Differential Gel Permeation Chromatography for Quality Control

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Synopsis

For the direct comparison of similar polymers, as, for example, for quality control, differential gel permeation chromatography provides a simple, sensitive technique that is relatively insensitive to operational variables. One polymer is chosen as a standard and a solution of that polymer is used as the eluent in an otherwise conventional GPC. Differential chromatograms of slightly different polymers are both positive and negative with respect to the baseline. Positive portions represent an excess and negative portions a deficiency as compared to the standard. As in conventional GPC, the elution volumes of the differences indicate the molecular size ranges of the differences. The algebraic sum of the differences is zero. Examination of the raw curves with only general information about calibration and operating conditions tells nearly as much about the differences as carefully executed conventional GPC with complex data reduction.

INTRODUCTION

Differential chromatography has been suggested for increasing sensitivity to small differences in composition in liquid and in gas samples.[1] In these cases, the problem is to detect changes in concentration of indvidual components, usually represented in the chromatograms by discrete peaks, identifiable by their elution volumes (V_r). In the comparison of polymers, differences are not discrete peaks but shifts in the distribution that merely change the shape of the continuum of molecular sizes as represented by the envelope of the conventional GPC curve.

It has been pointed out[2] that the relatively simple operation of subtracting normalized GPC curves from one another provides an easily interpreted difference curve. Differential gel permeation chromatography (DGPC) had been suggested earlier[3] for accomplishing the same result directly, but published work on this technique has been limited. Chuang and Johnson[4] examined the limits of sensitivity to narrow distribution polymers chromatographed in an eluent containing a broad polymer. Bartick and Johnson[5] used the observed retardation in V_r of the above peaks to study the size of polymer molecules in solution as a function of concentration. Otacka and Hellman[6] observed considerable loss of resolution in vacancy GPC.

None of these works showed a differential chromatogram in which the presence of one component was balanced by the lack of another. As far as can be seen, Chuang, Bartick, and Johnson[4,5] only added probes to the polymer-loaded eluent so they had no negative portion in their chromatograms. Johnson, in a talk before the Chicago section of the Society of Plastics Engineers,[7] described the

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differential curve of one polymer in another and predicted that it would be a useful tool in the comparison of polymers.

Following Johnson's suggestions,[4,7] we have demonstrated the feasibility and the great sensitivity and simplicity of DGPC for comparing polymers of a given type, and for following changes in molecular weight distribution of polymers during extrusion.

In DGPC for quality control, the mobile phase is a solution of a standard or reference polymer (reference polymer) of the type being examined, in a convenient solvent. The polymer sample (sample) to be examined is put into solution in the same solvent (without the reference polymer) at, or near, the same concentration as the reference polymer in the mobile phase, and injected as in GPC.

If the injected sample is the same as the reference polymer, the resulting chromatogram will be baseline only unless the concentration is different. In this case, there will be a chromatogram, positive if the sample concentration is greater than that of the standard and negative if it is less. The chromatogram will have the same normalized distribution as a conventional GPC of the standard, or as the vacancy curve.

Injection of pure solvent (no reference polymer) gives a vacancy chromatogram which has approximately the same shape (but opposite sign) as a conventional GPC at the same concentration. See Refs. 3 and 7.

If the injected sample differs from the standard in MWD or impurities, there will be a chromatogram—positive where the sample contains a larger weight fraction than the reference polymer and negative where there is less. If the sample concentration is exactly the same as that of the reference polymer, the algebraic sum of the positive and negative areas will be zero. (Note: These observations refer to the polymer portion of samples where detector response to all components is assumed to be constant. The presence of low-MW additives probably would be an exception.) If the sample concentration is greater or smaller than the reference, the sum will be positive or negative, respectively.

It is difficult to precisely match the concentration of the sample to the reference in the eluent, so the algebraic sum of the raw differential curve is seldom zero. It is not difficult to make an approximate correction for such a difference by constructing a new "baseline" having the same shape (MWD) as the reference or vacancy chromatogram and large enough to intersect the observed differential curve in such a way that the difference between the observed curve and the new baseline has zero as its algebraic sum. This new "base line" will be the curve that would have been observed if the sample had been the reference polymer, at the concentration of the sample. Its area is equal to the algebraic sum of the observed differential curve. Such base lines have been drawn in (by eye) for some of the differential curves of Figures 3, 4, and 5..

