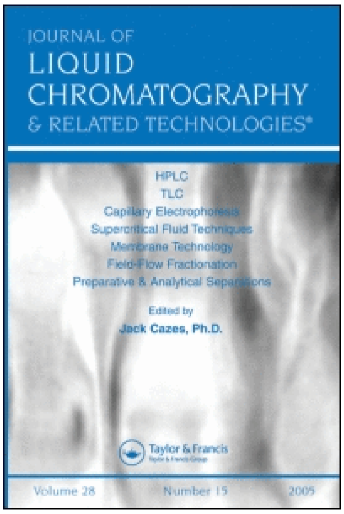

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Characterization and Properties of Macromolecules

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CHARACTERIZATION AND PROPERTIES OF MACROMOLECULES XVIII. THE EFFECT OF SOLVENT ON MOLECULAR WEIGHT DISTRIBUTIONS DETERMINED BY GEL PERMEATION CHROMATOGRAPHY

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ABSTRACT

The effect of solvent on the numerical results obtained from gel permeation chromatography has been evaluated. Columns packed with porous glass materials were evaluated, using three solvents. The narrow molecular weight distribution polystyrene standards were chromatographed in each solvent to calibrate the columns. The chromatograms of the standards were then analyzed to yield the molecular weight averages and their molecular weight distributions. The results indicate solvents of high viscosity should be avoided, especially for high molecular weight samples.

INTRODUCTION

Gel permeation chromatography, GPC, performed using a porous inorganic column packing, allows, in principle, an unrestricted choice of solvent. This work evaluates the effect of solvent on the determination of molecular weight averages and the differential molecular weight distributions, DMWD. The column packings employed were Corning Porous Glasses, CPG (*1*). These materials have been well-characterized (*2*) and have been shown to more efficient than other

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commercially-available packing materials (*3*). A previous report (*4*) has demonstrated that the universal calibration plot, M[η], is valid for polystyrene over a range of solvent power, viz., methylethylketone (MEK), dioxane, tetrahydrofuran (THF) and chloroform, for silica-based column packings but not for polystyrene gel packings. Other effects of solvent have been investigated; for example, the concentration dependence of polystyrene elution volume, using polystyrene gel columns, was found to be significant at higher molecular weight in a good solvent, THF, but negligible in a theta solvent, MEK (*5*). These authors showed that errors could arise in the calculation of molecular weight distributions for samples run at 3, 4 and 6 mg/ml if a calibration curve obtained at 0.3 mg/ml were employed. Mixed solvents have also been employed as theta solvents using polystyrene gel columns (*6*) and for porous silica column packings (*7*,*8*). For the latter column packings, the elution volume was found to be independent of sample concentration for theta solvents, but the universal calibration curve was not obeyed.

EXPERIMENTAL

The chromatograph used for these experiments was a Waters Associates ANA-PREP (*9*). The solvent flow rate was approximately 1.45 ml/minute for each solvent used, viz., tetrahydrofuran, THF, toluene or 1,2,4-trichlorobenzene, TCB. Flow rate was established gravimetrically. A syphon was employed to monitor flow rate during the course of each analysis. The polystyrene standards (*10*) were injected at 1 mg/ml in an injection volume of 2 ml. Detection was accomplished by differential refractometry run at a sensitivity setting to allow accurate quantitation of peak heights. The columns employed were six feet in length, 0.305 in. ID bent in a "U" shape. Four columns were used, packed with a single-pore diameter Corning porous glass, having the following diameters: 2000 Å, 1250 Å, 370 Å and 240 Å.

The calibration curves established by the polystyrene standards were employed to calculate the molecular weight averages and the distributions of the standards. Approximately 25 data points were taken for each chromatogram, and a computer program was used for the computations (*11*).

RESULTS AND DISCUSSION

Figure 1 shows the calibration curves obtained, using the polystyrene standards with these three solvents. The calibration curves for THF and toluene are superimposable. For all three solvents, the void volume, determined for a 7 x 10^6 molecular weight standard, and the total liquid volume, measured by n-hexane elution, are identical. However, at molecular wieghts lower than $\sim 10^5$, the calibration curve for TCB is displaced toward higher elution volumes. This retardation does not cause the sample to be eluted after the total liquid volume. The cause of this is speculated to be a specific interaction of the lower molecular weight polymers with the surface in the TCB solvent. Differences in elution volume due to sample viscosity effects would be expected to show up at the higher molecular weights.

