Gel Permeation Chromatography: Evaluation of Porous Glass-Column Packing Materials for Low Molecular Weight Solutes*

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Synopsis

Currently available small pore-size porous glass packing materials have been characterized as substrates for gel permeation-chromatographic separations. The elution volumes of narrow molecular weight-distribution polystyrene standards and hydrocarbon solutes have been determined using tetrahydrofuran as solvent. The results show that none has a sufficiently small pore diameter to enable low molecular weight oligomers to be separated. New smaller pore-diameter packing materials are required to enable these rigid materials to be used for separations of oligomer mixtures by GPC.

INTRODUCTION

The characterization and chromatographic properties of Corning porous glasses with pore diameters of approximately 2300 Å, 1400 Å, 790 Å, 370 Å, and 274 Å have been previously reported.[1] These are the commercial products designated CPG 10-2000, CPG 10-1250, CPG 10-700, CPG 10-370, and CPG 10-240, respectively. (Corning porous glasses are now manufactured and distributed by Electronucleonics Inc., Fairfield, New Jersey 07006.) The lower limit of separation for the CPG 10-240 was found to be ≥ 5000 for polystyrene dissolved in toluene. Some additional materials became available designated CPG 10-75, CPG 10-125, and CPG 10-175, which have pore diameters of 75 ± 10.5 Å, 124 ± 6.4 Å, and 171 ± 10.8 Å, respectively. The useful separating range has not been reported for these materials for separating synthetic polymers. The substrate CPG 10-75 was found to be useful for separation over two decades of molecular weight (polystyrene in tetrahydrofuran) 100–10,000. A search for porous glass substrates was made which will separate efficiently over the molecular weight range of 100–4000, similar to the organic gels of Heitz.[2] Corning porous glass 7930 was investigated because it has been reported to have a pore diameter of 25 Å.[3] This was calculated on the basis of cylindrical pore geometry using values of 173.2 m²/g for the surface area and 0.109

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cm³/g for the pore volume.   Additionally a sample of porous silica, with a pore diameter of 40 Å determined from the low-temperature nitrogen desorption isotherm was examined as a GPC substrate.

EXPERIMENTAL

All packing materials were treated with hexamethyldisilazane as previously reported[4] to eliminate or reduce adsorption.   Gel permeation chromatography columns were dry packed into a 6-ft U-shaped column made from ³/₈ in. O.D. aluminum tubing (0.035-in. wall).   (Corning glass 7930 was packed in stainless steel tubing ³/₈ in. O.D. (0.035 in. wall), 7 ft in length, consisting of two sections, one 4 ft and the other, 3 ft in length.)   Calibration was carried out using the narrow molecular weight distribution polystyrene standards (Pressure Chemical Co., Pittsburgh, Pa.) or hydrocarbons and the solvent was tetrahydrofuran, except for the column packed with Corning glass 7930 when toluene was used.   A Waters Associates ANA-PREP gel permeation chromatograph with a differential refractometer was used for obtaining the GPC calibrations.   Nitrogen adsorption–desorption isotherms and mercury penetration were determined for Corning porous glass 7930 as previously described.[4]

RESULTS AND DISCUSSION

The physical specifications given by the manufacturer for CPG 10-75, CPG 10-125, and CPG 10-175 are listed in Table I.   The columns packed with these materials were purged for 48 hr and then each column was calibrated using the narrow MWD polystyrene standards and the solvent at room temperature.   The calibration curves, Figure 1, plotted in the usual manner as the logarithm of the weight-average molecular weight M_w^- versus elution volume V_e.   The latter is expressed in peak counts which is the volume flowing between syphon dumps.   From these curves the useful separating ranges for polystyrenes in tetrahydrofuran for each material may be determined as follows:

Substrate	Separating range
CPG 10-75	$100 \rightarrow 10,000$
CPG 10-125	$3,000 \rightarrow 30,000$
CPG 10-175	$3,000 \rightarrow 60,000$

In view of their reported narrow pore-size distributions, it is surprising that these materials separate over such a wide molecular weight range.

