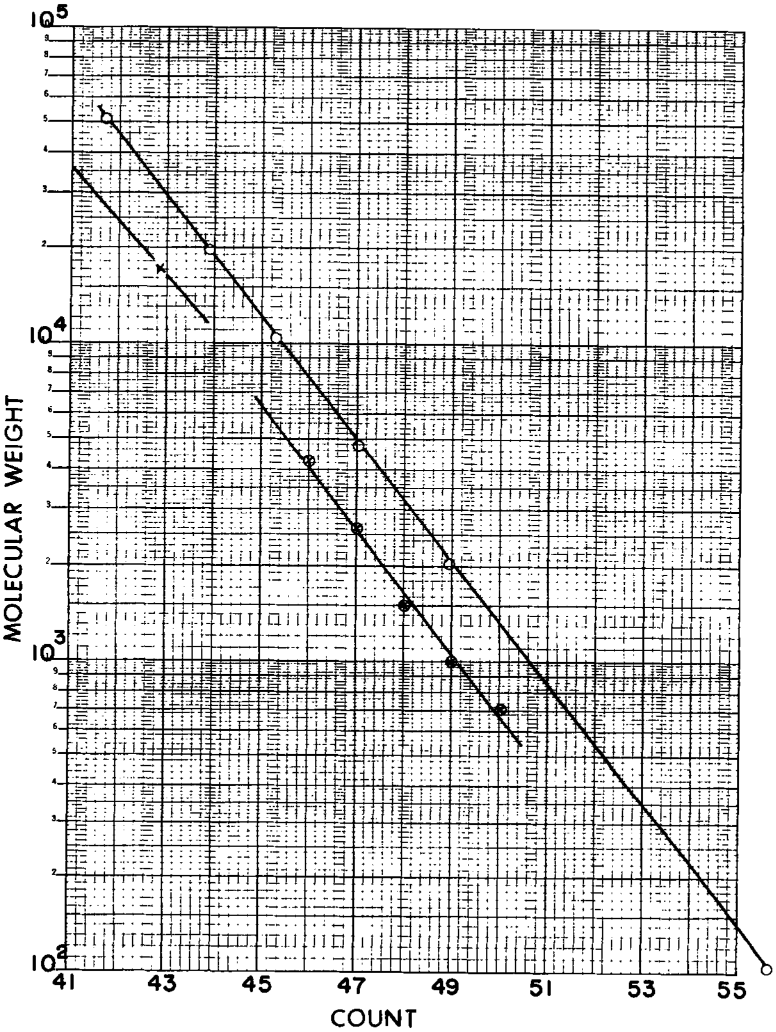

FIG. 4. Low molecular weight extension of polystyrene and polybutadiene calibration curves; ○, PS standards; ×, PBD standard (slope from Fig. 1); ⊗, PBD calculated.

TABLE 3

Low Molecular-Weight Polybutadiene Calibration. Averages from Seven Samples

Volume	Calc MW	Cor MW
44	5300	5000
45	(3800)	—
46	4600	4300
47	2900	2600
48	1800	1500
49	1300	1000
50	1000	700

The original sample was a blend of three materials; each of the three, and several broad distribution polymers, were chromatographed alone. The largest molecular-size portion of each sample was found to give low calculated molecular weights, that is, too much tetramer for the RI: these points were not included in the averages given in Table 3 which shows the results from seven samples. Figure 4 is a plot of these points along with the low molecular-weight end of the polystyrene and polybutadiene calibration curves of Fig. 1. The upper portion of the polystyrene curve is the same as it is in Fig. 1, but the present evidence indicates that if the polystyrene calibration is to be used as a size calibration, it must be extended (in this case) as a straight line from about molecular weight 4800 to monomer, rather than as indicated by the low molecular-weight samples.

Estimates of the molecular weight at which the peak of the various low molecular-weight polystyrene standards ought to be plotted are listed in Table 4.

TABLE 4

Recommended "Styrene Sizes" for Low Molecular-Weight Polystyrene Standards

Nominal MW	Source of standard[a]	Size scale
4800	2	4600
3600	1	4600
2030	2	3200
900	2	2500
600	2	1300

[a] 1: Arro Chemical Co. 2: Pressure Chemical Co.

In his work with polyethylene in *o*-dichlorobenzene at 130°C, Williams (*3*) found that normal paraffins fell on a straight line extrapolation of his higher calibration curve. He concluded that the nominal 4800 molecular-weight polystyrene ought to be plotted at 4350 ± 200, and the 900 molecular-weight polystyrene at 2100 ± 100. This is in good agreement with the present data.

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