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Effects of Porosity and Surface Area of Octadecyl-Derivatized Silica on Fractionations of Oligomers of 800 MW Polystyrene

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Abstract

Increasing the pore size of silica used to produce a C_{18}-derivatized column packing decreased the exclusion of the larger oligomers of an 800 MW sample of monodisperse polystyrene. More important was the decrease in surface area which degraded the fractionation of oligomers, which was based upon adsorption. Larger sample volumes and higher concentrations also degraded that fractionation, as expected.

INTRODUCTION

Fractionations of mixtures of oligomers provide very demanding tests of chromatographic columns, the associated hardware, and the separation procedures (*1*). As a result, the mixtures of oligomers found in different commercial preparations of polymers can be used advantageously to study the effects of different properties of the column packing on the separations (*2*). Specific surface area, pore size and volume, and the chemical nature of the surface are widely acknowledged to be major variables (*3*). The chemical nature of the surface is itself known to include not only the percentage and type of the organic group present, such as phenyl or octadecyl, but also the number and relative activities of the residual silanols (*1, 4*).

In our laboratory an earlier study used polystyrene samples to survey the fractionating capability of a variety of packings representing different derivatives: amino, cyano, phenyl, nitro, and octadecyl as well as silica itself

(*1*). However, those packings were obtained from a variety of suppliers and information about the extent of derivatization, endcapping, and porosity characteristics was usually missing. The importance of that missing information was emphasized later when the fractionation obtained using a new phenyl-derivatized silica was compared with that observed earlier. The second packing produced an excellent baseline fractionation of most of the oligomers from an 800 MW polystyrene sample whereas the original phenyl packing had produced only a large hump having small peaks upon it.

In the present study we have prepared packings from silica having different average pore sizes and specific surface areas. Our primary goal was to examine the effect of pore size on the resolution, particularly for pairs of the larger oligomers. However, the effects of concentration and volume of the sample as well as eluent composition and gradient steepness were also examined in an effort to find the best conditions for fractionating the oligomers of the 800 MW polystyrene.

The desirability of analyzing the packings for carbon content was recognized, but in this preliminary study, efforts have been limited to demonstrating that different batches could be made reproducibly from the same starting materials. The present study was also limited to the octadecyl derivative.

EXPERIMENTAL

Chemicals

Silica preparations having average particle sizes of 10 μm and average pore diameters of 100, 300, and 1000 Å were used (Lichrospher SI-100, SI-300, and SI-1000 from E. Merck, Gibbstown, New Jersey). According to the manufacturer, the specific surface areas were approximately 250 m^2/g for SI-100, 100 m^2/g for SI-300, and 20 m^2/g for SI-1000; the respective pore volumes were 0.8, 1.0 and 1.2 mL/g. Octadecyldimethylchlorosilane (ODCS) (Petrarch Systems, Bristol, Pennsylvania) and trimethylchlorosilane (TMS) (PCR Research Chemical, Gainesville, Florida) were used to derivatize and endcap the silica, respectively.

Two monodisperse polystyrenes, 800 and 110,000 molecular weight, were obtained from the Pressure Chemical Co. (Pittsburgh, Pennsylvania). Stock solutions of 100 mg/mL were prepared at least every 2 weeks in freshly distilled tetrahydrofuran (THF) and stored in the dark. More dilute solutions that were used as chromatographic samples were prepared each day from freshly distilled THF.

All organic solvents were obtained from J. T. Baker Chemical Co. THF (J. T. Baker Chemical Co., Phillipsburg, New Jersey) was used as a mobile phase and as a solvent for the samples. It was distilled over potassium to remove water and butylated hydroxytoluene. The later had been added to the THF as a stabilizer.

House distilled water was deionized and then distilled once again before being used as a mobile phase. Acetonitrile (ACN), methanol, and isopropanol were HPLC grade and were used without furthur purification. Toluene, benzene, pyridine, and ether were reagent grade. Nitrogen and helium were obtained from Selox Inc. (Atlanta, Georgia).

Apparatus

Two Varian Model 8500 pumps, one equipped with a solvent programmer (Varian Instrument Division, Palo Alto, California), were used to generate mobile phase gradients. Samples were introduced from loops of 2.5, 5, 10, and 25 μL by means of an air-actuated six-port valve, Model AC V-6 UHPA (Valco Instrument Co., Houston, Texas). The detector was an LC-55 variable wavelength detector (Perkin-Elmer Co., Norwalk, Connecticut) set at 265 nm. Chromatograms were recorded using a Linear Model 585 recorder.

Procedures

Preparation of packings. The procedure described in Berendsen et al. was followed (5). A weighed amount of silica support was acid-hydrolyzed before use in 0.1 *M* HCl at 90°C for at least 24 h and then thoroughly washed to neutrality with distilled water. Next, the physically absorbed water was removed by heating the silica overnight at 200°C under vacuum.

