

NOTES

*Interrupted Flow Gel Permeation Chromatography**

Infrared detectors for gel permeation chromatography can be used to monitor the concentration of eluting polymer^{1,2}; and additionally, with the solvent flow temporarily interrupted, complete spectra may be determined. The latter technique is useful for following functional group concentration in polymers³ and for identification of low molecular weight additives in polymers.

Zone broadening due to molecular diffusion will be increased during the period of interrupted flow. However, calculation of the average standard deviation, L , from the Einstein equation

$$L = (2Dt)^{1/2}$$

using a diffusion coefficient of 2×10^{-6} cm²/sec as representative of small molecules in the liquid phase, yields $L = 0.2$ cm with $t = 10^3$ sec. As $D \sim K/M^a$, where a ranges from 0.5 to 1, this zone broadening should decrease rapidly with increasing molecular weight. To confirm this, samples were run without interruption and compared with those where flow was interrupted for varying times, at approximately one-half the elution volume of the polymer.

A Waters gel permeation chromatograph with a differential refractometer detector operating at room temperature with toluene at a flow rate of 1.3 ml/min was used. Polystyrene standards (Pressure Chemical Company) having a narrow molecular weight distribution at concentrations of 0.088 g/100 ml and sample injection size of 2 ml were measured on two columns, a 16-ft by $3/8$ -in. diameter polystyrene gel with four 4-ft sections of nominal porosities of 45, 10^2 , 1.5×10^3 , and 10^6 Å and a 50-ft by $1/4$ -in. diameter silica gel column. Results are shown in Table I. Additional experiments with six Bio-Glas columns of varying porosities connected in series showed that identical chromatograms were obtained, up to at least a delay of 62 hr, for the 160,000 molecular weight solute.

TABLE I
Effect of Flow Delay on GPC Results

Polystyrene molecular weight	Analysis conditions	\bar{M}_w/\bar{M}_n	Columns
2,030	Normal	2.22	Polystyrene
	Delayed 17 days	2.31	Gel
10,300	Normal	1.20	Silica
	Delayed 90 min	1.21	Gel
51,000	Normal	1.42	Silica
	Delayed 85 min	1.40	Gel

For the 2030 molecular weight polymer after $\sim 1.5 \times 10^6$ sec, a small but probably significant difference in \bar{M}_w/\bar{M}_n was observed, although, as Figure 1 shows, the chromatograms were very similar. Within experimental error, no changes could be observed for the higher molecular weights at delay times of 85–90 min. The experimentally determined value of the diffusion coefficient for 2170 molecular weight polystyrene in toluene is 36.5×10^{-7} cm²/sec.⁴ A very rough estimate of D for the 2030 molecular

* Part XVII of a series on column fractionation of polymers.

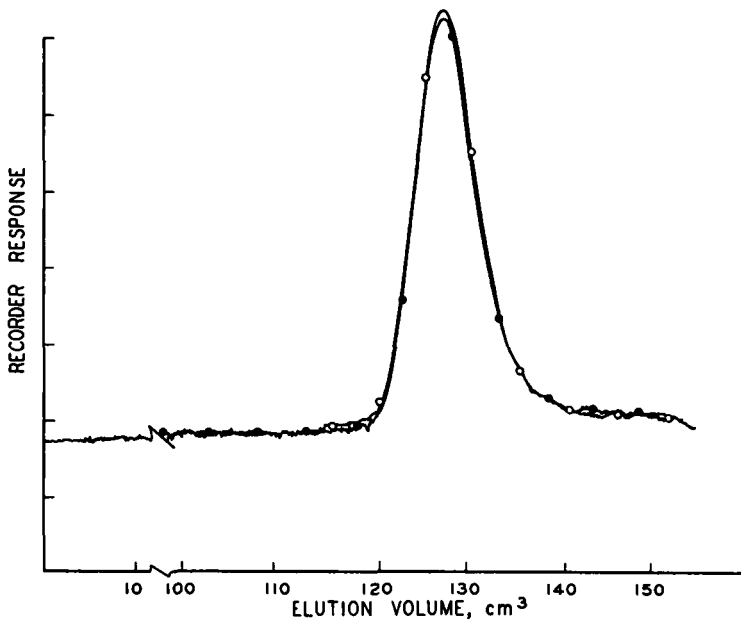


Fig. 1. Polystyrene-polystyrene gel column: Molecular weight; 2030. ● = normal; ○ = delayed, 17 days.

weight fraction by setting $L \leq 1$ cm gives a value of about 3×10^{-7} cm²/sec as an upper limit. This seems unreasonably low, and further work on this point is in progress. For any case of practical interest, it appears that no significant loss in resolution will be encountered using interrupted flow gel permeation chromatography.

References

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