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Multiple Detectors for Molecular Weight and Composition Analysis of Copolymers by Gel Permeation Chromatography

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Synopsis

The use of a single detector in gel permeation chromatography (GPC) for samples of varying composition leads to erroneous conclusions. With certain simplifying assumptions, a gel permeation chromatograph equipped with properly selected dual detectors yields composition and molecular weight distribution information that is meaningful. Examples discussed are a mixture of homopolymers and a sample supposed to have been a styrene–butadiene block copolymer. The ultraviolet absorption is used in conjunction with the refractive index trace to give qualitative information that is much more informative than could be obtained with one detector. Calibration of the relative responses of the detectors to each of the components of the mixture is described, and these calibrations are used to calculate point-by-point composition, molecular weights, and molecular weight averages.

INTRODUCTION

The great contribution of gel permeation chromatography (GPC) to the examination of polymers in solution depends on its ability to separate the polymer sample according to the size of the molecules in the sample.[1] Much effort has been expended in converting the data so obtained to true molecular weight distribution.[2,3] From the molecular weight distribution, the average molecular weights can be calculated.

While these averages have significance and convenience in comparing samples of a series of homopolymers, they are confusing when the sample is a copolymer of uneven composition or a mixture of two or more polymer types.

Owens and Cobler[4] discussed the difficulties of obtaining good quantitative data on the distribution of size or composition in mixtures or in copolymers and suggested the use of multiple runs with different solvents or of multiple detectors. Bartosiewicz[5] has described the use of various analytical methods on fractions collected from a gel permeation chromatograph. Terry and Rodriguez[6] described the use of infrared for monitoring the con-

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centration of various functional groups as a function of molecular size, using multiple runs with a monomeric material included to aid in relating the successive runs to each other quantitatively. Cantow and co-workers[7] have described the use of an ultraviolet monochromator in series with a differential refractometer for simultaneously determining the composition and the molecular size in styrene–butadiene copolymer rubbers. We have been using such a scheme for some time for the characterization of various styrene copolymers.

EXPERIMENTAL

The chromatograph used was a Waters Model 200, equipped with a Waters R-4 converted differential refractometer. An automatic sample valve with ten 1-ml loops was used for sample introduction. A eight-port Biotron valve was installed between the refractometer and the elution "dump" counter. This valve made it possible to connect other detectors in series with the refractometer.

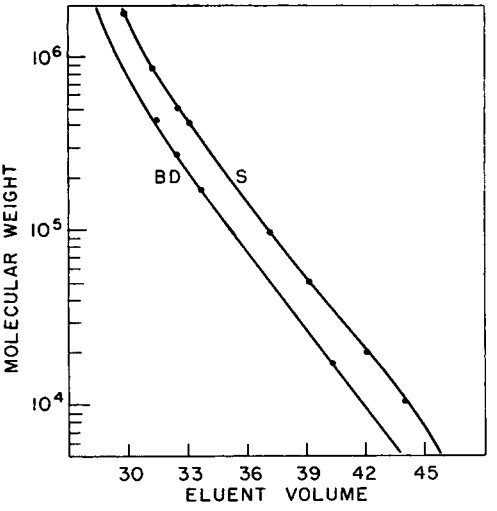

Fig. 1. Molecular weight–eluent volume calibration curves for anionic polystyrene and polybutadiene in THF on a six-column set.

A Beckman "DU" ultraviolet spectrophotometer using a hydrogen lamp and a Beckman power supply was used as a monochromator. For styrene-type polymers, the "DU" was set at 260 mμ.

For continuous monitoring of the transmitted light intensity, the photocell output of the "DU" was amplified by a Kiethley 601A electrometer. A Gilford Model 203 flowthrough cell, with 10 mm path and 70 μl volume, was connected to the eight-port valve with insulated $^1/_{16}$-in. stainless steel tubing. The volume of the tubing and cell after the refractometer was exactly 1.0 ml.