TABLE I
Physical Characteristics of Corning Porous Glasses

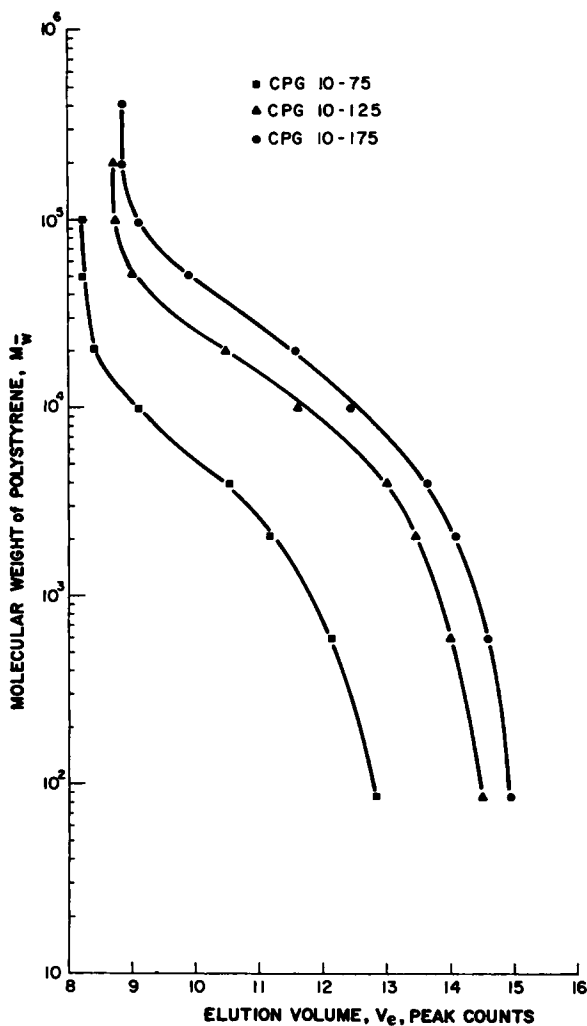| Sample	Pore diameter, Å	Pore volume, cm³/g
CPG 10-75	75 ± 10.5	0.44
CPG 10-125	124 ± 6.4	0.58
CPG 10-175	171 ± 10.8	1.07

Fig. 1. Calibration curves for Corning porous glasses using polystyrene
solutes and tetrahydrofuran solvent at 1.5 ml/min flow rate.

In order to detect any possible effect of pore size on efficiency of the
separation process, the ratio of weight- to number-average molecular
weight, M_w^-/M_n^-, has been calculated[5] for several solutes eluting from these
columns. Additionally the number of theoretical plates/ft,

$$n = \frac{1}{L}\left[\frac{V_e}{W_b/4}\right]^2$$

has also been included, where L = column length in feet, V_e = elution
volume, and W_b = peak width at the base. These values are collected in
Table II The M_w^-/M_n^- values are only meaningful when they are mea-
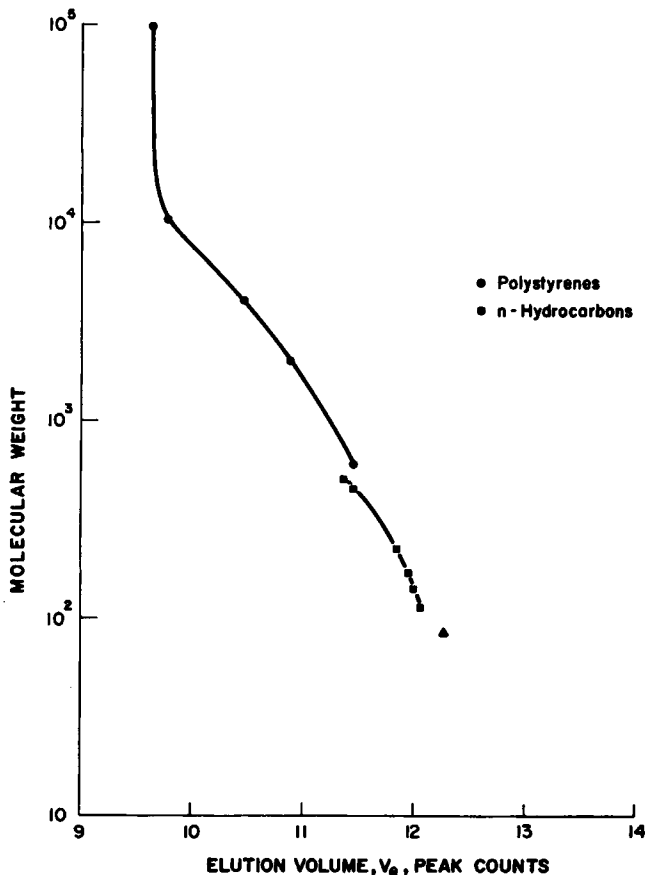sured for solutes which elute within the useful separating range of the

