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Gel Permeation Chromatography: Differential Operation

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Synopsis

Operation of gel permeation chromatographs in the differential mode provides a sensitive method for detecting small differences in molecular weight distribution between similar samples. The solvent used in this case is a dilute solution of the reference polymer in an organic solvent. This solution is used in both the reference and the separation column. Samples of the material to be compared are injected in the normal manner. Only differences between the samples are reflected in the resulting chromatogram. For process control, this offers a simplified data presentation and should lead to easier detection of changes in operating conditions.

INTRODUCTION

The use of gel permeation chromatography for process control in the polymer industry has been described.[1–3] Usually these have been conventional chromatographs operated in much the same fashion as analytical chromatographs. Malone, Suchan, and Yau[4] have described vacancy GPC in which the mobile solvent phase was a solution of polymer in solvent. In their case, the samples injected were the pure low molecular weight solvent only.

In differential operation in gel permeation chromatography, the solvent on mobile phase is a solution of the reference polymer with which comparisons are to be made in an organic solvent, in our case tetrahydrofuran. This dilute solution is circulated through both the reference side and the separation column of the gel chromatograph. The sample injected is a solution of the polymer to be compared with the reference polymer in tetrahydrofuran. The concentration of the polymer injected is the same as that of the reference polymer in solution. If the two polymers are identical, no signal is recorded on the chromatogram. Therefore, small differences in the sample should be more easily detected from differential operation. This type of operation has been examined and the results are described in the following section.

EXPERIMENTAL

A du Pont Model 820 liquid chromatograph (du Pont Instrument Products Division, Wilmington, Delaware) was used throughout these studies.

It was equipped with both refractive index and ultraviolet detectors. The columns were stainless steel, 1 meter in length, with an outside diameter of 0.64 cm and an inside diameter of 0.46 cm. The columns were packed with Corning controlled porosity glass, 200–400 mesh. Four columns in series were used. These were packed with CPG-75 Å + CPG-370 Å + CPG-1250 Å + CPG-1835 Å pore size, respectively. A Waters sample valve with a modified loop was used for sample injection. The pressure drop was about 170 to 200 psi, depending on the viscosity of solvent. The flow rate was 0.53 ± 0.03 ml/min throughout the studies. All measurements were made at room temperature. A recording syphon was used to determine elution volumes. The volume of the syphon was 2.44 ml per discharge.

The polystyrene used as the reference material was a commercial foamed polystyrene with a moderately broad distribution. The materials added were the narrow molecular weight anionic polystyrene fractions obtained from Pressure Chemical Company, Pittsburgh, Pennsylvania, and Waters Associates, Framingham, Massachusetts.

RESULTS AND DISCUSSION

Table I lists the amount and type of sample injected, the detector, and the detector sensitivity. Figure 1 shows first three injections of 0.159,

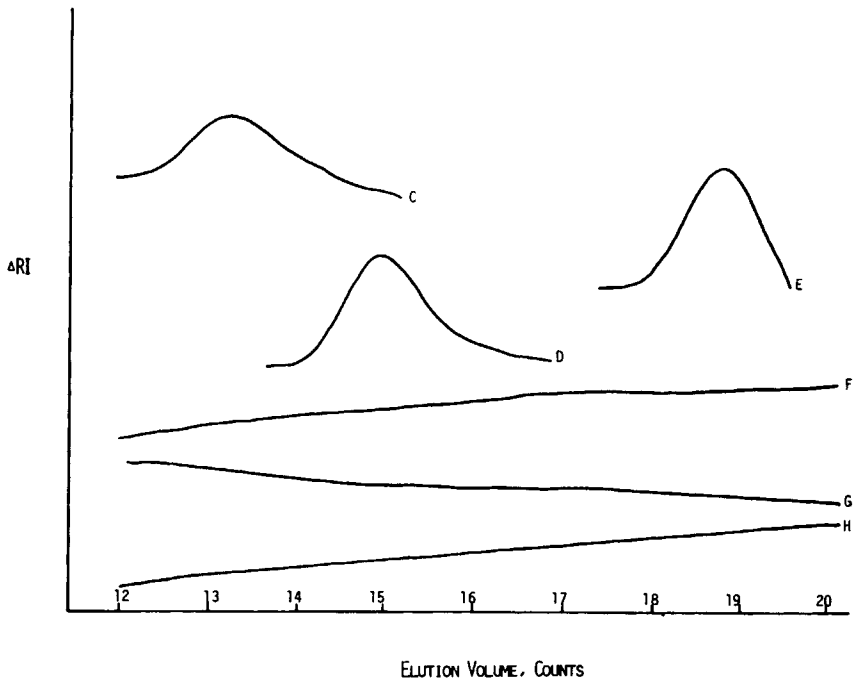

Fig. 1. Elution curves of broad-distribution polystyrene (4.1 mg) plus 10% narrow-distribution polystyrenes and baselines for injection of identical samples.

