

Molecular Weight Distribution of Poly(phenylene Sulfide) by High Temperature Gel Permeation Chromatography

CARL J. STACY, *Phillips Petroleum Co., Bartlesville, Oklahoma 74004*

Synopsis

Poly(phenylene sulfide) (PPS) has been characterized using a novel high temperature gel permeation chromatograph (GPC). Samples were injected in slurry form at ambient temperature, and redissolved by an in-line precolumn heater at 250°C. A viscometer consisting of a capillary tube with inlet and outlet taps connected to a sensitive differential pressure transducer was used as sole detector, with deflections converted to concentration using the column calibration. Columns and viscometer were operated at 210°C. Universal calibration was carried out using intrinsic viscosity/molecular weight relations for polystyrene and PPS, determined by light scattering. Satisfactory operation was confirmed by agreement between intrinsic viscosity calculated from GPC with independently measured values, and comparisons with melt flow data. Samples of PPS tested were found to be of relatively narrow distribution, with M_w/M_n typically less than two.

INTRODUCTION

Poly(phenylene sulfide) (PPS) has become an important engineering plastic since Phillips Petroleum Company's introduction of much improved versions of the polymer.^{1,2} Due to the high crystalline melting temperature ($T_m = 285^\circ\text{C}$) and high solution temperatures ($>200^\circ\text{C}$) of PPS, molecular weight and rheological characterization are very difficult.³ Obviously such studies would be greatly facilitated by the availability of gel permeation chromatography (GPC), which has become indispensable for predicting and correlating performance as well as understanding polymerization mechanisms of many commercial polymers.⁴ In particular, "universal calibration" of GPC⁵ has become widely useful as it allows use of well characterized standard samples of different chain structure.^{6,7} Unfortunately, solution temperatures of PPS are beyond the range of commercial instruments, which at best extend to 150°C.⁸ Limitations exist with all components but are particularly serious with injector valves and detectors. The described procedure allows operation of the injector at room temperature. Further, in-line viscometric detectors previously used in conjunction with other detectors for elimination of calibration⁹ or for characterizing chain branching^{10,11} appeared to have no inherent temperature limitations. However, such a detector senses viscosity rather than concentration so that if used alone it is necessary to convert the signal in some way to a response in concentration. It will be shown that this can be done using the same calibration information

used for calculating molecular weights. Assembly, calibration, and applications of a chromatograph based on the above considerations is described in this report.

EXPERIMENTAL

Materials. Solvent 1-chloronaphthalene (Aldrich Chemical Co., C5,765-0) was purified by passage through a silica gel column and 0.5 μm Millipore filter before use. Polystyrene (PS) standards (ARRO Laboratories, Pressure Chemical Co.) have been characterized previously by low-angle laser light scattering.¹² PPS samples were all made by the Phillips process.^{1,2} Unlaminated Teflon membranes (Millipore FHUP 0.5 μm) were used for solution filtration.

Light Scattering. Instrumentation previously developed and applied to polyethylene and hydrogenated polybutadiene characterization^{13,14} was modified for use with PPS in 1-chloronaphthalene at 220°C by installation of a higher temperature scattering cell, solid-state ratiometer, and He-Ne laser light source.¹⁵ At incident wavelength 632.8 nm fluorescence was minimized though it was still necessary to make corrections. Using a modified Brice-Phoenix differential refractometer, specific refractive increment for PPS was found to be 0.167 mL/g. All solutions were prepared, filtered, and scattering measured within three hours to minimize degradation, as evidenced by a slow increase in fluorescence and low-angle scattering. To improve precision for these low-molecular weight polymers, seven angles (45–135 degrees) were measured on each of four independently prepared concentrations (0.002–0.008 g/mL) of each sample. After extrapolation of reciprocal scattering to zero angle, extrapolation to zero concentration was carried out using square root plots.¹³

Intrinsic viscosity was determined in 1-chloronaphthalene at 208°C using a Cannon-Fenske #50 viscometer in a tetralin vapor bath. Plots of $\ln \eta_r/c$ versus concentration gave very low slopes over the whole range of intrinsic viscosity and concentration, allowing good extrapolations.

Melt flow (in g/10 min) was determined using a melt indexer at 315°C, 5 kg load, with a die of 0.209 cm diameter and 0.8 cm length.

Gel Permeation Chromatography. Injection and injector valve operation at 210°C would give serious problems with polymer solution transfer, gasket wear, and leakage. In preliminary experiments it was found that freshly precipitated PPS slurries contained particles fine enough to pass through 0.25 mm tubing and a standard injector, and could be readily dissolved. Thus it was possible to inject the sample in slurry form at room temperature.