The bonding reaction was carried out under dry nitrogen in toluene that had been dried over sodium. To a mixture of 50 mL toluene, 1.8 g silica, and 4 mL pyridine (dried by CaH_2) was added a fourfold excess of octadecyldimethylchlorosilane (assuming 4 silanol groups per nm^2). This mixture was heated for 120 h at 95–105°C. Occasionally, the mixture was gently stirred using a magnetic bar or shaken carefully by hand, in each case taking care to minimize damage to the particles. The bonded packings were washed consecutively with dry toluene, dry methanol, 1:1 methanol–water, water (to remove the pyridine hydrochloride salt), methanol, and ether. Finally, the derivatized silica was dried for 12 h at 200°C *in vacuo*.

All bonded packings were then posttreated with trimethylchlorosilane in the same way as described above except that the reaction temperature was 45–50°C.

Column Preparation. A weighed amount of dry packing material was added to the column packer (Micromeritics, Norcross, Georgia) followed by 1:1 isopropanol–methanol and a magnetic stirring bar. A Varian 8500 pump was used to force the suspension into a 0.46-cm i.d. × 10 cm 316 stainless steel column using pure isopropanol as the medium. Then the medium was changed to freshly distilled THF before removing the column for storage or use.

Chromatography. Unless otherwise stated, all fractionations involving adsorption of the oligomers were performed using a starting composition of 1:1 THF/water, an increasing gradient of 0.2% THF/min, and a flow rate of 60 mL/h. The steric-exclusion experiments were performed in pure THF using a 10-μL sample of 2 mg/mL and eluting with pure THF at a flow rate of 10 mL/h.

RESULTS

Preliminary Exeriments

A test of the reproducibility with which derivatizations could be done is shown in Fig. 1. The features of primary concern were the shape and height of the underlying "hump" and the absence of a peak produced when pure THF was passed through the column. Such a peak, one of which is shown in Fig. 2, indicated that active silanols were present. Pure THF was required to desorb the last traces of polystyrene. (The higher hump in Fig. 2 was apparently the result of using a large sample, as discussed below.)

It is worth noting that the active silanols resulted from the addition of the trimethylchlorosilane to a hot suspension rather than to a cold one. Fortunately, after the packing had been removed and treated properly with endcapping reagent, the resulting column showed no evidence of either a final desorption peak for polystyrene at 100% THF or a degraded separation of the higher oligomers in its chromatograms obtained under the same conditions as before.

Effect of Sample Volume and Concentration

In Fig. 3, Curves a, c, d, and b show that as the sample volume increased, the height of the hump increased, especially at the higher molecular weight

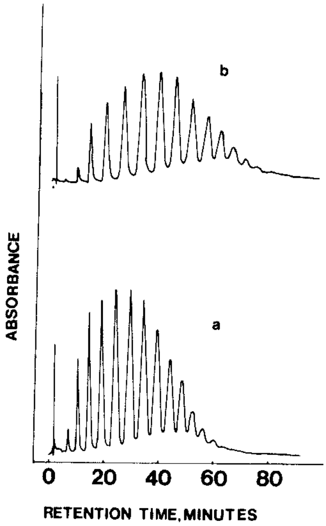

FIG. 1. Reproducibility of derivatizing two portions of Lichrospher-100 Å as indicated by the fractionation of 800 MW polystyrene. Starting solvent 1:1 THF/water; gradient, 0.2% THF/min at 60 mL/h; sample, 2.5 μL of 100 mg/mL polystyrene.

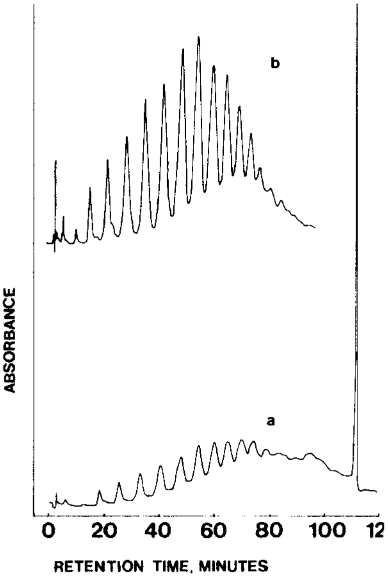

FIG. 2. Effect of incomplete endcapping on the fractionation of 800 MW polystyrene. Same conditions as Fig. 1 except a sample size of 5.0 μL. (a) Before second endcapping. (b) After second endcapping.

