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Gel Permeation Chromatography: The Effect of Treatment with Hexamethyldisilazane on Porous Glass Packings*

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Synopsis

Porous glass column packings have been shown to be an effective substrate for gel permeation chromatography. When carbon tetrachloride is used as a solvent in conjunction with infrared detection, the porous glass exhibits adsorptive properties with polystyrene and polyisobutene. A procedure to eliminate these undesirable properties by treatment with hexamethyldisilazane has been developed. Experiments showed complete elution of all injected polymer. The treatment thus permits quantitative fractionation studies using infrared detection.

INTRODUCTION

Porous glass has been shown to be an effective column packing for gel permeation chromatography (GPC) for a variety of polymer-solvent systems.[1-4] The utility of infrared detectors for monitoring concentration of eluting polymer and measuring complete spectra for identification purposes in GPC has also been demonstrated.[4-6] Infrared detection requires the use of halogenated solvents to allow the carbon-hydrogen absorption region to be monitored. The adsorptive properties of porous glass are enhanced by these solvents. Thus, Ross and Castro[4] found inordinately large elution volumes for polystyrenes on porous glass columns using tetrachloroethylene as the solvent at 110°C even though the glass had been treated with hexamethyldisilazane and dimethyldichlorosilane. They were able to overcome this difficulty temporarily by the injection of organic silicone or highly polar compounds to block the active sites. Using untreated porous glass we found that polystyrene would not elute at 25°C using either tetrachloroethylene or carbon tetrachloride as solvents. Under these conditions, however, polyisobutenes were eluted and were, therefore, used to evaluate the effect of treating the porous glass on elution volume and column efficiency.

* Part XIX of a series on Column Fractionation of Polymers.

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Apparatus and Materials

The gel permeation chromatograph used a Perkin-Elmer Model 112 infrared spectrometer as a detector. A heated microflow cell (Carle Instruments, Inc., Anaheim, California) was modified using a Teflon spacer to increase the path length to 5 mm and width to 1.25 mm. Sodium chloride flats 3.5 mm thick were used as windows. A constant solvent flow was delivered from a pneumatic pump (Waters Associates, Framingham, Massachusetts) and regulated by adjusting the air pressure and capillary tube length on the pump exit. Flow rates were 1 ml/min. Degassing the solvent was necessary. The syphon volume was 5.6 ml. The spectrometer was operated at a wavelength of 2940 cm^{-1}. Column lengths were 4 ft of stainless steel tubing of internal diameter $^5/_{16}$ in.

The porous glass was a developmental product ("Bio-Glas," Bio-Rad Laboratories, Richmond, California) with the physical characteristics listed in Table I.

TABLE I
The Effect of Hexamethyldisilazane Treatment of Porous Glass on the Pore Structure

Method	Untreated	Treated
Nitrogen Adsorption-*Desorption Isotherms*		
BET Area, m^2/g	61.6	48.3
Liquid Nitrogen Micropore Volume, (<500 Å Pore Radius), cc/g	0.29	0.26
Mercury Porosimeter	0.50	0.47
Pore Volume, (22–67,000 Å Pore Radius), cc/g		
Macropore Volume, (500–67,000 Å Pore Radius), cc/g	0.21	0.21
Micropore Volume, (22–500 Å Pore Radius), cc/g	0.29	0.26

Hexamethyldisilazane Treatment

A convenient test for effectiveness of the hexamethyldisilazane treatment is water flotation. Completely treated porous glass will float indefinitely, partially treated sinks. The manufacturer's recommended treatment for aqueous applications is evacuation in a heated tube at 130°C under vacuum for several hours, closing off the vacuum and opening a valve to a flask containing hexamethyldisilazane. This gave incomplete blockage of the surface hydroxyl group. Method I consisted of heating under vacuum at 250°C for two hours and then opening the valve to the flask. This gave complete surface coverage. Two methods of in situ treatment were tried but were only partially successful. In Method II, a heating tape was wrapped around a packed column, evacuated at 130°C,

and the valve to the flask opened. This was repeated several times. For Method III, dry nitrogen at 0.5 ml/min was passed through the column heated to 130°C followed by six successive injections of 1-ml portions of hexamethyldisilazane through the injection septum.

Results and Discussion

The results of mercury porosimetry and nitrogen adsorption-desorption experiments are shown in Table I. Mercury porosimetry shows that the macropore volume is unaffected by the hexamethyldisilazane treatment. Micropore volume (determined by nitrogen adsorption) is decreased by ~10% after treatment. There is very little pore volume having a pore

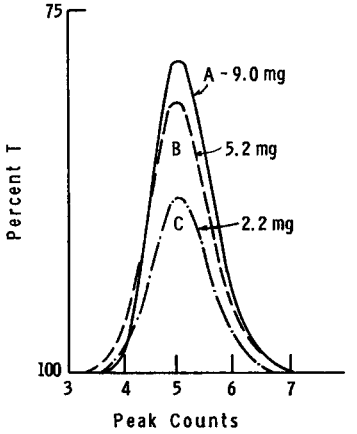

Fig. 1. Elution of standard polystyrene (molecular weight 160,000) from a porous glass column (4 ft). (*A*) Treated by Method II; (*B*) treated by Method I; (*C*) treated by Method I.

