

Molecular Weight Distributions of Standard Polystyrene Samples by GPC and by Sedimentation Velocity Analysis*

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Synopsis

In precision gel permeation chromatographic (GPC) work, the spreading (zone spreading) characteristics of the instrument must be calibrated. Standard samples of anionic polystyrene have been used for this purpose. The molecular weight distributions of these standard samples, nevertheless, have not been determined carefully. In this work, several standard polystyrene samples obtained from Pressure Chemical Company were examined by GPC and by sedimentation velocity analysis. The results show that (1) the high molecular weight polystyrene samples have skewed molecular weight distributions as has been suspected and that (2) the present data treatment technique for GPC is effective for these very narrow-distribution samples.

INTRODUCTION

The narrow-distribution polystyrene samples distributed by the Pressure Chemical Company of Pittsburgh, Pennsylvania, have been used extensively as standards for gel permeation chromatography (GPC). Precise knowledge of their molecular weight distributions (MWD) is therefore important. Conventional methods of fractionation are powerless for these extremely narrow-distribution samples. Tung, Moore, and Knight¹ have used a reverse flow technique to obtain reliable molecular weight distribution results from GPC. Nevertheless, for the extremely narrow-distribution samples, the results by GPC depend greatly on the validity of the mathematical procedure of correcting spreading. Sedimentation velocity analysis on an ultracentrifuge is a more direct method. It has been shown² that for broad-distribution samples, the results determined by GPC and sedimentation agreed well. In the present work, both methods are used to study the molecular weight distributions of these narrow-distribution polystyrene standard samples.

GEL PERMEATION CHROMATOGRAPHY

The GPC instrument was a Waters Model 200. Two column sets were used in the experiments. Both consisted of column sections 4 ft long,

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packed with Styragel beads. The porosities of the beads, in nominal Å units, were as follows:

Column A. Six 4-ft sections: (1) $7 \times 10^6 + 5 \times 10^6$; (2) 10^6 ; (3) all purpose (10^6 , 10^5 , 10^4 , 10^3 , 10^2 in equal amounts); (4) 5×10^4 ; (5) 10^4 ; (6) 3×10^2 .

Column D. Four 4-ft sections: (1) $7 \times 10^6 + 5 \times 10^6$; (2) all purpose (same as the section in column A); (3) 1.5×10^6 ; (4) 3×10^4 .

Column A was used in all except one run on a broad-distribution sample. Tetrahydrofuran was the solvent. Flow rate was 1 ml/min. To correct for the spreading, a trial-and-error method was used. This method contained a damping step to damp out the artificial oscillations which occurred frequently when narrow-distribution chromatograms were being corrected for spreading.³ Gaussian spreading was assumed in the correction.

SEDIMENTATION EXPERIMENTS

A Spinco Model E analytical ultracentrifuge equipped with a photoelectric scanning system was used for the sedimentation velocity experiments. When the Schlieren optical system was used, polystyrene solutions lower than 0.1 g/100 ml in concentration could not be satisfactorily measured. As described by McCormick,⁴ an elaborate concentration correction procedure must be applied to these data obtained at high concentrations. Using a 265- μ light source and the photoelectric scanner, ten times more dilute solutions may be used. The errors caused by intermolecular interferences can be ignored at such dilutions and the uncertainties introduced by the concentration correction procedure can be avoided.

In the highly diluted solutions, distortions attributable to thermal disturbances appeared frequently in the cell during centrifugation. Scholte and Rietveld,⁵ in their high-temperature centrifugation work, used metal shields to protect the cell from exposure to the radiations from the heaters. The rotor at the present working temperature of 35°C was heated only by the intermittent heater located near the mercury cup. A simple aluminum ring, shown in Figure 1 fitted on top of the heater-mercury cup assembly, was found sufficient to prevent the thermal disturbances.