Standard concentration detectors such as differential refractometer or UV-vis absorption contain optical and electronic components incapable of operation at 210°C. Attempts were made to use Waters model 440 absorption detector, after in-line precipitation of the fractionated polymer. Scattering at 546.1 nm was highly sensitive, but deposition of polymer on cool optical surfaces was a serious problem. Thus a viscometric detector was considered, in spite of low sensitivity at low molecular weight.

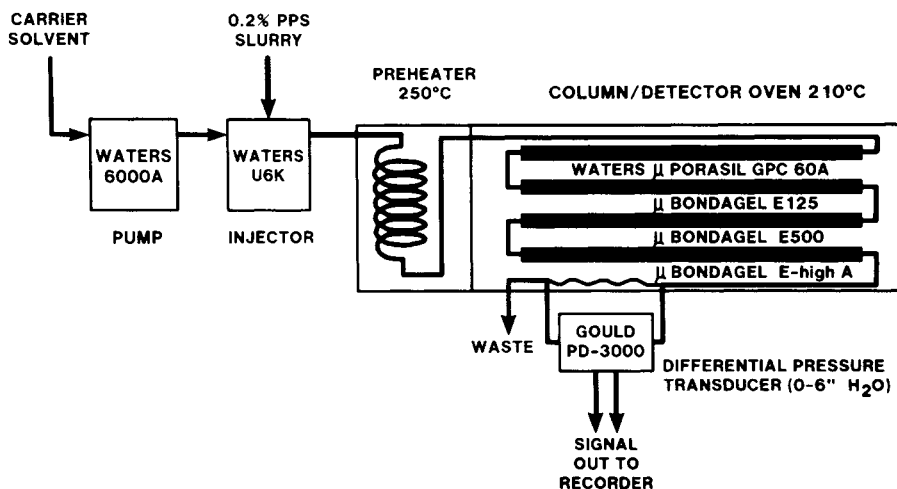


Fig. 1. Poly(phenylene sulfide) GPC system.

A block diagram of the instrument is shown in Figure 1. Solvent reservoir with magnetic stirrer, Waters 6000A pump, and U6K injector are all operated at room temperature. The preheater consists of 1.5 m of 0.25 mm tubing, wound on a 2.5 cm brass rod. It is regulated at 250°C to redissolve the sample before it enters the column array. The columns are Waters μ -Porasil GPC60A, μ -Bondagel E-125, E-500, and E-high A, operated in a column oven regulated at 210°C. The capillary viscometer detector, also in the oven, consists of 200 mm of 0.25 mm bore tubing followed by a similar section to provide additional pressure drop, and finally a short section of larger bore to exit the oven without clogging at the cold end. Tubing from T fittings at the ends of the viscometer are connected to a Gould PD-3000 differential pressure transducer (range 0–15 cm water) outside the oven. The transducer, with both chambers liquid-full, is operated in a separate enclosure at room temperature. After initial installation, the columns were pre-aged at operating temperature until the recorded baseline signal from the transducer stabilized. The solution is prepared in a small pressure container fitted with valve and filter holder. Weighed polymer and solvent is purged with nitrogen, sealed, and magnetically stirred at 220°C until solution is complete. The container is then quickly inverted and the valve opened; internal pressure drives the solution into a small flask at room temperature to form a finely divided, dilute slurry. A 100 μ L portion is then injected, while marking the exact time on the trace. A typical chromatogram is shown in Figure 2.

CALCULATIONS

Intrinsic Viscosity Molecular Weight Correlations. Universal calibration requires good values for the parameters K and a in the Mark-Hou-

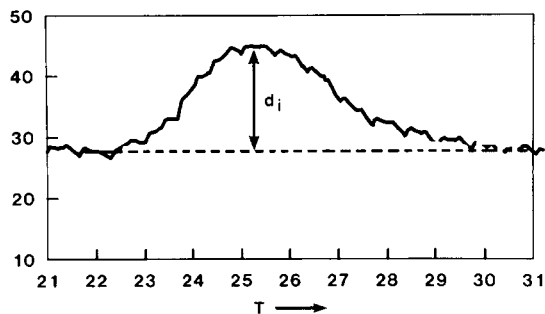


Fig. 2. Typical poly(phenylene sulfide) GPC run.