EXPERIMENTAL

The instrument used in these experiments was assembled from commercially available components except for the column and siphon which were fabricated in our laboratory. Any GPC with reasonable resolution would have been suitable. The column used was a coil of $\frac{1}{8}$-in. stainless steel tubing, 2.2 mm i.d., 24 ft (7.3 m) long, packed with a mixture of controlled porosity glass (CPGHS,

TABLE I
Controlled Porosity Glass for General Purpose GPC

Nominal pore size (Å)	Pore volume (cc/g)	Wt % in mixture
3000	0.82	8.3
2000	0.87	10.3
1000	1.19	10.3
700	1.68	8.7
500	1.50	9.3
370	1.21	13.0
170	1.07	10.1
125	0.58	8.7
75	0.45	15.8

Electronucleonics) of pore sizes 75–3,000 Å, nominally 10 μm particles, washed on a 60 μm (coarse) sintered glass filter to remove fines.[8] The mixture of pore sizes was chosen to provide an approximately even distribution of pore sizes over the range from 75 Å to 3,000 Å so as to give as long a straight line log(MW)-V_r calibration as possible. Table I shows the weight fractions of the various pore sizes used. Packing was done in a water slurry, using an ultrasonic bath, with pressures up to 5,000 psig. The column temperature was controlled at 100°C, and a stainless steel restrictor, 0.005 in. i.d. ($^1/_{16}$ in. o.d.), 10 ft long, at room temperature, was inserted before the refractometer detector to prevent boiling in the column.

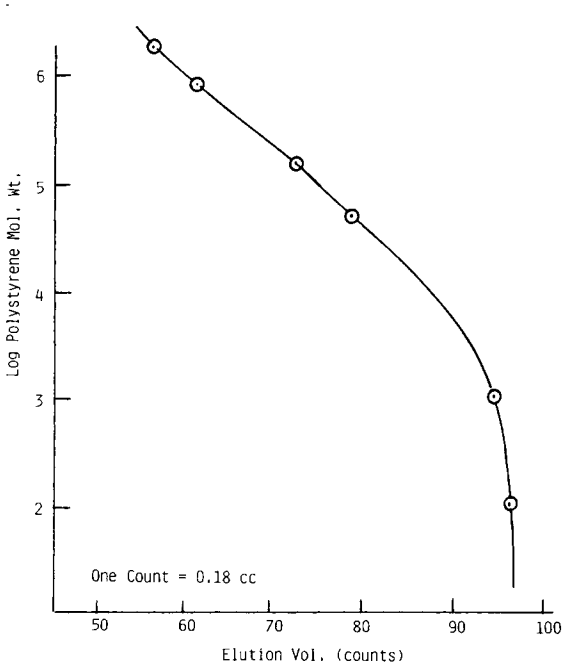

Fig. 1. Calibration of general purpose controlled porosity glass column. CPG pore sizes 75–3,000 Å (see Table I); 24 ft coil, 2.2 mm i.d.; eluent, 0.4% general purpose polystyrene (P1) in tetrahydrofuran; temperature, 100°C; flow rate, 1.2 cc/min. Standards: anionic polystyrenes from Waters Associates.

The air operated sample valve had a 50 μL sample loop and was actuated by an electronic timer.[9] Since the flow rate was 1.2 mL/min, injections were 2 s, or approximately 40 μL. A micro siphon, 0.18 mL/count, fabricated in our shop, was used to monitor eluent volume.

The solvent was tetrahydrofuran (THF), loaded with 4.00 g polymer/L. Sample solutions were made at the same concentration in THF. Our column was calibrated just as it was for GPC, using narrow distribution standards from Waters Associates dissolved in the polymer loaded eluent. Our chromatograms did not show the loss of resolution observed by Otacka and Hellman.[6] Figure 1 shows our calibration curve.

RESULTS

It is common experience that detecting the difference between two nearly identical signals, or two similar chromatograms, is difficult and is best done by computer. Figure 2 shows three conventional chromatograms from a Waters Model 200 GPC equipped with a general purpose set of four Styragel columns. The three curves are nearly identical in total area. The three samples were a general purpose polystyrene (Pl), the same polymer after extrusion from a hot laboratory extruder—once (P2) and three times (P3). The only obvious change in these chromatograms is the shift of the peak toward count 24 (lower molecular weight) after extrusion. Table II shows the average molecular weights calculated from the curves using Tung's[10] resolution correction and data reduction schemes.

