

Effect of Concentration and Second Polymer on Elution Volumes in Gel Permeation Chromatography

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Synopsis

Shifts have been observed in the elution volumes of solutions of polystyrene, polybutadiene, and mixtures of the two in gel permeation chromatography using tetrahydrofuran as solvent. Such shifts are examined in terms of the effect on the hydrodynamic volumes of concentration, of molecular weight, and of the presence of an incompatible polymer. Suitable concentration ranges to minimize these shifts have been found.

INTRODUCTION

Gel permeation chromatography (GPC) is used to separate macromolecules according to their sizes, or more precisely, their hydrodynamic volumes. The elution volume (V_e) of a polymer is characteristic of the polymer sample for a given GPC column set and solvent and increases with decreasing molecular weights.

In our earlier work on phase equilibria of multicomponent polymer systems,¹⁻³ the phases were analyzed using GPC. It was discovered then that peak elution volumes (position of the peak) of the polymers shifted due to the concentration effects of the two polymers. These chromatograms were used only to calculate the concentration of the polymers and not for computing the polydispersity, since both polymers had narrow molecular weight distributions. If these chromatograms were used for calculating the polydispersity, a significant error could be introduced due to shifts in the position of the peaks. A desire to use these chromatograms to evaluate the polydispersity of the polymers in the conjugate phases in our future work has led us to take a closer look at the effect of concentration of the individual polymers on their elution volumes and also the effect of concentration of a second polymer on the elution volume of the first one.

Many workers⁴⁻¹⁰ have investigated the effect of concentration on the peak elution volume of individual polymers. The effect of a second polymer on the peak elution volume of the first polymer (in a mixed polymer system) has also been recognized and reported in the past,¹⁰ although not extensively.

The purpose of this article is to report the observed effects of concentration on the elution volumes of polystyrene (PS), and polybutadiene (PBD) polymers and also the effect of concentration of a second polymer on the elution volume of the first polymer in the mixed polymer systems of PS and PBD.

EXPERIMENTAL

Choice of System

The four PS samples used in these experiments were narrow molecular weight distribution (MWD) samples with average molecular weights of 9,000; 110,000; 233,000; and 390,000, respectively. These samples were supplied by Pressure Chemical Co. The two PBD samples used were also narrow MWD samples with average molecular weights of 17,000 and 170,000, respectively. They were supplied by Phillips Petroleum Co. The characteristics of the PS samples with molecular weights of 9,000 and 110,000 and those of the PBD samples were reported in our earlier article.¹ The polydispersity ratios for the PS samples with molecular weights of 233,000 and 390,000 are less than 1.06 according to the data supplied by the manufacturers.

Preparation and Analysis of Polymer Solutions

The polymer solutions were prepared by weighing out an exact amount of the polymer needed for a desired concentration in a 10-ml volumetric flask and then dissolving it in tetrahydrofuran (THF). Solutions of various concentrations ranging from 0.2 to 8.0 mg/ml were prepared. In the case of mixed polymer systems, an exact amount of each of the polymers needed for a desired concentration (of each polymer) was weighed into a 10-ml volumetric flask and then THF was added to dissolve the polymers.

The analysis of the samples was done on a Waters 200 GPC equipped with an ultraviolet (UV) detector using monochromatic light of wavelength 254 nm and a differential refractive index (RI) detector using white light. The detectors were positioned in series along the eluant path and their outputs were recorded on a dual-channel Texas Instruments recorder. The GPC was used with four columns containing styragel packing of the following size designations: 2000–5000; 15,000–50,000; 150,000–700,000; and 5,000,000 Å. The flow rate was 1 ml/min and the injected sample size was 2.0 ml.

RESULTS AND DISCUSSION

The results are presented in Figures 1–4. In the case of PS alone (Fig. 1), we find that there is a threshold concentration (we call it C_t) below which there is a negligible increase in peak elution volume, but above which there is a fairly linear increase of peak elution volume with concentration. Some of the data of other workers (Table II in Cantow, Porter, and Johnson⁵ and Figure 1 in Boni, Sliemers, and Stickney⁶) support this conclusion, although Boni et al.⁶ preferred to fit their data to a simple straight line. The value of this threshold concentration becomes smaller for higher molecular weight PS samples. Thus, for PS with molecular weights of 233,000 the value of C_t is approximately 4 mg/ml while it is about 3 mg/ml for PS with a molecular weight of 390,000.

It was noted that the effect of concentration on peak elution volume is virtually negligible for narrow MWD PS samples with molecular weights below 110,000 (the highest molecular weight PS used in our phase studies so far). The shift in peak volumes is greater the higher the molecular weight of the sample. This is true with both PS and PBD samples (Figs. 1 and 2).