Fig. 2. Calibration curve for Corning glass Code 7930 for polystyrene and hydrocarbon solutes, toluene solvent at 2.41 ml/min flow rate.

column. Historically, the value of n for small solutes eluting at the total liquid volume of the column has been reported and is included here for comparison purposes. Where comparisons are possible, for the same solute analyzed on different columns, there appears to be very little difference between M_w^-/M_n^- values. This shows that the number of theoretical plates, calculated using small molecule solutes, is not a valid criterion for column efficiency when analyzing polymers. The data of Table II indicate there is no large effect of pore size on efficiency at a given molecular weight as previously reported.[6] In an attempt to define the pore diameter required for oligomer separations, we have examined Corning porous glass Code 7930. The GPC calibration curve for this material is shown in Figure 2. This was determined using polystyrene and hydrocarbon solutes dissolved in toluene and using a flow rate of 2.41 ml/min. This material is capable of performing GPC separations over the range of 100–10,000 (polystyrene molecular weights) very similar to CPG 10-75. This is surprising since previous work had indicated a pore diameter of 25.2 Å for this material

TABLE II
Experimental Values for M_w^- and M_w^-/M_n^- and the Number of Theoretical Plates n

Solute n-hexane		Column CPG 10-75 (230 plates/ft)		Column CPG 10-125 (83 plates/ft)		Column CPG 10-175 (129 plates/ft)	
$M_w^{-\text{a}}$	$M_w^-/M_n^{-\text{a}}$	M_w^-	M_w^-/M_n^-	M_w^-	M_w^-/M_n^-	M_w^-	M_w^-/M_n^-
Polystyrene							
51,000	1.06	b	b	b	b	50,360	1.39
20,400	1.06	b	b	20,200	1.21	18,300	1.21.
10,000	1.10	11330	1.35	10,840	1.30	9,840	1.34
4,000	1.10	3740	1.43	b	b	b	b
2,000	1.10	1980	2.0	b	b	b	b

a Manufacturers values.

b GPC traces not analyzed because chromatograms extend beyond upper or lower limit of the calibration curves.

(vide supra). This material is not a good packing material for GPC columns because its pore volume is small.