Cyclohexane distilled grade was purchased from Burdick and Jackson Laboratory of Muskegon, Michigan. It was redistilled before use. The optical density of the redistilled solvent at 250 μ wavelength light was less than 0.012. Its density at 35°C was 0.7643. The equation relating the sedimentation constant and molecular weight of polystyrene in this solvent was found to be

$$S = 0.0148 \times M^{0.5} \quad (1)$$

where M represents the molecular weight and S , the sedimentation constant in Svedberg units. The coefficient in eq. (1) reported by McCormick

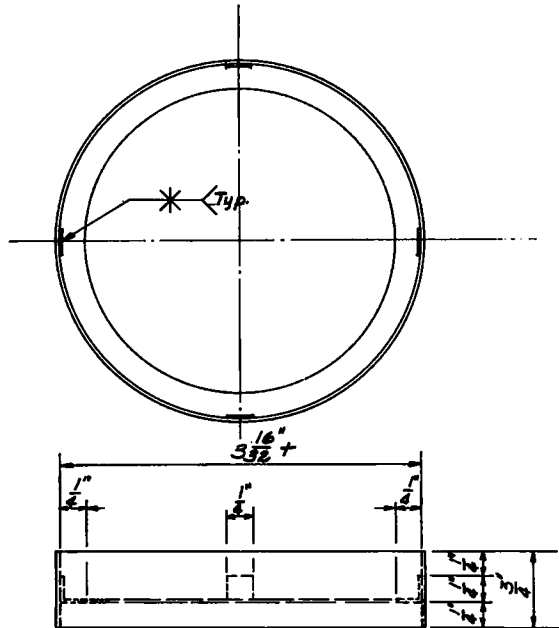


Fig. 1. Heat shield ring for Spincro Model E analytical ultracentrifuge.

was 0.0155.⁴ A slight difference in solvent density could account for this discrepancy.

Figure 2 shows the recorder trace of a typical sedimentation boundary as measured by the photoelectric scanner. The raw data read from such a chart were differentiated numerically to obtain the concentration gradient profile at the boundary. Hydrostatic pressure correction was then applied. The pressure correction coefficient was determined to be 1.62×10^{-9} cm²/dyne; it is within the 1.1 to 3×10^{-9} range reported in the literature.^{6,7}

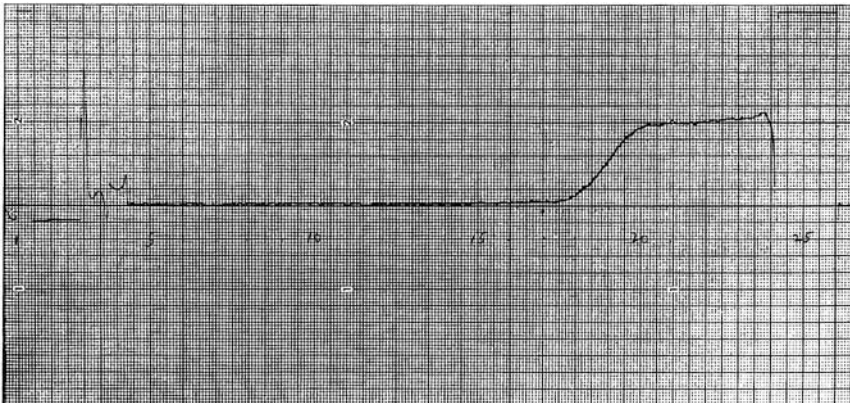


Fig. 2. Photoelectric scanner output of Spincro Model E analytical ultracentrifuge.

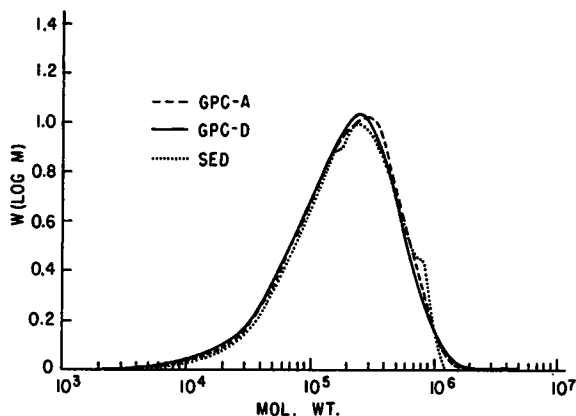


Fig. 3. Molecular weight distribution (MWD) of a broad-distribution polystyrene.

The effect of diffusion was not corrected in the present work, mainly because the method of extrapolation for correcting diffusion often distorts the shape of the distribution curve. To minimize the diffusion effect, the sedimentation boundary at a time just before it reached the bottom of the cell was used for the analysis.