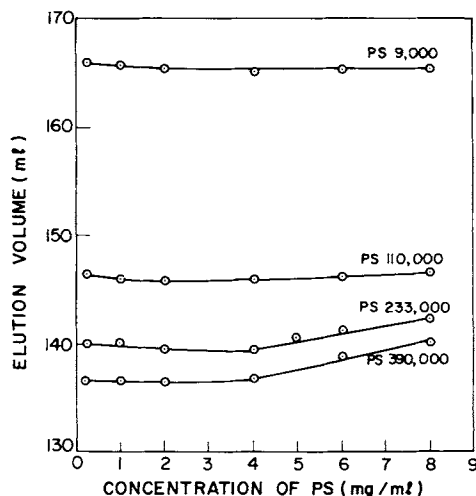


Fig. 1. Effect of concentration on elution volume of PS of different molecular weights. $T = 23^{\circ}\text{C}$.

The fact that increasing polymer concentration in the injected sample leads to increased peak elution volumes has been reported by several workers.⁴⁻¹⁰ It is also known that the higher the molecular weight of the polymer the more pronounced is this shift. Several theories have been advanced to explain this phenomenon. It is generally assumed that the effective hydrodynamic volume of macromolecules dissolved in good solvent decreases with increasing concentration thus leading to an increase of the peak elution volume.⁸

Maron, Nakajima, and Krieger¹¹ studied solutions of polystyrene in different solvents. They concluded that with increasing concentration, there is a sharp decrease in the effective swelling of the solvated macromolecule. This decrease in molecular dimensions was attributed to the crowding of the macromolecular chains in the solutions and the resultant lack of available space for chain extension.

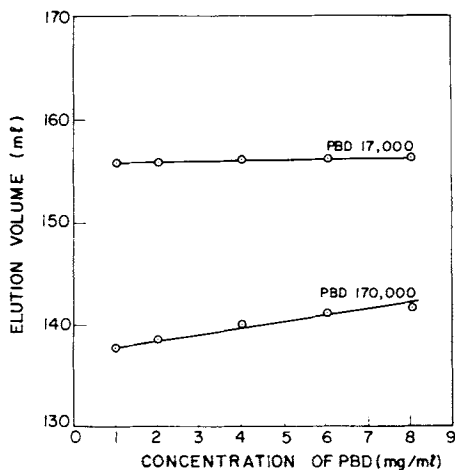


Fig. 2. Effect of concentration on elution volume of PBD of different molecular weights.

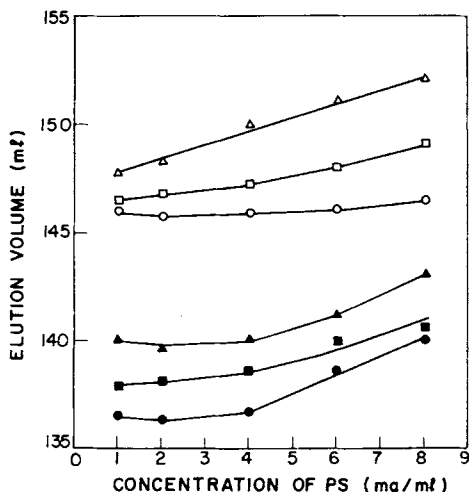


Fig. 3. Effect of concentration of PBD on elution volumes of PS samples of different concentrations. ○, PS 110,000; □, PS 110,000+2 mg/ml of PBD 170,000; △, PS 110,000+4 mg/ml of PBD 170,000; ●, PS 390,000; ■, PS 390,000+2 mg/ml of PBD 170,000; ▲, PS 390,000+4 mg/ml of PBD 170,000.

Weissberg, Simha, and Rothman¹² and Simha and Zakin^{13,14} have shown that compression of macromolecular coils in good solvents arises from a balance between intra- and intermolecular repulsion of chain segments. On close approach of two or more such macromolecules in a good solvent, each will assume a configuration corresponding to a smaller average radius than at infinite dilution, that is, the coils shrink. This effect, of course, depends on concentration. At reasonably high concentrations, each solute molecule is surrounded by a cage of neighboring polymer molecules, the effect of which may be approximated by a uniform pressure on the central molecule, which leads to a shrinkage of the molecule from its volume at infinite dilution.

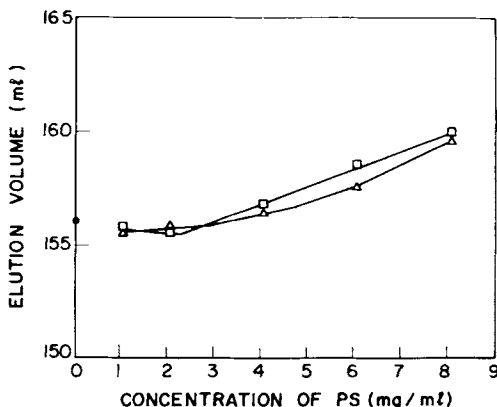


Fig. 4. Effect of concentrations and molecular weight of PS on elution volume of PBD having fixed concentration of 4 mg/ml and molecular weight of 17,000. ●, no added PS; △, with PS 233,000 added; □, with PS 390,000 added.