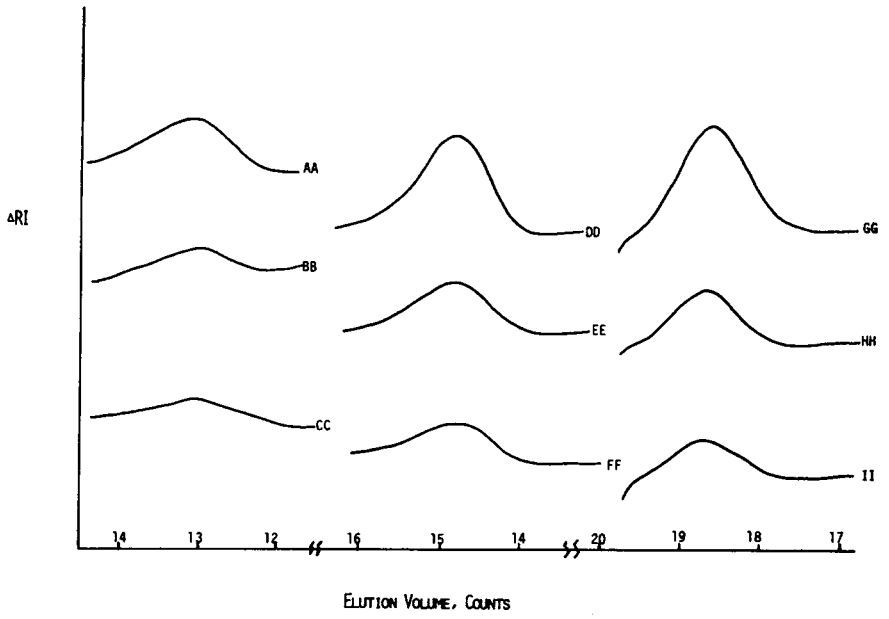

Fig. 2. Elution curves of broad-distribution polystyrenes (4.1 mg/ml) plus 5%, 2.5%, and 1% narrow-distribution polystyrene.

0.318, and 0.636 ml, respectively, of the reference polymer into the solution containing the reference polymer. No detectable change in baseline was observed. This illustrates the use of larger samples to increase sensitivity of the method if desired. On the same figure are shown the resulting chromatograms for the broad-distribution polystyrene to which has been added 10% of narrow molecular weight distributions of 498,000, 200,000, and 19,850, respectively. In this case the concentration of the broad-distribution polymer in the THF was relatively high, 4.1 mg/ml. Even at this high concentration, it is possible to detect changes of 1% readily, as is shown in Figure 2, where chromatograms for a relative weight concentration of 5%, 2.5%, and 1% for three different molecular weights of the narrow distributions are shown.

Lower concentrations of the reference polymer permit use of an increased sensitivity, particularly with the ultraviolet detector. Figure 3 shows results, again for three different molecular weights, for concentrations ranging from 10% to 0.5%. Even lower concentrations could be detected by use of increasing sample size and higher detector sensitivity, if required. For contrast, Figure 4 shows a normal gel permeation chromatogram of the broad distribution alone plus the broad distribution to which 1% of a narrow distribution of molecular weight 51000 has been added. Careful examination shows a change in the chromatographs; but it would not be possible to readily observe this, particularly if the output of the chromatogram alone were used. Computer recording of the data would probably