All runs were made at 48,000 rpm and at a concentration of 0.03 g/100 ml. The conversion of the distribution of sedimentation constants to molecular weight distribution was done via eq. (1).

RESULTS AND DISCUSSION

It has been shown earlier² that for a broad-distribution polystyrene sample the molecular weight distribution determined by GPC and by sedimentation agreed well. This test was repeated here using a broad-

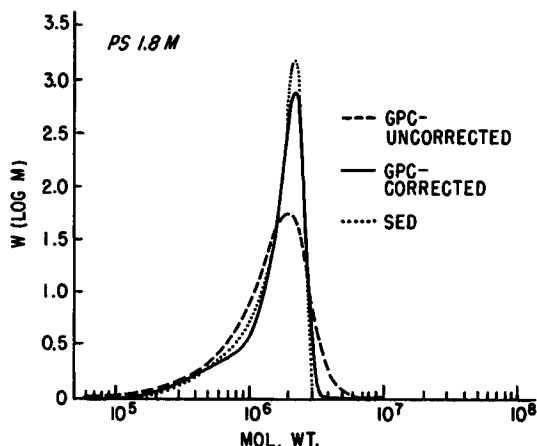


Fig. 4. MWD of Pressure Chemical Co. Sample 14a.

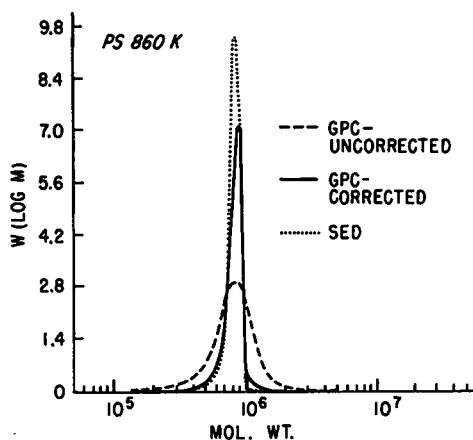


Fig. 5. MWD of Pressure Chemical Co. Sample 6a.

distribution polystyrene as the sample. Two GPC runs were made, one with column A, one with column D. The results of both GPC runs were plotted together with that determined by sedimentation in Figure 3. The agreement among all three runs is shown to be good. Difficulty in obtaining smooth numerical differentiation of the scanner curve is responsible for some of the unsmoothness of the sedimentation curve shown in the figure.

The narrow-distribution polystyrene samples from Pressure Chemical Company were the same seven samples that were recommended for the calibration of GPC spreading characteristics.⁸ Table I gives the nominal molecular weights (furnished by the Pressure Chemical Company) and the average molecular weights determined by GPC and sedimentation in this work. The molecular weight distribution curves are shown in Figures 4 to 10. In these figures, the spreading-corrected distribution and the

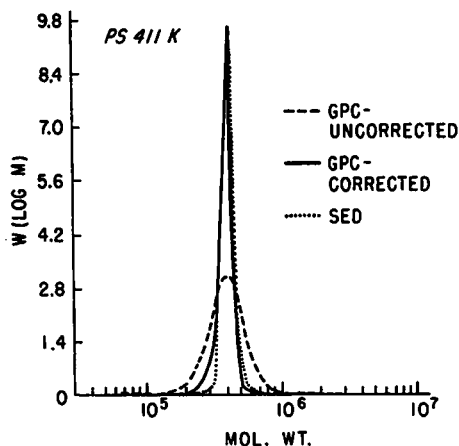


Fig. 6. MWD of Pressure Chemical Co. Sample 3a.

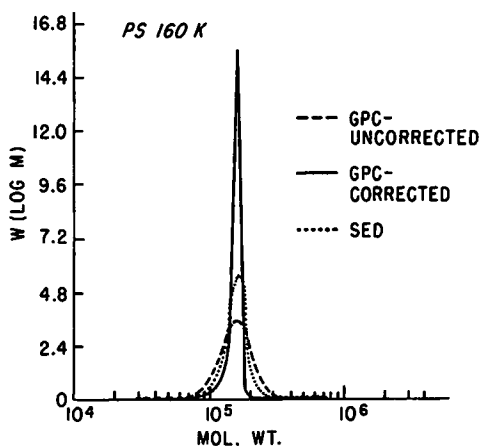


Fig. 7. MWD of Pressure Chemical Co. Sample 1a.