The elution volumes at different concentrations of PBD samples are plotted in Figure 2. The effect of concentration seems to be negligible in the case of the lower molecular weight PBD (MW 17,000). In the case of the higher molecular weight PBD (MW 170,000), there is a linear relationship between concentration and peak elution volume. The effect, as expected, is more pronounced in the higher molecular weight sample. The foregoing theories could explain this behavior as they did that of the PS samples. The refractive index output was used in the case of the PBD samples since the UV response at 254 nm was found to be zero.

The effect of concentration of a second polymer on the peak elution volume of the first polymer is of considerable interest and importance when dealing with mixed polymer systems. In Figure 3, the data pertaining to the effect of concentration of PBD on the elution volume of PS are presented. It can be seen that for a given concentration of PS, its elution volume increases with increasing concentration of the second polymer (PBD). Also, the effect seems to be more pronounced in the region of higher concentrations of PS. From the data, it can be seen that if the concentration levels of PS and PBD are kept in the vicinity of 1 mg/ml each, the resultant shift in peak elution volume is reasonably small (less than 1%). This shift should be kept in mind when analyzing concentrated polymer mixtures by GPC, such as conjugate phases, in that the dilution of the phases must be done to keep the concentration of the polymers to the desired level before analyzing through GPC.

In Figure 4 some data on the effects of concentration and molecular weight of PS on the elution volume of PBD at a fixed concentration of PBD are presented. To solutions of 4 mg/ml of PBD (MW 17,000), differing amounts of PS were added and the shifts in the peak elution volume of PBD were measured. It is seen that as the concentration of PS is increased there is a significant increase in the elution volume of PBD. Also the result is more pronounced with the higher molecular weight PS sample. There is also a threshold concentration C_t which is approximately 2.5 mg/ml of PS. Bakos, Berek, and Bleha¹⁰ had similar results when they worked with systems of PS and poly(methyl methacrylate) (PMMA) in a "binary eluant" of PS-THF. They have accounted for the observations of changes in peak elution volumes by coil shrinkage resulting from polymer incompatibility. They have also discussed other factors like sorption effect, secondary exclusion, and high viscosity of eluant as possible causes for the peak shifts. It can be predicted from theories concerning the behavior of macromolecules in a thermodynamically good solvent that the addition of a chemically different macromolecule to a solution of a particular polymer would lead to a change in the effective hydrodynamic volume of the macromolecular chains. This change is caused by mutual interactions between the two dissimilar polymers which are, in most cases, repulsive. This reduction in volume or the coil shrinkage of the one polymer in the presence of another polymer brings about an increase in the elution volume of the first polymer with respect to its binary system of polymer and solvent. The greater the incompatibility, i.e., the greater this repulsive force between the two polymers in question, the more pronounced would be the expected dimensional changes of the macromolecular chains, and hence, the greater would be the corresponding increase in the peak elution volume.

CONCLUSIONS

It can be concluded that GPC can be used as a method to study the size variations of macromolecules especially in the ternary system of incompatible polymers in a common solvent, when the concentration levels of the two polymers are kept at suitably low levels. In phase studies, the chromatograms obtained for the conjugate phases can be used to evaluate size variation, and hence, the possible changes in polydispersity of the polymers involved, if either the molecular weights or the concentrations of the polymers involved are relatively low.

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References

1. V. Narasimhan, D. R. Lloyd, and C. M. Burns, *J. Appl. Polym. Sci.*, **23**, 749 (1979).
2. D. R. Lloyd, V. Narasimhan, and C. M. Burns, *Polymer Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **20**(1), 897 (1979).
3. D. R. Lloyd, V. Narasimhan, and C. M. Burns, *J. Liquid Chromatogr.*, **3**(8), 1111 (1980).
4. J. L. Waters, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **6**, 1061 (1965).
5. M. J. R. Cantow, R. S. Porter, and J. F. Johnson, *J. Polym. Sci. Part B*, **4**, 707 (1966).
6. K. A. Boni, F. A. Sliemers, and P. B. Stickney, *J. Polym. Sci. Part A-2*, **6**, 1567 (1968).
7. A. Rudin, *J. Polym. Sci. Part A-1*, **9**, 2587 (1971).
8. D. Berek, D. Bakos, L. Soltes, and T. Bleha, *J. Polym. Sci. Polym. Lett. Ed.*, **12**, 277 (1974).
9. D. Berek, D. Bakos, T. Bleha, and L. Soltes, *Makromol. Chem.*, **176**, 391 (1975).
10. D. Bakos, D. Berek, and T. Bleha, *Eur. Polym. J.*, **12**, 801 (1976).
11. S. H. Maron, N. Nakajima, and I. M. Krieger, *J. Polym. Sci.*, **37**, 1 (1959).
12. S. G. Weissberg, R. Simha, and S. Rothman, *J. Res. Natl. Bur. Stand.*, **47**, 298 (1951).
13. R. Simha and J. L. Zakin, *J. Chem. Phys.*, **33**, 1791 (1960).
14. R. Simha and J. L. Zakin, *J. Colloid. Sci.*, **17**, 270 (1962).

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