The results of the calculation of molecular weight averages from these chromatograms are shown in Table I. At each molecular weight, the calculated ratio of weight to number average molecular weight, $\bar{M}_w/\bar{M}_n$, increases as the viscosity of the solvent increases. At molecular weights of 411,000 and 670,000, the weight average molecular weight is significantly below its true value when TCB is used as the solvent. The value of $\bar{M}_w$ calculated for the 670,000 molecular weight standard is also low when toluene is used. For all other samples and solvents, the calculated $\bar{M}_w$ is in good agreement with the true value. The chromatograms for the 670,000 molecular weight polystyrene standard are shown in Figure 2. Although these chromatograms are obtained in the region where the calibration curves are superimposable, the chromatogram in TCB is extended to higher elution volumes. When the differential molecular weight

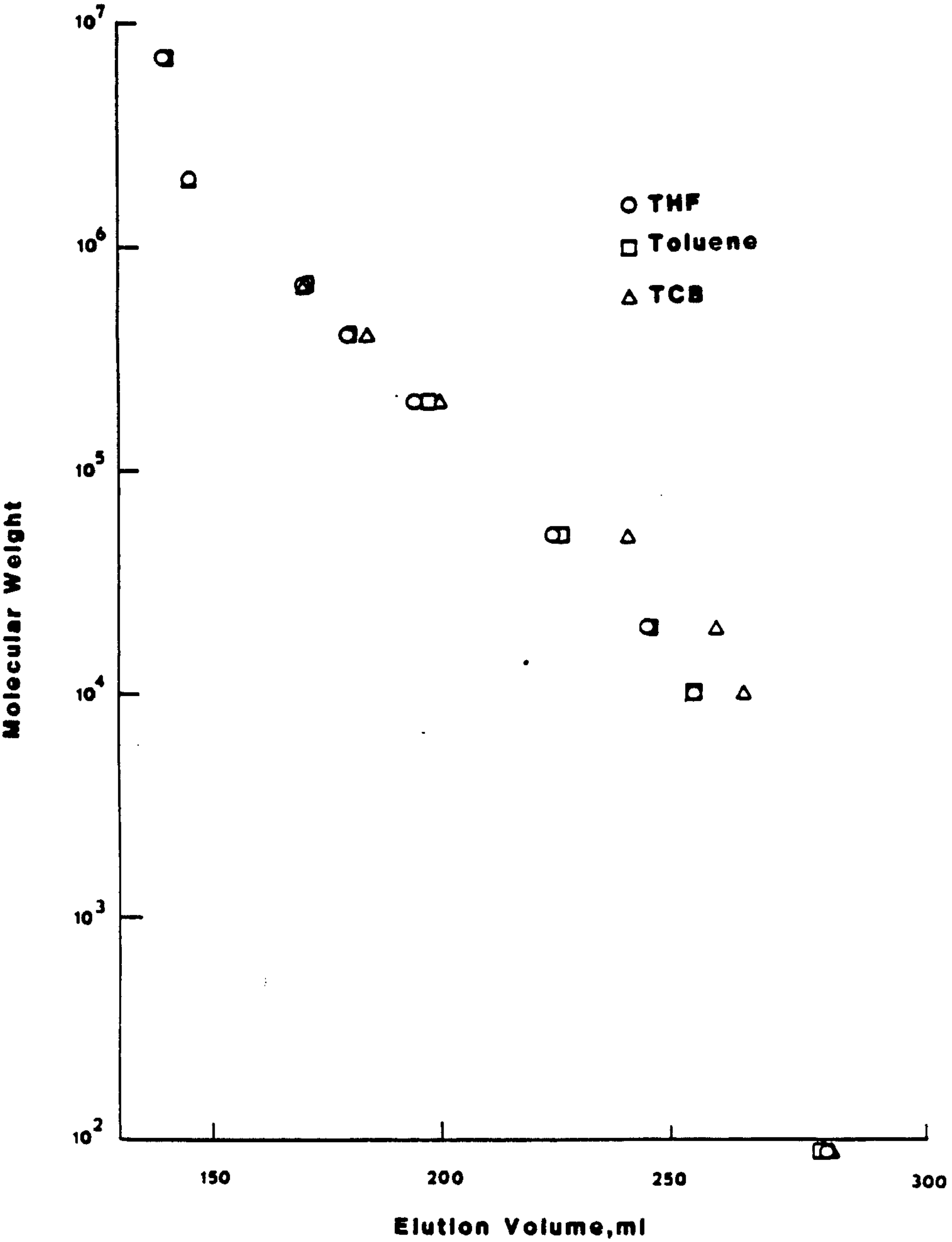

Figure 1 GPC calibration curves for Corning CPG glass columns for polystyrene, using tetrahydrofuran (THF), toluene and 1,2,4-trichlorobenzene (TCB)

TABLE 1

Calculated Molecular Weight Averages*

Solvent	Tetrahydrofuran		Toluene		1,2,4-Trichlorobenzene	
Viscosity cp @ 20°C	0.486		0.59		1.4225	