Signal recording was done with a dual-pen Brown recorder with 25 mV range for the refractometer and 12.5 mV for the ultraviolet detector. The recorder chart was used for visual inspection of the results and for selecting the endpoints of the baseline for use in data reduction. In addition to the recorder, the signals were monitored by an IBM 1800 time-sharing computer, and calculations were done both in the 1800 computer and in a Burroughs 5500 computer.

For infrared monitoring, a Beckman IR9 was used as a monochromator, utilizing the maximum scale expansion features and dual 10-mm Wilks microflowthrough cells.

Six Waters columns containing Styragel packing (styrene–divinylbenzene) (Waters Associates, Framingham, Mass.) of the following size designations were used: 10^6 Å, 10^5 Å, 5×10^4 Å, 3×10^3 Å, and 800 Å. Figure 1 shows the calibration curves obtained with this set, using standard anionic polystyrenes obtained from Pressure Chemicals and narrow molecular weight distribution polybutadiene samples from Phillips Petroleum Company. Uninhibited freshly distilled tetrahydrofuran (THF) was used as the eluting solvent at 23°C. The flow rate was from 1 to 2 ml per min. The sample size in most cases was about 1.6 mg, in 0.16% solution. The prepared solutions were filtered through UF sintered glass filters (Pyrex #36060) before loading them in the sample loops. Injection time is sufficient for 1.0 ml of the solution to enter the system.

Calibration of Detectors

It is impractical to determine the relative responses of GPC detectors by direct comparison of solutions of known concentrations, because the concentrations involved are extremely low and minute amounts of im-

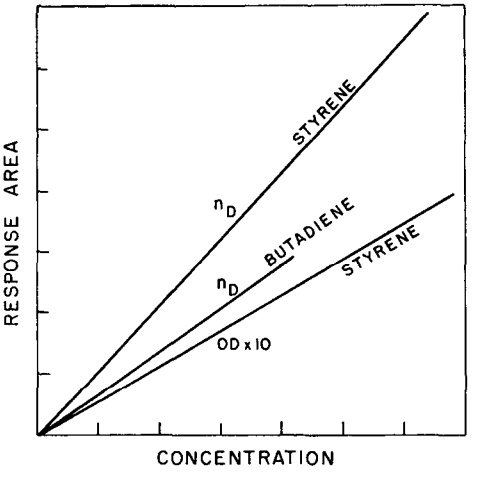

Fig. 2. Response areas for polystyrene and polybutadiene in THF, on differential refractometer (n_D) and UV spectrometer (OD) at 260 mμ. Samples injected were 0.2 mg to 6.4 mg.

purities, dissolved air, or water can give spurious readings larger than the reading desired.

In GPC, impurities, air, monomer, etc., are separated from the polymer, so we injected carefully measured amounts of homopolymers and integrated the areas under the polymer peaks. The resulting integrals (Fig. 2) showed that at a given concentration in THF, polystyrene gives 1.4 times the signal given by polybutadiene on the Waters differential refractometer, and that the area of the refractive index (RI) curve for polystyrene was 35.6 times the area of the optical density curve. (The units of these integrals are millivolt-milliliters for the refractometer and optical density-milliliters for the ultraviolet monochromator.) We found that the sensitivity of the ultraviolet spectrometer to polystyrene was linear with concentration and insensitive to changes in light intensity (slit width or lamp age), temperature, flow rate, or pressure. The differential refractometer, on the other hand, was extremely sensitive to temperature, pressure, condition of the refractometer cell, or the fine adjustment of the optics. As a continuous check on the condition of the refractometer, and the operation in general, our data-reduction program for each sample calculated reported the integral of each curve. Accurately measured samples of homopolymers of styrene and of butadiene were run periodically to establish the ratio of the RI integral to the optical density (OD) integral for polystyrene. The ratio of the RI integral for polystyrene to that for an equal weight of polybutadiene was found to be constant.