TABLE I
Chromatographic Operational Conditions

Run designation	Sample injected	Volume injected, ml	Detector	Detector sensitivity
A	PS-B(4.1 mg/ml) PS-51000(0.041 mg/ml)	0.318	UV	16×
B	PS-B(4.1 mg/ml)	0.318	UV	16×
C	PS-B(4.1 mg/ml) PS 498000(0.41 mg/ml)	0.318	RI	4×
D	PS-B(4.1 mg/ml) PS 20000(0.41 mg/ml)	0.318	RI	4×
E	PS-B(4.1 mg/ml) PS 19850(0.41 mg/ml)	0.318	RI	4×
F	PS-B(4.1 mg/ml)	0.159	RI	4×
G	PS-B(4.1 mg/ml)	0.318	RI	4×
H	PS-B(4.1 mg/ml)	0.636	RI	4×
I	PS-B(0.667 mg/ml) PS 670000(0.0667 mg/ml)	0.318	UV	8×
J	PS-B(0.667 mg/ml) PS 670000(0.033 mg/ml)	0.318	UV	8×
K	PS-B(0.667 mg/ml) PS 670000(0.016 mg/ml)	0.318	UV	8×
L	PS-B(0.667 mg/ml) PS 670000(0.00667 mg/ml)	1.272	UV	4×
M	PS-B(0.667 mg/ml) PS 670000(0.0033 mg/ml)	1.272	UV	4×
N	PS-B(0.667 mg/ml) PS 411000(0.0667 mg/ml)	0.318	UV	8×
O	PS-B(0.667 mg/ml) PS 411000(0.016 mg/ml)	0.318	UV	8×
P	PS-B(0.667 mg/ml) PS 411000(0.016 mg/ml)	0.318	UV	8×
Q	PS-B(0.667 mg/ml) PS 411000(0.0667 mg/ml)	1.272	UV	4×
R	PS-B(0.667 mg/ml) PS 411000(0.0033 mg/ml)	1.272	UV	4×
S	PS-B(0.667 mg/ml) PS 51000(0.0667 mg/ml)	0.318	UV	8×
U	PS-B(0.667 mg/ml) PS 51000(0.033 mg/ml)	0.318	UV	8×
V	PS-B(0.667 mg/ml) PS 51000(0.016 mg/ml)	0.318	UV	8×
W	PS-B(0.667 mg/ml) PS 51000(0.00667 mg/ml)	1.272	UV	4×
X	PS-B(0.667 mg/ml) PS 51000(0.0033 mg/ml)	1.272	UV	4×
AA	PS-B(4.1 mg/ml) PS 498000(0.20 mg/ml)	0.636	RI	4×
BB	PS-B(4.1 mg/ml) PS 498000(0.1 mg/ml)	0.636	RI	4×
CC	PS-B(4.1 mg/ml) 498000(0.041 mg/ml)	1.272	RI	4×

(*continued*)

TABLE I (*continued*)

Run designation	Sample injected	Volume injected, ml	Detector	Detector sensitivity
DD	PS-B(4.1 mg/ml) PS 200000(0.20 mg/ml)	0.636	RI	4×
EE	PS-B(4.1 mg/ml) PS 200000(0.1 mg/ml)	0.636	RI	4×
FF	PS-B(4.1 mg/ml) PS 200000(0.041 mg/ml)	1.272	RI	4×
GG	PS-B(4.1 mg/ml) PS-19850(0.20 mg/ml)	0.636	RI	4×
HH	PS-B(4.1 mg/ml) PS-19850(0.10 mg/ml)	0.636	RI	4×
II	PS-B(4.1 mg/ml) PS-19850(0.041 mg/ml)	1.272	RI	4×

pick up the small difference; but as in any analytical technique, determination of small differences between two large signals is more difficult than in the differential case.

The elution volumes of the narrow molecular weight distribution samples are a function of the concentration of the broad polymer in the tetrahydrofuran. Figure 5 shows plots of log molecular weight versus elution volume for the conventional gel permeation chromatography and for dif-

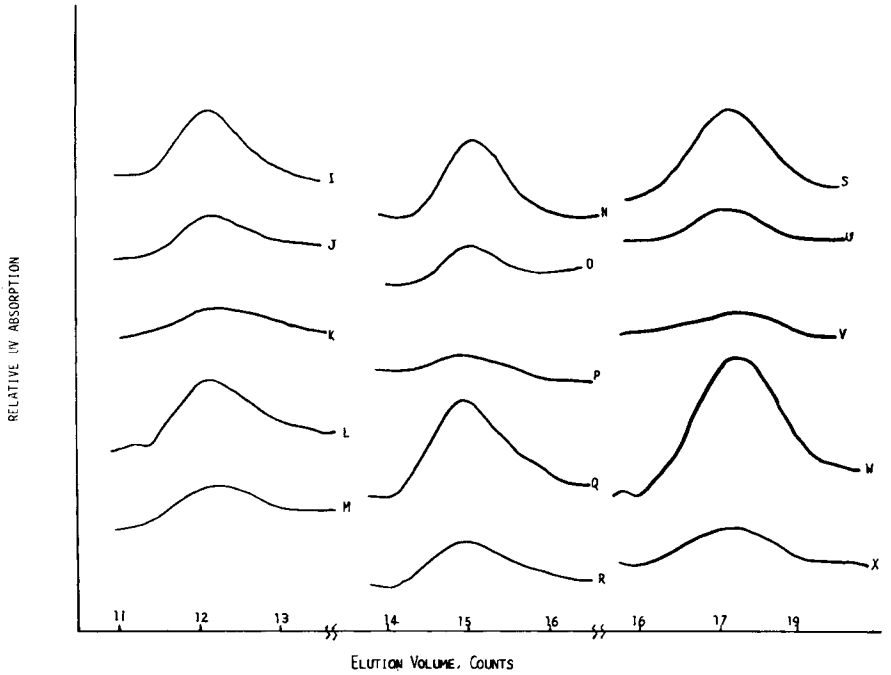

Fig. 3. Elution curves of broad-distribution polystyrene (0.667 mg/ml) plus narrow-distribution polystyrene, from 10% to 0.5% by weight.