Sample	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
670,000	643,500	1.13	607,600	1.14	594,200	1.22
	(643,700	1.13)				
411,000	413,300	1.12	418,200	1.10	364,400	1.19
	(421,300	1.12)				
200,000	204,800	1.10	215,100	1.15	196,100	1.24
					(213,800	1.21)
51,000	52,260	1.11	49,580	1.14	52,310	1.20
(51,000	52,500	1.105)				
19,800	19,000	1.21	19,080	1.33	19,780	2.35
10,000	10,140	1.46	10,900	1.49	11,750	2.53

* Duplicate analyses shown in parentheses.

distribution (DMWD) is calculated (see Figure 3), a pronounced distortion of the low molecular weight end is seen.

At lower molecular weights, the distinctly different TCB calibration curve causes the chromatograms to be non-superimposable. The chromatograms for the 51,000 molecular weight polystyrene are shown in Figure 4. The peak of the chromatogram obtained using TCB solvent is displaced to higher elution volumes. When the DMWD is calculated, however, the distributions for the three different solvents are in reasonable agreement. The band broadening which occurs for all solvents has a profound effect on the number average molecular weight because the tail of the chromatogram at high elution volumes in TCB is assigned a molecular weight close to that of the solvent. This is evident in Figure 5, and is reflected in the high

