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Note

High-performance vacancy gel permeation chromatography

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Gel permeation chromatography (GPC) is widely used for characterizing the molecular weight distribution of polymers [1]. When a polymer solution is injected into a GPC column with a solvent as the mobile phase, a regular GPC curve is obtained. If a polymer solution is used as the mobile phase and the pure solvent is injected as a sample, the chromatogram obtained will be a mirror image of the regular GPC curve of the polymer sample. This is called vacancy chromatography. Otocka and Hellman [2] reported vacancy chromatography with a conventional GPC column. Their results indicated a difference (Δv) in elution volumes between the regular GPC mode and the vacancy mode, and Δv increases with increase in molecular weight and flow-rate. As a result, the calibration graphs obtained for regular GPC and vacancy chromatography were not identical. It has been suggested that this discrepancy could be minimized by using a high-performance GPC column. In this paper, vacancy chromatography was studied in high performance GPC and the concentration dependences in the regular GPC mode and the vacancy mode were examined.

EXPERIMENTAL

The instrument employed was a Waters Assoc. Model ALC/GPC 244 chromatograph with UV and refractive index detectors. A single μBondagel column was used at a flow-rate of 1 ml/min. The polystyrene (PS) samples used were Waters Assoc. narrow-distribution standards and laboratory-made anionic polymerized PS samples (molecular weight 6000–1 800 000). Tetrahydrofuran (THF) was used as a solvent.

RESULTS AND DISCUSSION

A calibration graph was obtained using the regular GPC mode, the above PS samples at a concentration of $0.3 \cdot 10^{-2}$ g/ml being injected into the column. Another calibration graph was obtained using the vacancy technique in which the column was eluted separately with PS solutions of different molecular weight at the same concentration of $0.3 \cdot 10^{-2}$ g/ml while pure THF solvent was injected as a sample into the column.

The results showed that the two calibration graphs are not identical, and the differences increase with increasing molecular weight, as shown in Fig. 1. However, by

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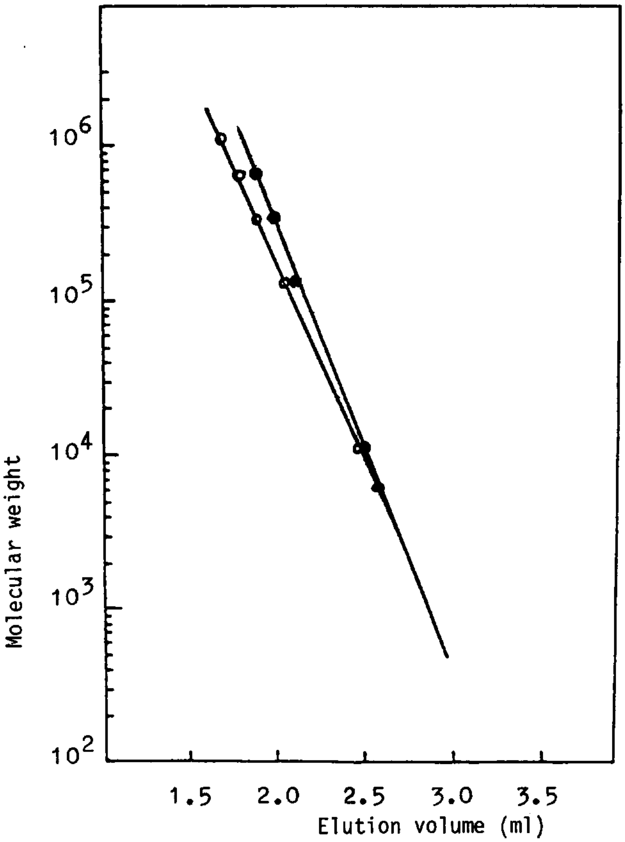

Fig. 1. Comparison of calibration graphs for the regular (○) and vacancy (●) mode on a μBondagel column. PS concentration = $0.3 \cdot 10^{-2}$ g/ml.

lowering the concentration we obtained a vacancy chromatogram that is exactly the mirror image of the regular GPC trace as shown in Fig. 2. The calibration graphs obtained for vacancy and regular GPC for PS–THF at a concentration of $0.03 \cdot 10^{-2}$ g/ml are identical. These results indicate that the discrepancy in the elution volumes between two modes should be attributed to a concentration dependence rather than to the column performance.