Methyl acrylate–methyl N-vinylcarbamate copolymer was prepared by methanolysis of the methylacrylate vinylisocyanate copolymer prepared in high conversion by the methods of Iwakara et al.[8]

Examples

A Mixture of Homopolymers. The lower curve of Figure 3 is the chromatogram obtained with a differential refractometer for a synthetic mix-

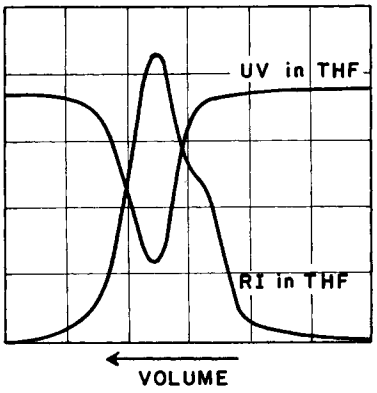

Fig. 3. Gel permeation chromatograph of a synthetic mixture of equal weights of polystyrene and polybutadiene, both of about 400,000 mol wt. RI trace and UV trace at 260 mμ.

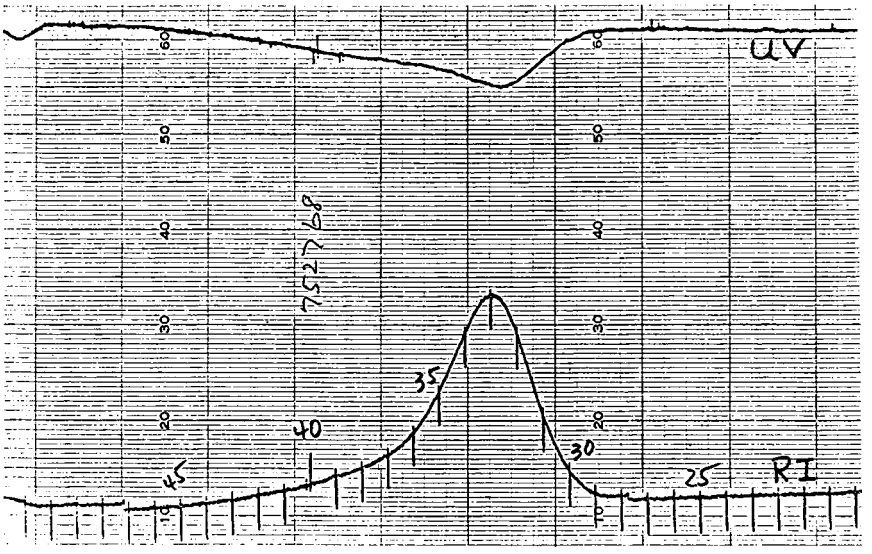

Fig. 4. Gel permeation chromatograph of styrene–butadiene copolymer, 1.6 mg in THF at room temperature. UV transmitted light intensity at 260 mμ and differential refractometer signal on "2X." Numbers on RI curve are "dumps," each one 5 cc. The two pens are offset in time just enough to compensate for the liquid holdup between detectors.

ture of equal amounts of two homopolymer samples of the same molecular weight, one polystyrene and the other polybutadiene. The upper curve is the response of a ultraviolet spectrophotometer set at 260 mμ. At this wavelength, polybutadiene is transparent and polystyrene has a strong absorption; so the apparently larger fraction must be a styrenelike polymer and the other, a butadienelike polymer. Reference to Figures 1 and 2 shows that in spite of their different sizes and elution volumes, the two portions of the chromatogram represent fractions of about the same molecular weight and the same amounts of polymer.

The response of the Waters refractometer has been demonstrated to be linear with concentration for many materials; but it is easily seen that its response varies widely from one compound type to another since it depends on the *difference* in refractive index between the solvent and the dissolved polymer. This difference can be in either direction, over several orders of magnitude, or it could be zero. In fact, it is sometimes expedient to use a solvent whose refractive index is the same as that of the solution of one component of a mixture[4]; but if this situation should arise unexpectedly, the result would be quite misleading.