Figure 3 shows an inverted vacancy chromatogram (the result of injecting pure

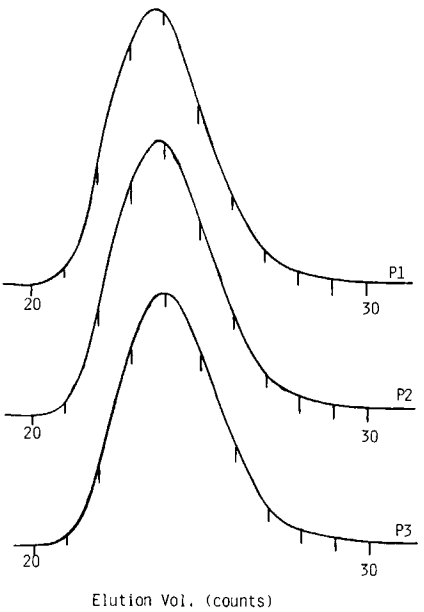

Fig. 2. Conventional GPC of a general purpose polystyrene, P1, and the same polymer after one extrusion, P2, and three extrusions, P3, run in a Waters Model 200; room temperature; 1 cc/min; 5-mL counts; 0.5 min injection from 1 cc loop.

TABLE II
Average Molecular Weights from Conventional GPC of a General Purpose Polystyrene before and after Extrusion

Sample	M_n	M_w	M_z	M_w/M_n
P1 original	130,000	277,300	457,000	2.13
P2 once extruded	118,300	262,960	438,200	2.22
P3 extruded three times	106,900	242,600	410,200	2.27

THF as sample), and differential chromatograms of P2 and P3, run in an eluent containing P1 as the reference polymer. The dotted lines are "eyeball" corrected baselines. The detector sensitivity of the differential curves was four times that used for the vacancy chromatogram, so the differences are magnified. These differential curves clearly show that extrusion has changed these samples, lowering the molecular weight. In addition, they show the range of molecular weight which is subject to degradation; and, since there is no appreciable signal in the range below 7,000 molecular weight, the products of degradation either were volatile or were of moderate molecular weight.

In order to investigate the use of DGPC for quality control, several samples, all of which met specifications for "general purpose" polystyrene, were obtained. One, P4, was chosen as the standard or reference polymer and the others were run in DGPC mode, with P4 dissolved in the eluent. Figure 4 shows differential chromatograms of two, P5 and P6. Included in Figure 4 are a vacancy chromatogram (inverted), run at the same sensitivity as the samples, and a differential chromatogram of the reference polymer itself, run at a slightly higher concentration than the eluent.

Both samples P5 and P6 have somewhat broader MWD as is evidenced by the

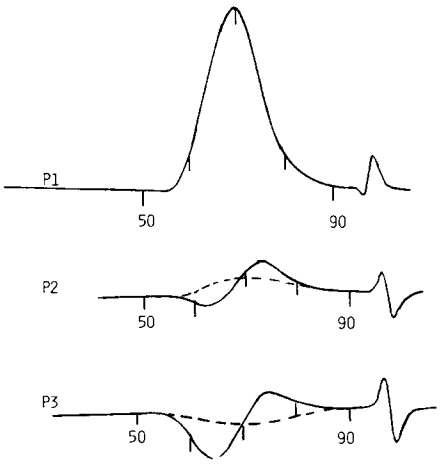

Fig. 3. Differential GPC of two extruded polystyrene samples of Figure 2, in 0.4% unextruded polymer P1 in THF. Under the same conditions as Figure 1, 40 μL injections. The hatch marks indicate every tenth count; 0.18 mL/count. The dotted lines are estimated corrected baselines. The curve P1 is a vacancy chromatogram, inverted and attenuated.

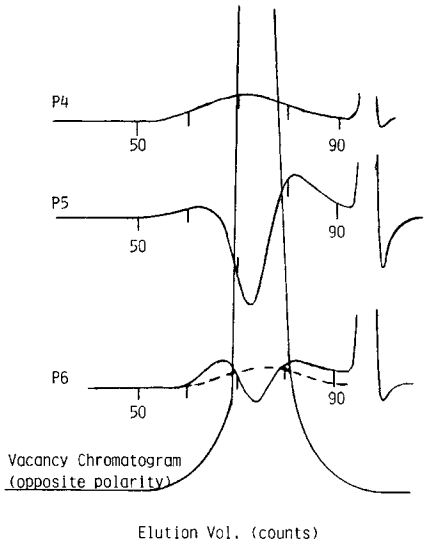

Fig. 4. Differential GPC curves for general purpose polystyrene samples P4, P5, and P6 and a vacancy curve all in 0.4% polymer P4 in THF at the same conditions as Figures 1 and 3.