Fig. 3 gives an example of the difference in elution volumes for a PS solution at a concentration of 0.6%. The initial slope of the peak elution volume *vs.* concentration plot of PS (mol.wt. $6.9 \cdot 10^5$) in the vacancy mode is much larger than that in the regular mode, as shown in Fig. 4. This is due to a macromolecular crowding effect. When the concentration of the polymer solution is increased, the dimensions of the individual macromolecular chains begin to contract as compared with the size at infinite dilution. In the regular GPC mode there is no polymer in the pores of the column packing, whereas in the vacancy mode the solute polymer is present in the pores of the packing. Hence in the latter instance the macromolecular crowding effect

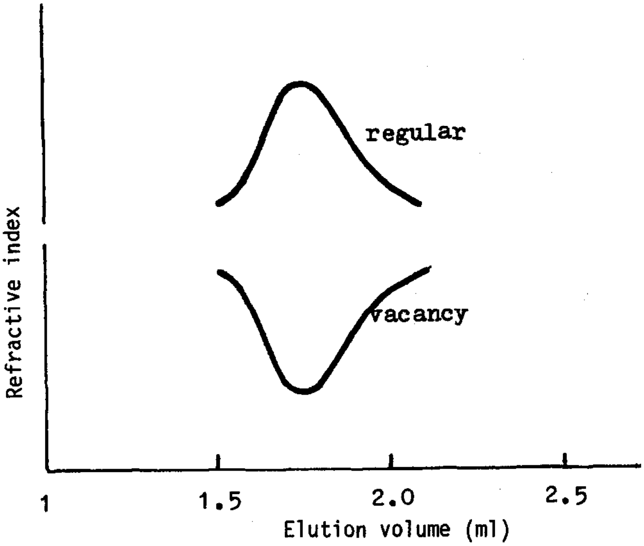

Fig. 2. Comparison of regular chromatogram with 0.03% PS–THF injected in THF and vacancy chromatogram with THF injected in 0.03% PS–THF.

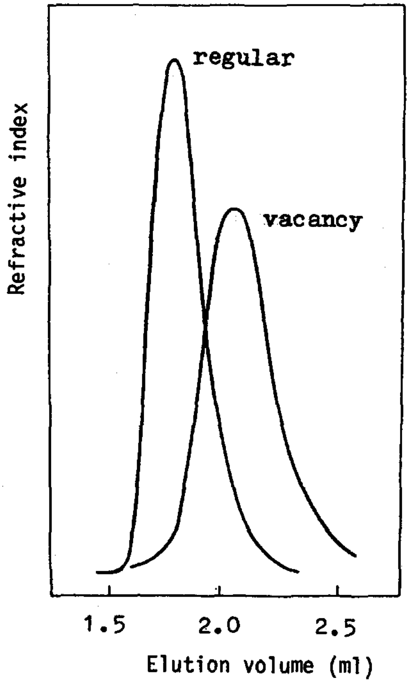

Fig. 3. Comparison of vacancy and regular GPC chromatograms for PS of molecular weight 6.9 · 10^5. PS concentration = 0.6 × 10^{-2} g/ml.

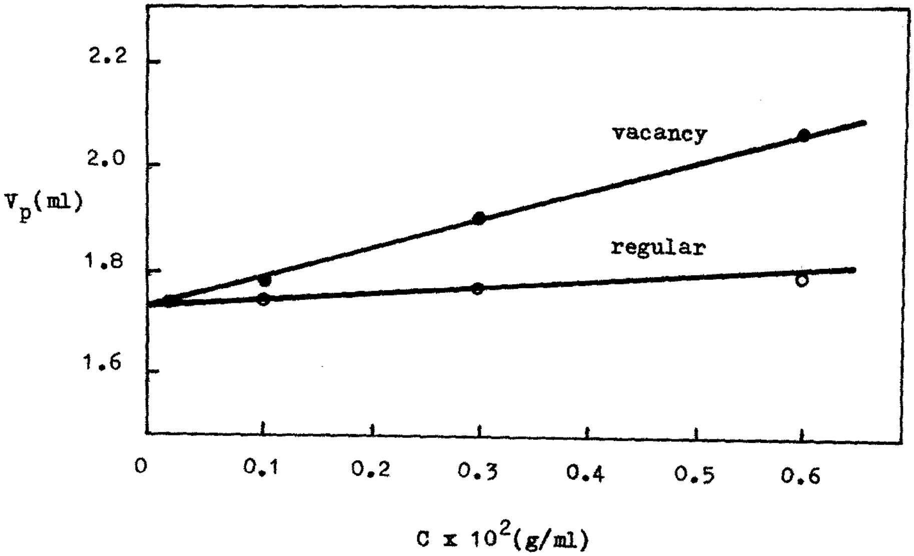

Fig. 4. Comparison of concentration (C) dependences in vacancy and regular GPC for PS of molecular weight $6.9 \cdot 10^5$. V_p = peak elution volume.

would be expected to be more pronounced. This explains the greater concentration dependence in the vacancy mode than in the regular mode.

REFERENCES

1 W. W. Yau, J. J. Kirkland and D. D. Bly, *Modern Size Exclusion Liquid Chromatography*, Wiley, New York, 1979.
2 E. P. Otocka and M. Y. Hellman, *J. Polym. Sci., Polym. Lett. Ed.*, 12 (1974) 439.