Styrene–Butadiene Copolymers. Figure 4 shows the GPC response curves for a sample supposed to be a styrene–butadiene block copolymer. Visual inspection indicates that the composition is not the same across the molecular size range. It is possible, with the calibration of the detectors, to proceed with calculating the composition at each point. Table I shows

TABLE I
GPC Composition Calculations for a Styrene–Butadiene Copolymer Sample

V (dumps)	*F2V* (RI)	*F1V* (OD)	*F2* styrene	(*F2V* − *F2*)	*F1* (BD)	*FV* (*F1* + *F2*)	*W1* (% BD)	M_s*
28	0.	0.	0.	0.	0.	0.	—	—
29	0.07	0.001	0.04	0.03	0.04	0.80	50	3.65×10^6
30	0.3	0.002	0.07	0.23	0.32	0.39	82	1.61×10^6
31	0.96	0.009	0.32	0.54	0.90	1.22	74	9.54×10^5
32	1.92	0.018	0.64	1.28	1.79	2.43	74	6.29×10^5
33	2.36	0.021	0.75	1.61	2.25	3.00	75	4.28×10^5
34	1.95	0.019	0.68	1.27	1.78	2.46	72	3.03×01^5
35	1.29	0.016	0.57	0.72	1.01	1.58	64	2.10×10^5
36	0.8	0.013	0.46	0.34	0.48	0.94	51	1.45×10^5
37	0.57	0.012	0.43	0.14	0.20	0.63	32	1.03×10^5
38	0.42	0.012	0.43	—	0.	0.43	0	7.4×10^4
39	0.34	0.010	0.37	—	0.	0.37	0	5.3×10^4
40	0.29	0.009	0.32	—	0.	0.32	0	3.9×10^4
41	0.19	0.008	0.28	—	0.	0.28	0	2.8×10^3
48	0.15	0.006	0.21	—	0.	0.21	0	2.0×10^3
43	0.09	0.003	0.11	—	0.	0.11	0	14.7×10^3
44	0.07	0.002	0.07	—	0.	0.07	0	10.5×10^3
45	0.04	0.002	0.07	—	0.	0.07	0	7.0×10^3
46	0.02	0.001	0.04	—	0.	0.	0	4.5×10^3
47	0.	0.	0.	—	0.	0.	0	2.7×10^3
					8.77	14.63	60	

* Molecular weight, styrene scale, from Figure 1.

the net signal as determined by the IBM 1800 computer (gross signal minus the chosen baseline) and calculations of point-by-point composition. For simplicity, only about one third of the number of data points taken was used in these calculations and those of Table III.

Calculations

The optical density, $F1V$, is used to calculate the styrene contribution, $F2$, to the corrected response curve, as follows:

$$F2 = F1V \times K_2$$

where K_2 is the ratio of the slopes of RI and OD curves for styrene in Figure 2 (in this instance, 35.6). The butadiene contribution, $F1$, to the corrected response curve is the residue of refractometer response after subtracting the styrene contribution, multipled by the relative response factor (styrene/butadiene), K_1 (in our instruments, 1.4):

$$F1 = (F2V - F2) \times K_1.$$

The total corrected response is the sum of individual contributions:

$$FV = F1 + F2.$$

The per cent butadiene at point i is

$$W1_i = F1_i/FV_i \times 100$$

or, for the whole sample,

$$W1 = \Sigma F1/\Sigma FV \times 100.$$

Table I shows the results of these calculations and Figure 5 shows the computer plot of $F1$, $F2$, FV, and $W1$ versus molecular weight.

The several functions together with the eluent volume V and the styrene calibration curve of Figure 1 were used to calculate average molecular weights (Table II). $F2V$ gives the usual result. $F1V$ would be a poor choice for a styrene–butadiene copolymer. For this sample, the molecular weight, calculated from FV on a styrene scale, is not appreciably different from that from $F2V$ because, for most of the sample, the composition is constant. The small difference reflects the lower sensitivity of the refractometer to butadiene. None of these calculations gives a "true"

TABLE II
Molecular Weights of Styrene–Butadiene Copolymer Calculated from Different Functions

	M_n	M_w	M_w/M_n
Refractometer trace $F2V$	131,765	434,613	3.30
UV optical density $F1V$	66,295	316,561	4.78
Corrected response curve FV	128,742	442,401	3.44
FV (copolymer scale)	107,504	270,044	2.52