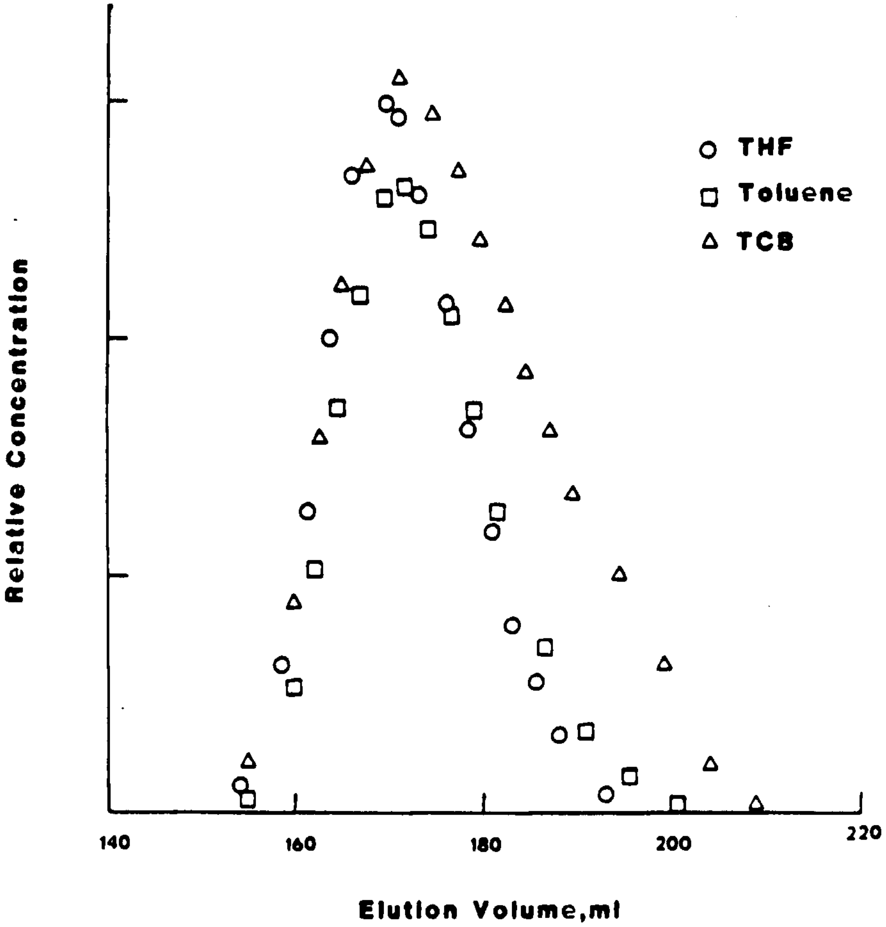

Figure 2 GPC chromatograms of polystyrene, $\bar{M}_w$ 670,000, eluted for Corning CPG glass columns, using THF, toluene and TCB

values of $\bar{M}_w/\bar{M}_n$ for TCB solvent. In Figure 4, the chromatogram in toluene extends to higher elution volume than the chromatogram obtained in THF, even though the calibration curves are superimposable.

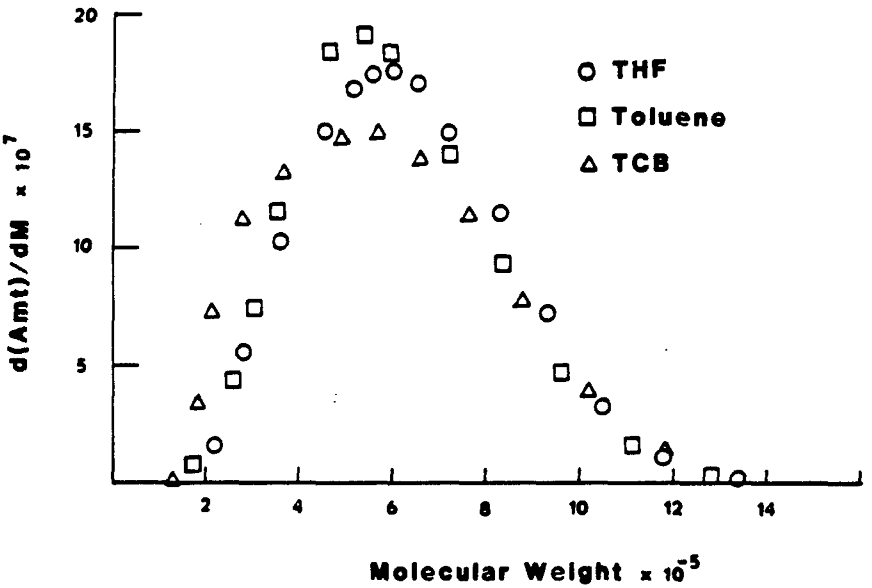

Figure 3 Differential molecular weight distribution (DMWD) of polystyrene, $\overline{M}_w$ 670,000, determined with Corning CPG glass columns, using THF, toluene and TCB

CONCLUSIONS

For Corning porous glass column packing materials, the low molecular weight end of the chromatograms extend to higher elution volumes as the viscosity of the solvent increases from THF to toluene. This causes a larger value for the ratio $\overline{M}_w/\overline{M}_n$ at any given molecular weight. Chromatograms obtained in TCB exhibit further extension to higher elution volumes for high molecular weight samples, and, at lower molecular weights, the peak of the chromatogram is shifted to higher elution volumes. At higher molecular weights, this causes the calculated values for $\overline{M}_w$ to be lower than the true values. At lower molecular weights in TCB solvent, band broadening causes a further increase in the calculated value of $\overline{M}_w/\overline{M}_n$ because of the lower molecular weight assigned to the high elution volume tail of the chromatogram.