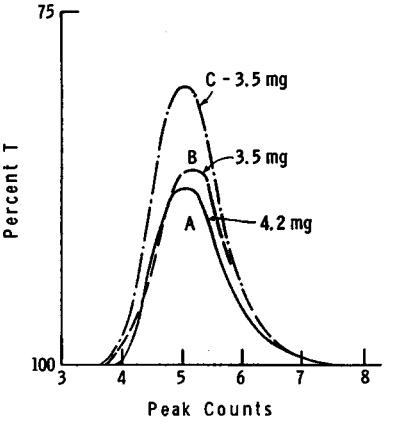

Fig. 2. Elution of a polyisobutene ($\bar{M}v$ = 78,500) from a porous glass column (4 ft). (*A*) Untreated; (*B*) treated by Method III; (*C*) treated by Method I.

TABLE II
Effect of Hexamethyldisilazane Treatment on Column Efficiency and Polymer Recovery

	Untreated Column			Treated Column			
Sample	n*	% Recovery	Figure	Treatment Method	n*	% Recovery	Figure
Toluene	173	100	3A	I	114	100	3B
Polystyrene		Did not Elute		I	86	100	1B
$\bar{M}_w$ = 160,000				II	89	65	1A
Polyisobutene	64	60	2A	I	95	100	2C
$\bar{M}_v$ = 78,500				III	83	76	2B
Polyisobutene	47	29		I	73	100	
$\bar{M}_v$ = 145,700							

* n is the number of theoretical plates for a 4 ft column.

radius of 22 Å or less, determined from the nitrogen desorption isotherm; thus, the micropore volumes from nitrogen adsorption and mercury porosimetry agree in these cases. The volume of the pores available to these polymers, which is mostly in the macropore region, is essentially identical for both the treated and the untreated columns used.

The chromatograms shown in Figures 1 and 2 are for a narrow molecular weight distribution polystyrene ($\bar{M}_w$ 160,000) and a polyisobutene fraction of $\bar{M}_v$ 78,500. The polymers were injected by displacement from a loop having a volume of 0.56 ml; and the amount of polymer injected, in milligrams, is shown on each chromatogram. A plot of concentration of injected solution versus peak area produced straight lines, passing through the origin, for each polymer eluted from the column treated by Method I.

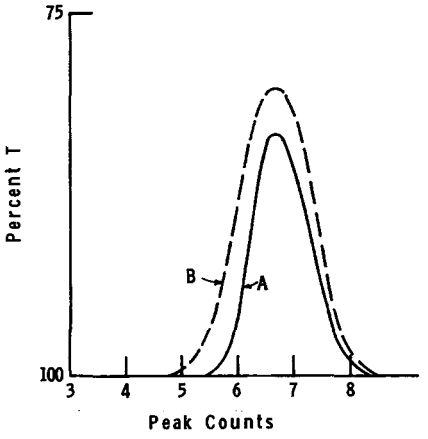

Fig. 3. Elution of toluene from a porous glass column (4 ft). (*A*) Untreated; (*B*) treated by Method I.

This proved that all of the polymer injected was eluting within the peak. Comparison of areas then allowed the percentage recovery from columns treated by other methods to be calculated. The values are shown in Table II. The number of theoretical plates per column, n, calculated from $n = (4\ Ve/W)^2$ is also shown in Table II (where Ve is the elution volume at the peak maximum and W is the distance on the base line between the points where the tangents to the inflection points cross). The results obtained using another polyisobutene fraction, $\bar{M}_v$ = 145,000, and toluene are also included in Table II.

Polystyrene ($\bar{M}_w$ = 160,000) did not elute from an untreated column but was eluted completely from a column treated by Method I, Figures 1 *b* and *c*. These figures also show that elution volume is independent of sample size and that the sensitivity attainable with infrared detection is similar to that of refractometric detection. Figure 1*a* shows the elution from a column treated by Method II; the efficiency is the same as a properly treated column, but the recovery is only 65%.

Figure 2*a* shows that on the untreated column the polyisobutene fraction, $\bar{M}_w$ = 78,500, elutes unsymmetrically with tailing and 60% recovery (Table II). Incomplete treatment by Method III increases the efficiency and recovery, Figure 2*b*. Complete treatment further increased the efficiency and allowed 100% recovery from the column, Figure 2*c*. A comparison of the recoveries from the untreated columns of the two polyisobutene fractions (Table II) shows that adsorption increases with increasing molecular weight. Thus, a whole polymer will be partially fractionated during the GPC elution; and the GPC curve will not represent the injected material. Toluene exhibits decreased efficiency when chromatographed from the column treated by Method I, Figure 3*b*, compared with the elution from an untreated column, Figure 3*a*. The peak center and end are approximately the same on both columns, but the leading edge on the treated column elutes earlier. This could result from different packing arrangements in the columns. Recovery in both cases was 100%.

Complete suppression of the adsorptive properties of porous glass towards polystyrene and polyisobutene using carbon tetrachloride solvent can be attained by correct treatment with hexamethyldisilazane. The treatment is permanent when the columns are used at room temperature.

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