This material was characterized using the techniques of low-temperature nitrogen adsorption–desorption isotherms and high-pressure mercury porosimetry. The analysis of the nitrogen adsorption isotherm using the BET approach showed the surface area to be 109 m²/g. The liquid nitrogen micropore volume was found to be 0.211 ml/g which allows the average pore diameter of 77 Å to be calculated. The mercury porosimetry results showed the pore volume to be 0.194 ml/g. This, however, measures only those pores with radii greater than 21 Å and is expected to be smaller than the value obtained from the nitrogen adsorption experiment. From these results it appears the material used by us is significantly different from previous samples of this material. Additionally, from the desorption isotherm and mercury porosimetry the differential pore volume distribution may be obtained. These results are plotted in Figure 3. The agreement between the two methods is very good considering the number of experimental variables used in the computations. Both methods show a bimodal distribution of pore diameters, one centered around 40–60 Å and the other, at 80–100 Å. With these results it is readily seen why this material has similar GPC characteristics to CPG 10-75. A porous silica sample (kindly provided by Owens-Illinois, Toledo) with a narrow pore-size distribution having a pore diameter of 40 Å was examined to see if this would be capable of oligomer separations. The differential pore volume distribution is shown in Figure 4. The surface area was determined by the BET approach to be 781 m²/g, and the total pore volume was found to be 0.524 cm³/g. On the basis of cylindrical pore geometry, the pore diameter may be calculated as 26.8 Å. A column packed with this material was characterized using the following solutes: polystyrene having molecular weight 600, 2,100, 5,000, 10,000, 20,400, and 51,000 and n-hexane. All these materials eluted at the same volume, 8.3 peak counts, which for this column is equal to the void volume or interstitial volume.
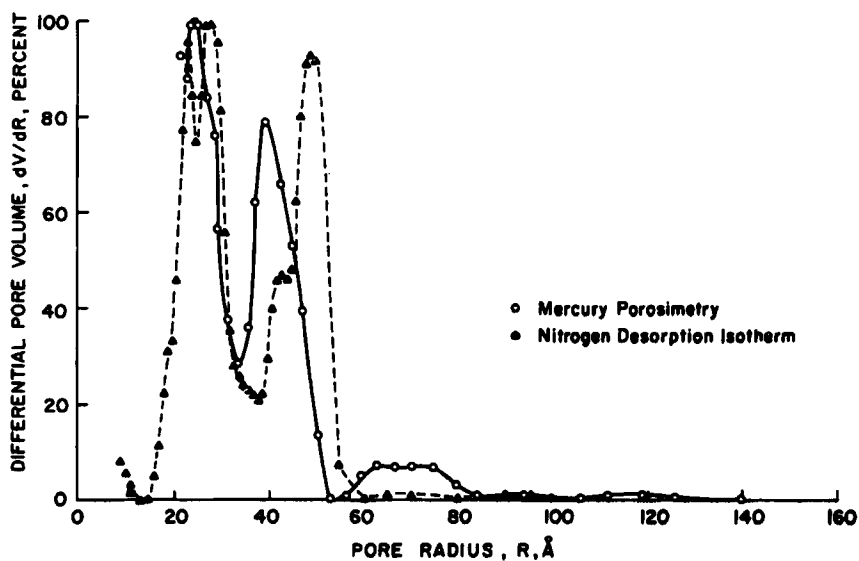
Fig. 3. Differential pore volume distribution of Corning porous glass Code 7930.
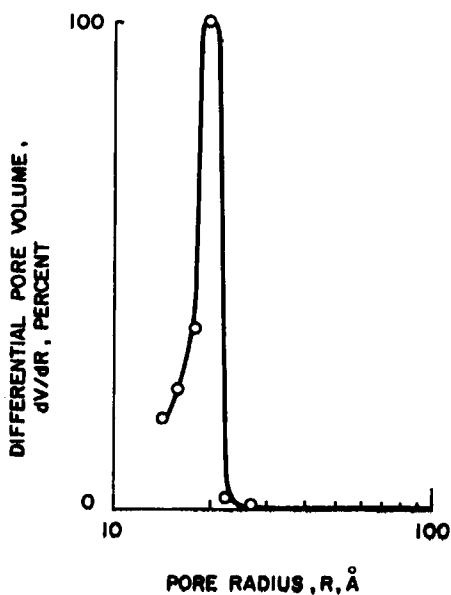

Fig. 4. Differential pore volume distribution of experimental silica.

The extended chain length of polystyrene having a molecular weight of 600 may be calculated to be 14 Å. This is approximately half of the pore diameter or one third, depending on which method of calculation is used. Even if these molecules could not enter the pore, it is surprising that n-hexane cannot enter the pore either.

CONCLUSIONS

Several porous glasses have been characterized as column packing materials for gel permeation chromatography. The molecular weight range (polystyrene) has been determined over which each of these materials will produce separation. None of these materials was found to have narrow separating ranges similar to those of porous crosslinked polymer gel materials. The latter have been shown to be capable of high-resolution separations of oligomer mixtures.

References

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