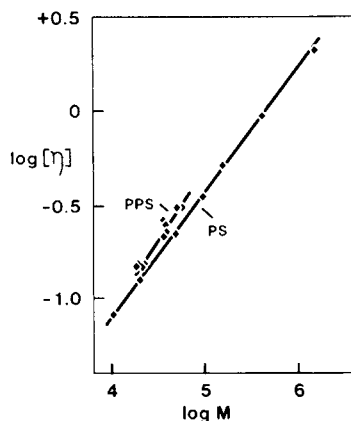


Fig. 3. Intrinsic viscosity/molecular weight relationships for polystyrene and poly(phenylene sulfide) in 1-chloronaphthalene at 208°C.

wink-Sakurada (MHS) equation:

$$[\eta] = KM^a \quad (1)$$

Plots of $\log [\eta]$ versus $\log M$ for PS and PPS in 1-chloronaphthalene at 208°C are shown in Figure 3. For PS, the good fit over the whole range indicates that little degradation has taken place during the 45–60 minutes needed to complete a viscosity measurement. Results for PPS covered a shorter range and deviations were greater, primarily due to difficulties in the light scattering characterization. MHS parameters from these plots are as follows:

	K	a
PS	1.86×10^{-4}	0.657
PPS	8.91×10^{-5}	0.747

Calibration. Universal calibration⁵ is based on a “hydrodynamic volume” V defined as

$$V = [\eta]M \quad (2)$$

which is a function of elution volume v

$$V = f(v) \quad (3)$$

Since column separation is based on molecular size, the same function applies to a wide variety of polymer structures (for a given set of columns and operating conditions). Combining with the MHS equation yields

$$V = KM^{a+1} \quad (4)$$

In the present case, $\log V$ is treated as a cubic in time t after injection:

$$\log V = C_3t^3 + C_2t^2 + C_1t + C_0 \quad (5)$$

After establishing coefficients $C_3 - C_0$ for standard polystyrenes, the correlation is used to calculate V for each point on the chromatogram.

Polymer Concentration. The in-line capillary viscometer measures

$$P_i - P_o = kd \quad (6)$$

where P_i is pressure at equal volume increments on the curve, P_o is baseline (solvent) pressure, d is recorder deflection above the baseline, and k is an instrument constant. To calculate concentration, recall that

$$[\eta] = \left[\frac{\eta_{sp}}{C} \right]_{C \rightarrow 0} \quad (7)$$

where

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} = \frac{P - P_o}{P_o} = \frac{kd}{P_o} \quad (8)$$

At low concentration,

$$\frac{kd}{P_o C} = KM^a \quad (9)$$

or

$$C = \frac{kd}{P_o KM^a} \quad (10)$$

Concentration at the increment i relative to the total curve is given by

$$C_i = \frac{\frac{kd_i}{P_o KM_i^a}}{\frac{k}{P_o K} \sum_i \frac{d_i}{M_i^a}} = \frac{\frac{d_i}{M_i^a}}{\sum_i \frac{d_i}{M_i^a}} = \frac{\frac{d_i}{V_i^{a+1}}}{\sum_i \frac{d_i}{V_i^{a+1}}} \quad (11)$$

where absolute pressure P_o , instrument constant k , and MHS coefficient K need not be known.

Random Branching. Long-chain branching can be introduced into PPS by incorporating a small amount of trifunctional monomer trichlorobenzene (TCB). From the known amount of TCB one may calculate (for each species) a branching index G , the ratio of intrinsic viscosity of branched polymer to linear polymer of the same molecular weight.

$$G = [\eta]_b / [\eta]_l \quad (12)$$

Such information may then be used to calculate an average G for the whole polymer, and a corrected molecular weight distribution.

Assuming random incorporation, that is, each molecular species contains the same mole fraction of TCB,¹⁶ then

$$n_i = LM_i \quad (13)$$

where n_i is number of branches per molecule of molecular weight M_i and L is number of branch points per molecular weight unit. From n_i , a branching parameter g_i for random branching in each species may be calculated from the following approximate equation for trifunctional branching¹⁷

$$g_i = \left[\left(1 + \frac{n_i}{7} \right)^{1/2} + \frac{4n_i}{9\pi} \right]^{-1/2} \quad (14)$$

which is related to G by the equation¹⁸

$$G_i = g_i^{1/2} \quad (15)$$

The hydrodynamic volume V_i as given by experiment is therefore a function of both G_i and M_i :

$$V_i = G_i K M_i^{\alpha+1} \quad (16)$$

With G_i less than one and a known function of M_i , branching is taken into account by solving for M_i . Successive approximations converge rapidly to corrected M_i and G_i .