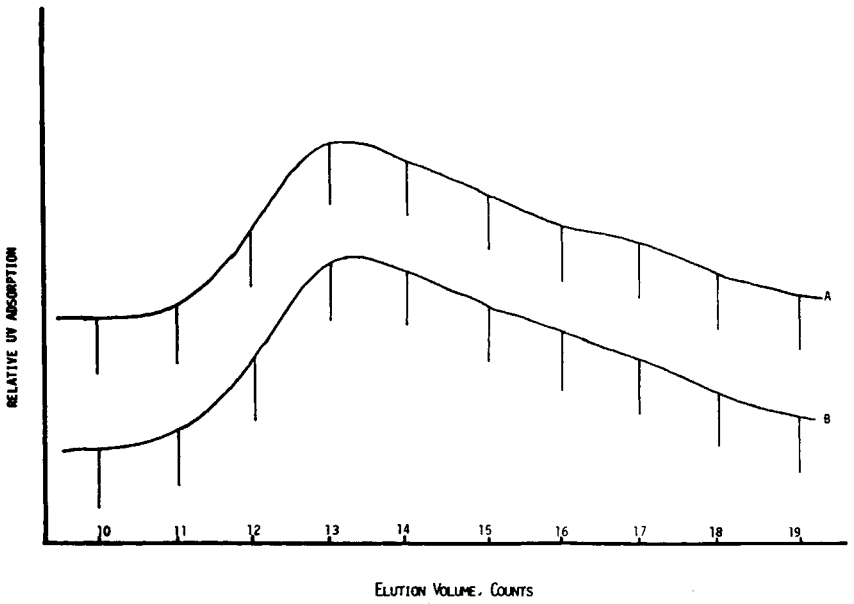

Fig. 4. Comparison of normal GPC curves of broad-distribution polystyrene, with and without adding narrow-distribution polystyrene, PS-51000.

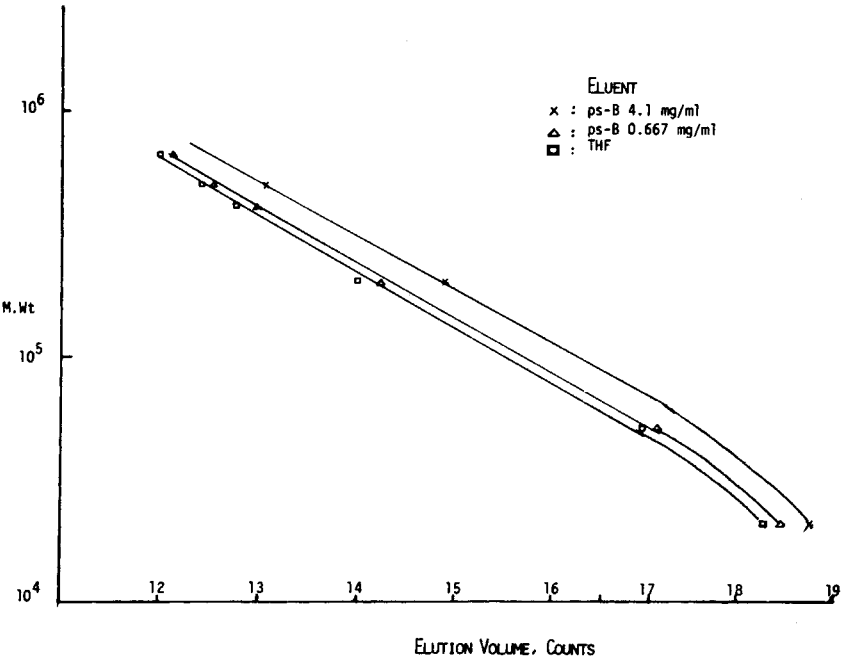

Fig. 5. Calibration curves.

ferential operation at two concentrations. To obtain quantitative results, it would be necessary to calibrate at the concentration of reference sample employed. The increase in elution volume associated with increasing concentration of the reference polymer in tetrahydrofuran shown in Figure 5 is directionally the same as that observed in normal gel permeation chromatography with increasing sample size (see, for example, reference 5). This increase in elution volume is associated with the experimentally established decrease in the hydrodynamic volume of macromolecules with increasing concentration. Recently, a model to permit computation of the change in elution volume with concentration has been developed and tested.[6,7]

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