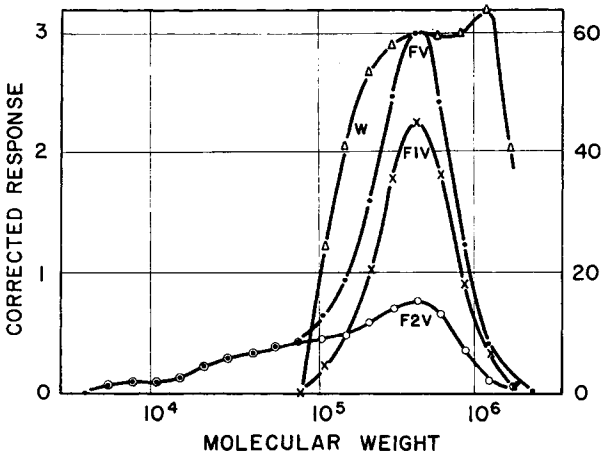

Fig. 5. Computer-calculated and plotted corrected response curves for styrene–butadiene copolymer. *F1V* is butadiene component; *F2V*, the styrene component; *FV* is sum of the two, the corrected response curve; *W* is wt-% BD.

molecular weight. The numbers reported are the molecular weights of a mixture of polystyrenes that have the same size distribution as the sample. To get a number that more nearly represents the true molecular weights, the averages of the last line were calculated using "copolymer" molecular weights described below.

Copolymer Molecular Weight Estimation

It is usual to report the results of a chromatogram "on the styrene scale," that is, to relate the signal *FV* to the molecular weight of straight-chain polystyrene that would have the same *size* in the same dilute solution. This method provides good agreement with other methods when applied to homopolymers of the type used for calibration, but fails when one is examining samples of uneven composition. Its usefulness depends on the detector response being linear with weight throughout the molecular weight range and for all the species present. This can hardly be the case with mixtures or copolymers.

If one has calibrations for all the homopolymers involved relative to the styrene calibration and if one makes the assumption that the *size* of a copolymer molecule is the sum of the sizes of the two portions of the molecule as though each were a homopolymer, then it is possible to calculate a distribution on a "copolymer scale."

We have been studying styrene–butadiene block copolymers and mixtures and have estimated copolymer-scale molecular weights for these samples. The "copolymer molecular weight," M_c, we have used is obtained by "linear interpolation on a log scale." This interpolation defines the copolymer molecular weight at a given volume increment as

$$M_c = M_S^{W_S} \cdot M_B^{W_B}$$

or

$$\log M_c = W_S \log M_S + W_B \log M_B$$

where W_S and W_B are the weight fractions of styrene and butadiene at that volume increment and M_S and M_B are the respective homopolymer molecular weights at that same volume.

TABLE III
GPC Molecular Weight Calculations for Styrene–Butadiene Copolymer

V (dumps)	FV[a] $(F1 + F2)$	W_B	M_S	log M_S	log M_c	M_c
28	0.	—	—	—	—	—
29	0.08	0.50	3.65×10^6	6.562	6.407	2.55×10^6
30	0.39	0.82	1.61×10^6	6.207	5.960	9.11×10^5
31	1.22	0.74	9.54×10^5	5.980	5.757	5.72×10^5
32	2.43	0.74	6.29×10^5	5.798	5.575	3.76×10^5
33	3.00	0.75	4.28×10^5	5.632	5.406	2.54×10^5
34	2.46	0.72	3.03×10^5	5.482	5.265	1.84×10^5
35	1.58	0.64	2.10×10^5	5.323	5.130	1.35×10^5
36	0.94	0.51	1.45×10^5	5.162	5.009	1.02×10^5
37	0.63	0.32	1.03×10^5	5.013	4.917	0.826×10^5
38	0.43	0.	7.4×10^4	4.67		0.74×10^5
39	0.37	0.	5.3×10^4	4.724		0.53×10^5
40	0.32	0.	3.9×10^4	4.592		0.39×10^5
41	0.28	0.	2.8×10^4	4.447		0.28×10^5
42	0.21	0.	2.0×10^4	4.301		0.20×10^5
43	0.11	0.	14.7×10^3	4.168		14.7×10^3
44	0.07	0.	10.5×10^3	4.021		10.5×10^3
45	0.07	0.	7.0×10^3	3.845		7.0×10^3
46	0.04	0.	4.5×10^3	3.653		4.5×10^5
47	0.	0.	2.7×10^3	3.432		2.7×10^5

[a] From Table I.