Intrinsic Viscosity from GPC. From MHS parameters, G values, and concentrations, intrinsic viscosity of the whole polymer is

$$[\eta] = \frac{\sum_i C_i G_i K M_i^{\alpha}}{\sum_i C_i} \quad (17)$$

Data Processing. GPC data were processed using an Apple IIe micro-computer equipped with graphics tablet, ProFile hard disk, Epson FX-80 printer, and user-produced software. Chromatograms were taped to the tablet and carefully traced, smoothing pressure fluctuations which followed the

pump cycle. Data points at preselected elution time intervals are stored in a permanent disk file by run number.

Data for any individual run are then retrieved for calculations. After five-point smoothing,¹⁹ a linear baseline is interpolated between smoothed end points and subtracted from each point on the curve. Hydrodynamic volume is then calculated from each elution time using Eq. (5), and molecular weights for each species from Eq. (4).

For random branching the correction procedure is (i) an estimate of n and G are calculated at each point from the initial M value, (ii) this is used to correct M , (iii) a new n and G are calculated, then (iv) the process is repeated until successive values of M agree within 1%. Three iterations were usually enough. The successive approximation is carried out for each point on the curve.

Concentrations are calculated from recorder deflections, using Eq. (11).

Molecular weight averages M_z , M_w , and M_n , intrinsic viscosity and average G^7 are then calculated from the appropriate summations.

Molecular weight distribution $F(\log M)$ and branching factors G are plotted vs. $\log M$ and printed in the final report, along with the various averages.

RESULTS AND DISCUSSION

Overall Precision. Standard deviation of individual molecular weights was estimated by four independent runs on each of six samples in the $M_w = 24,000$ to $32,000$ range. The result for M_w was 7% of the value; for M_z , 6%; for M_n , 10%; for M_z/M_w , 6%; and for M_w/M_n , 5%. These results reflect the greater sensitivity of the detector at higher molecular weight. No correction was made for bandspreading.²⁰ The ratio M_w/M_n found for standard polystyrenes in this system are comparable to previous work,¹² indicating that peak broadening is small (corrected $M_w/M_n \sim 7\%$ lower).⁷

Comparison of GPC with Intrinsic Viscosity. Results for laboratory samples covering a wide molecular weight range are shown in Table I. Plots of molecular weight distribution are given in Figure 4. In spite of wide variations in MWD, intrinsic viscosities directly determined and independently calculated from GPC are in excellent agreement. This is evidence that the complete procedure, including universal calibration, is working satisfactorily. For instance, failure of the detector to sense low-molecular

TABLE I
Comparison of Intrinsic Viscosity Calculated From GPC with Directly Measured Values

Sample	M_w	M_n	M_w/M_n	Calc. [η]	Obs. [η]
1	4,000	3,800	1.03	0.043	0.05
2	13,300	8,900	1.50	0.102	0.09
3	24,800	13,900	1.79	0.161	0.16
4	31,600	14,600	2.16	0.190	0.19
5	46,900	23,400	2.00	0.258	0.23
6	50,400	24,400	2.06	0.270	0.27

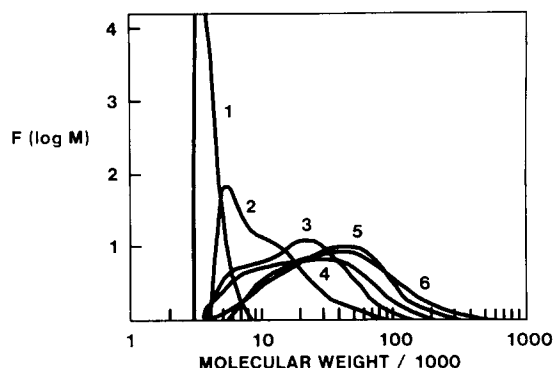


Fig. 4. Molecular weight distributions for laboratory samples.

weight material would have been reflected in a high intrinsic viscosity from GPC.

Molecular Weight Distribution. Results for selected PPS polymers are shown in Table II. Note that M_w/M_n runs somewhat lower than two, the expected result for condensation polymers.²¹ Correction for bandspreading would make M_w/M_n even lower. This prompted a more detailed comparison with theoretical distributions. A plot of the experimental results for sample A2 are compared in Figure 5 with the usual probability distribution²¹ and a log normal curve, both chosen to match M_w and M_w/M_n of the experiment. Clearly the log normal curve matches the experiment more closely, with the probability curve predicting a much too long low-molecular weight tail. It is unlikely that this much material, extending well into the polymeric range, would have been lost in polymer recovery. It also seems unlikely that this much material would have been missed in the GPC measurements