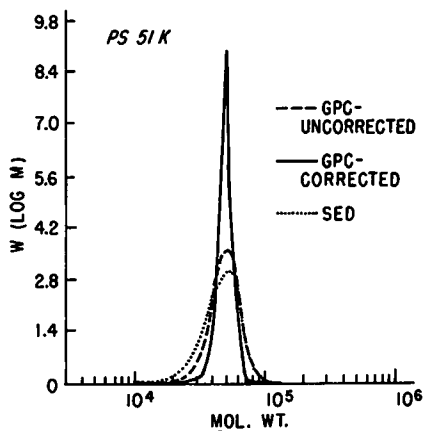


Fig. 8. MWD of Pressure Chemical Co. Sample 7a.

TABLE I
Molecular Weights and Weight- to Number-Average Molecular Weight Ratios of
Standard Polystyrene

Samples		by GPC			by Sedimentation		
Sample no.	Nominal mol wt $\times 10^{-3}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
14a	1800	1134	1635	1.443	1124	1605	1.428
6a	860	780	829	1.063	798	824	1.033
3a	411	394	405	1.027	414	418	1.011
1a	160	157.3	159.1	1.012	156.6	161.1	1.029
7a	51.0	49.3	50.6	1.026	43.9	48.4	1.104
2a	19.8	18.59	19.91	1.071	—	—	—
8a	10.3	9.51	10.28	1.081	—	—	—

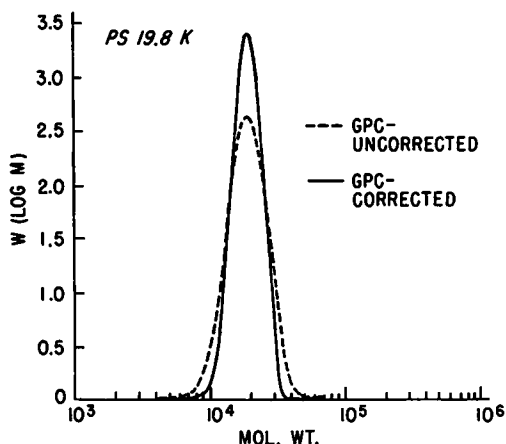


Fig. 9. MWD of Pressure Chemical Co. Sample 2a.

uncorrected distribution from GPC were plotted together to show the importance of spreading correction for narrow-distribution samples.

The agreement between the GPC and sedimentation results is excellent for the three high molecular weight standard samples. For the 160,000 molecular weight sample, the distribution determined by sedimentation appears broader. The effect of diffusion in sedimentation was more pronounced for the lower molecular weight samples. For the 51,000 molecular weight sample, the sedimentation result is broader even than the uncorrected GPC results. For this reason, the distributions for the other two lower molecular weight samples were not measured by sedimentation.

The agreement for the three high molecular weight standard samples confirms the earlier observation⁸ that these samples were skewed in molecular weight distribution. It also confirms the effectiveness of the present procedure of correcting the spreading in GPC.

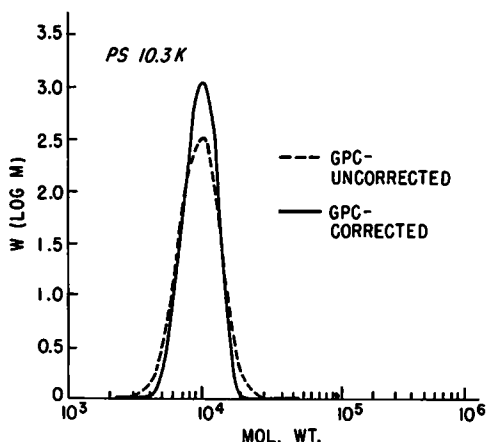


Fig. 10. MWD of Pressure Chemical Co. Sample 8a.

For lower molecular weight samples, the extent of spreading in GPC is less severe and GPC should be more reliable than sedimentation. But even for the three high molecular weight samples, GPC results appear to be more reliable. For example, in Figure 6, the sedimentation result was narrower at the low molecular weight end of the distribution. The lack of precision in reading the scanner curve where the boundary concentration was barely above the baseline contributed to this discrepancy.

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