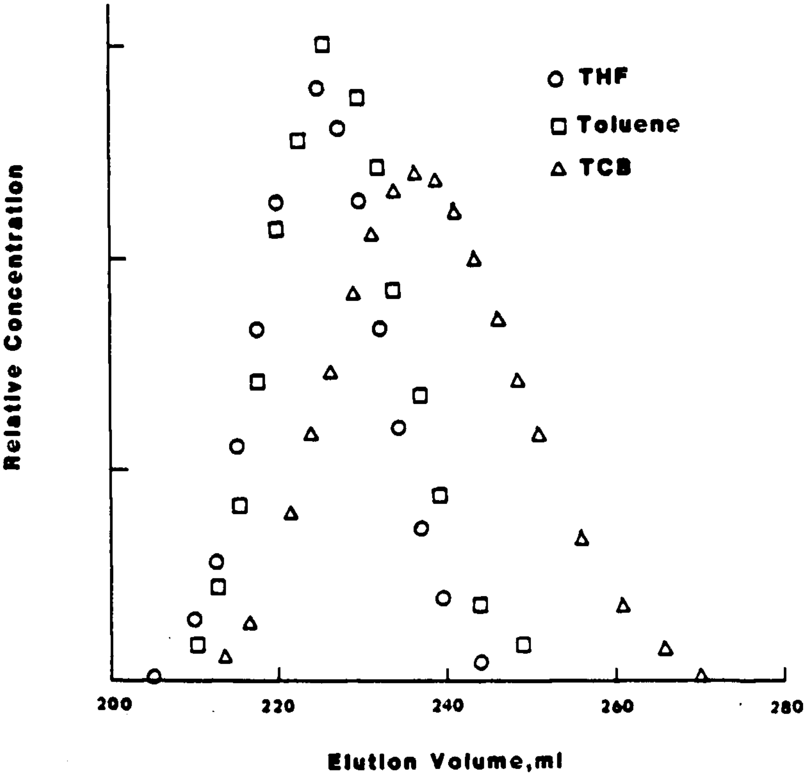

Figure 4 GPC chromatograms of polystyrene, $\overline{M}_w$ 51,000, eluted from Corning CPG glass columns, using THF, toluene and TCB

If a particular solvent of high viscosity must be employed, the use of elevated temperatures should be considered to reduce the viscosity.

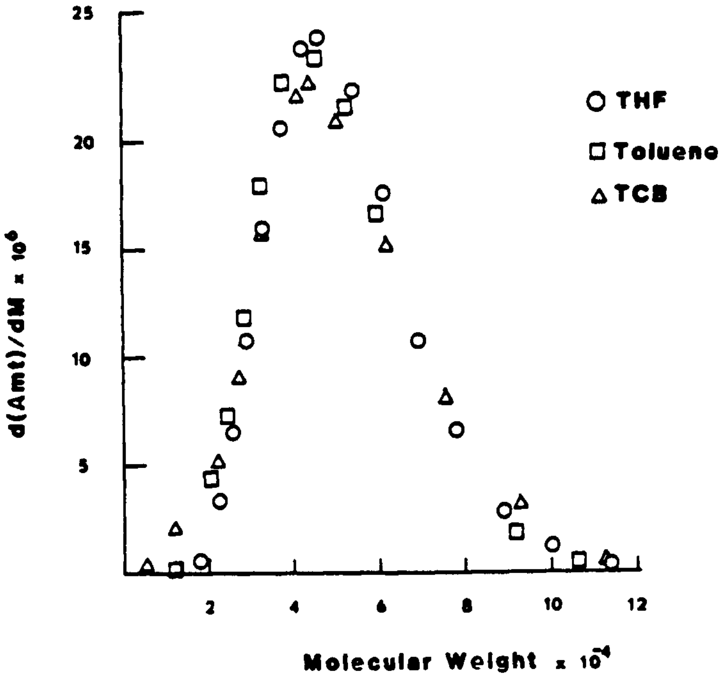

Figure 5 Differential molecular weight distribution of polystyrene, $\bar{M}_w$ 51,000, determined with Corning CPG glass columns, using THF, toluene and TCB

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