TABLE II
Miscellaneous Poly(phenylene sulfide) Products

Sample	TCB	$M_w/1000$	M_z/M_w	M_w/M_n	Melt flow
A1	—	49	1.4	1.4	185
2	—	53	1.4	1.4	207
3	—	63	1.8	1.5	138
4	—	51	1.6	1.5	147
5	—	53	1.9	1.7	271
6	—	27	1.3	1.2	6950
7	—	24	1.4	1.3	4900
8	—	24	1.4	1.4	5800
9	—	25	1.5	1.4	7100
10	—	25	1.3	1.2	17500
11	—	22	1.4	1.3	8500
B1	0.13	75	1.6	1.5	60
2	0.13	82	2.3	1.7	48
3	0.2	68	1.8	1.8	73
4	0.2	62	1.6	1.6	123
5	0.2	73	1.5	1.4	55
6	0.2	78	1.5	1.4	57

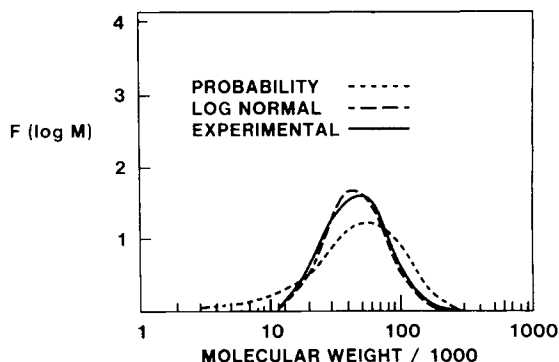


Fig. 5. Comparison of results for sample A2 with theoretical molecular weight distributions.

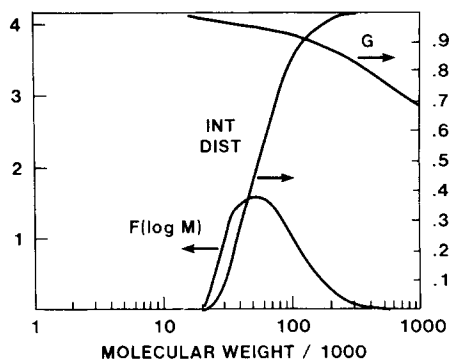


Fig. 6. Molecular weight distribution and random branching curve for sample B5.

through lower sensitivity of the viscosity detector. The consistent observation that M_z/M_w is very close to M_w/M_n also supports the log normal distribution. The significance of this apparent deviation from simple random condensation statistics is under investigation.

Branching. Figure 6 shows MWD and G for sample B5. Correction for random branching increased M_z , M_w , and M_n by 9, 5, and 3% for 0.2 mol% TCB. The G value dropped below 0.8 at the high end, with average $G = 0.92$. Thus, a highly precise value of TCB content is not necessary, and some variation in branching pattern will have little effect on the results. Further, branching characterization using, for instance, independent intrinsic viscosity data^{6,7,10,11,16} would probably not have sufficient sensitivity to detect this level of branching.

Melt Flow. Standard melt-flow measurements are also included in Table II. Melt flow of linear PPS has been found previously to be correlated with zero shear viscosity and molecular weight by the equation³

$$\eta_o = \frac{3.3 \times 10^5}{MF} = 2.06 \times 10^{-20} M_w^{4.86} \quad (18)$$

based on M_w from light scattering. M_w from GPC for the present series of

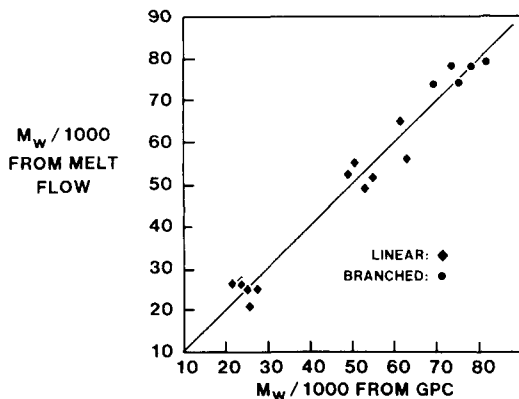


Fig. 7. Comparison of molecular weight from poly(phenylene sulfide) GPC with molecular weight from melt flow.

linear products (A1–A11) is directly compared with M_w from melt flow in Figure 7. The values are seen to be consistent within the scatter of the data, lending further support to the validity of the high temperature GPC results. Branched samples (B1–B6) gave low M_w from Eq. (18), reflecting the effect of chain branching on melt flow. Below a critical molecular weight range, effective molecular weight in flow should be gM .²² Above this range, viscosity of the branched polymer may be much greater.^{23,24} Assuming M to be below the critical range, average branching factor from GPC and random branching was used to correct M_w from melt flow. Corrected values are consistent with the comparison in Figure 7.

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