positive portions of the curves at both the high and the low molecular weight ends of the chromatogram. P6 was run at slightly higher concentration than the eluent causing the differential chromatogram to be considerably more positive than negative. The dotted line is an approximation (drawn "by eye") of the differential chromatogram that would have been seen if P4 had been run at this higher concentration. The true differential chromatogram of P6 is the difference between the observed chromatogram and the dotted line. Even without the

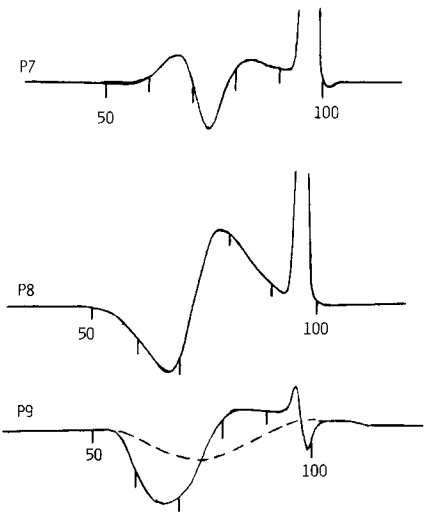

Fig. 5. Differential GPC curves for general purpose polystyrene samples P7, P8, and P9, as in Figure 4 except that the shorter distance between hatch marks indicates a slightly higher flow rate.

corrected baseline, it can easily be seen that P6 has more high molecular weight fraction than P5.

A small amount of ethylbenzene was added to each of the sample solutions which accounts for the late peaks in the chromatograms. This was included as an internal standard.

The three samples, P7, P8, and P9 (Fig. 5), apparently were run at a slightly higher temperature or flow rate as the time from injection to the ethylbenzene peak is slightly less. This difference would have made a time-based conventional GPC anaysis faulty; but in DGPC, without reference to any calibration and in spite of the change in operating conditions, there is no question that all three samples differ from the reference polymer and from each other. P7 is quite like P6, and P8 and P9 are considerably lower in molecular weight and quite different from each other.

Johnson[7] pointed out the possibility of degradation of the reference polymer in storage or in passage through the pump, etc. To avoid this, he used a syringe-type pump. To check the stability of polystyrene in our system, which included a reciprocating pump (Waters M6000), we recycled the effluent of our system to a half-liter inventory, at 1.2 mL/min, overnight. Injecting a sample of unrecycled eluent into this system showed no sign of degradation after 18 h. It is probable that many polymers would not survive this treatment.

DISCUSSION

It has long been the opinion of the author that, although several average molecular weights ($\overline{M}$) may properly define a polymer, they really are only shorthand for molecular weight distributions (MWD) and that neither of them, $\overline{M}$ or MWD, gives as clear a picture of the distribution of molecular weights of a polymer as a plot of weight fraction, $f_{(M)}$, vs. molecular weight or log-molecular weight. To use the various $\overline{M}$ as specifications for a commercial polymer means that a GPC must be run, the raw data converted to MWD, and then to $\overline{M}$. The job is not yet complete. On discovery that the sample polymer is high or low in $\overline{M}$, one must go back to the MWD to determine what has caused the deviation. Actually, one then mentally develops the differential curve suggested by Hassell et al.,[2] though plotting it is seldom done.

This conventional approach requires impeccable technique, a reliable and current calibration, and complex mathematical manipulation. Variations in technique, flow rate, temperature, column aging, etc., are unacceptable hazards.

With DGPC, the comparison of the sample with the accepted standard is done by the chromatograph itself. Operational variables may shift a "difference" a little in elution volume, but *no variable will cancel the difference.* Variations in flow rate, viscosity, column characteristics, etc., are simultaneously affecting both the sample and the reference polymer to which it is being compared. As the chromatogram appears, one sees that there is (or there is not) an excess (or a deficiency) in the molecular weight range that is emerging. Specifications could be written that give the allowable deviation for various critical ranges of molecular weight, and action could be taken without recourse to precise calibrations or sophisticated calculations.

It has been pointed out that in a modern polymerization plant, several poly-

merization trains may be in operation simultaneously, each having its own product specification, and that these specifications may change fairly frequently. Using DGPC for quality control in these circumstances probably would require a chromatograph for each train. The use of rigid packings such as CPG, and rugged columns such as described in this paper, facilitates rapid changeover from one reference polymer to another.

Mathematical treatment of the differential curve can yield the conventional MWD and $\overline{M}$, though the results are subject to about the same limitations as those obtained in conventional GPC. Discussion of these calculations and further interpretation of differential curves will be the subject of our next report.

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