The log molecular weight versus elution volume curves (Fig. 1) for polystyrene and for polybutadiene are very nearly parallel so that M_B is $M_S \times c$, where c is a constant—in this case, 2.0.

Some of the data of Table I are repeated in Table III and used to calculate copolymer molecular weights by the method described.

DISCUSSION

Generalization of Composition Analysis

The styrene–butadiene application was a relatively simple one, since the polybutadiene had no absorption in the ultraviolet at the wavelength chosen. A more general case would be a copolymer in which both species contribute to both signals. Then

$$F1V = \frac{aW1 + bW2}{100}$$

and

$$F2V = \frac{cW1 + dW2}{100}$$

where $W1$ and $W2$ are weight per cent and a, b, c, and d are sensitivity or response factors. In the general case, the composition calculation would involve solution of the two simultaneous equations in two unknowns. In the case where one of the monomers gives no signal on one of the detectors, e.g., styrene–butadiene copolymers, the factors can be combined as follows:

$$K_1 = c/d,\ K_2 = c/a, \qquad \text{and} \qquad b = 0.$$

Several Detectors

For more complex polymers, even more detectors can be used. Simple algebra tells us that the solution of a problem of N unknowns requires N equations, so a terpolymer would require three detectors.

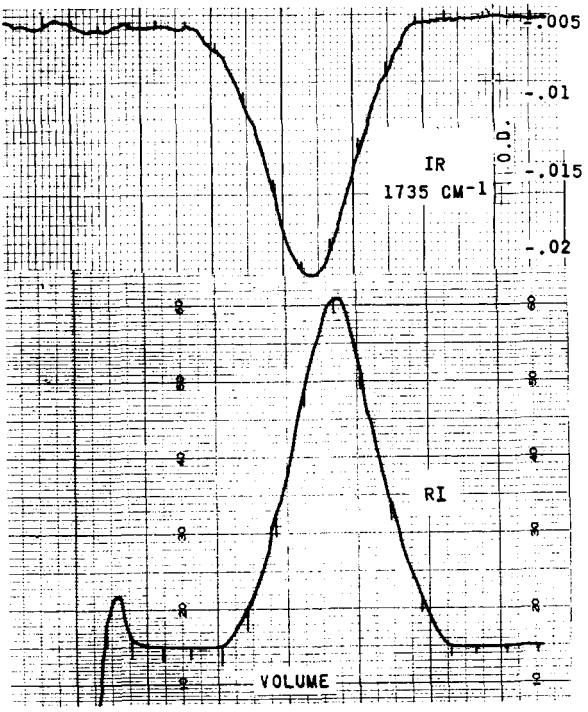

Fig. 6. Composite chromatogram of approximately 60 mg methyl acrylate–methyl N-vinylcarbamate copolymer run at room temperature in THF, with a set of low-porosity columns. The liquid volume between refractometer and IR cell (approx. 4 cc) is indicated by the later appearance of the IR peak. Conditions in IR: 0.1-mm cells, max. scale expansion (full scale is 90% transmission).

Other Detectors

As was reported by Rodriguez and Terry,[5] infrared absorption at a single wavelength can be used as a detector in GPC. Figure 6 shows the refractometer (RI) and infrared (IR) traces obtained with a methyl acrylate–methyl carbamate copolymer.[8] The IR spectrometer was set at 1735 cm^{-1} to monitor the carbonyl band. We have not treated these curves mathematically, but it seems evident that the sample was of fairly even composition.

SUMMARY

The use of selective detectors in gas–liquid chromatography to distinguish compound types is common, as is the use of several classification reagents in TLC, etc. We have demonstrated that with proper calibration, the simultaneous use of two or more detectors with a gel permeation chromatograph can give point-by-point composition information which, besides being useful in itself, aids in obtaining correct size distributions.

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