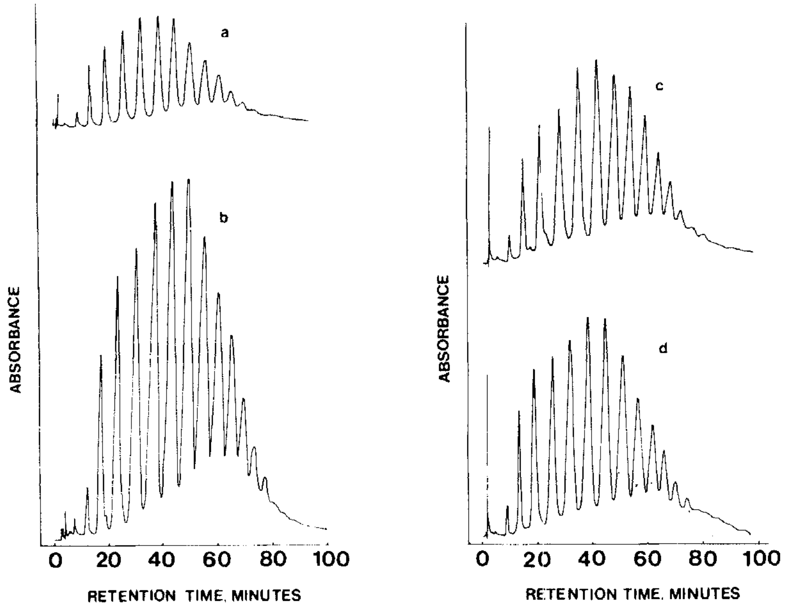

FIG. 3. Effect of sample volume on the fractionation of 800 MW polystyrene using all other conditions that were used in Fig. 1. (a) 2.5 μL; (b) 25.0 μL; (c) 5.0 μL; (d) 10.0 μL.

end. As expected, when the volume was held constant but the sample concentration changed, a similar effect was found, and the curves were very similar to those in Fig. 3. However, to illustrate that effect we have chosen to show the corresponding data for the 300 Å column (Fig. 4). Note that the hump for the most concentrated sample, 4d, was not only much larger than those for the other concentrations, but also larger than the corresponding sample, 3b, on the 100 Å column. This suggested that the smaller specific area of the 300 Å packing was the important factor.

Effect of Specific Surface Area and Pore Size

The original reason for using different pore sizes was to decrease any contribution to the hump as a result of steric exclusion of the larger oligomers. In that case, the hump should have decreased as the pore size increased. Figure 5 shows that exactly the opposite was true. Furthermore, the hump began at a smaller oligomer for the largest pore size. Hence the smaller specific surface area of the larger pore packings must have been the controlling factor.

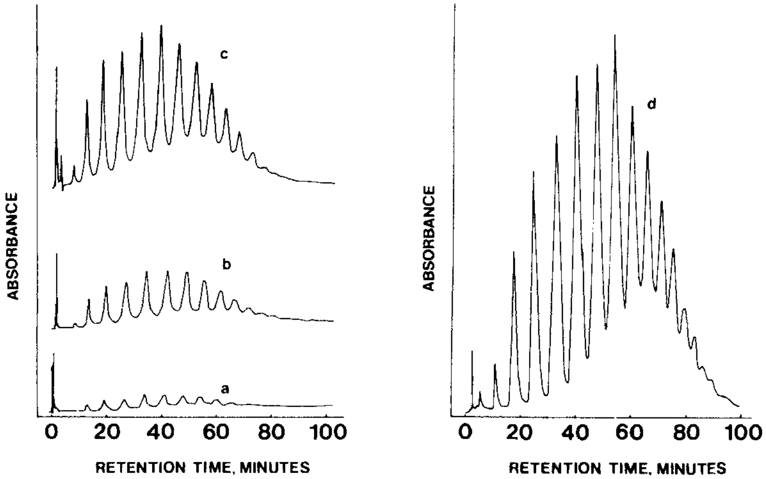

FIG. 4. Effect of sample concentration and pore diameter on the fractionation of 800 MW polystyrene using Lichrospher-300 Å with a sample volume of 25 μL and other conditions the same as Fig. 1. (a) 5 mg/mL; (b) 20 mg/mL; (c) 50 mg/mL; (d) 100 mg/mL.

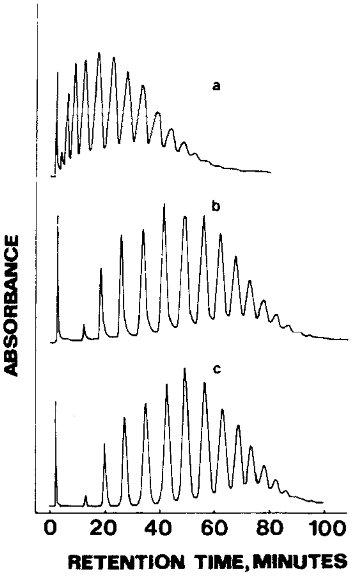

FIG. 5. Effect of pore size on the fractionation of 800 MW polystyrene using a 10-μL sample of 50 mg/mL polystyrene and the same starting solvent and gradient as Fig. 1 but at a flow rate of 40 mL/h. (a) 1000 Å; (b) 300 Å; (c) 100 Å.

That conclusion was confirmed by performing a series of steric exclusion experiments using pure THF as the eluent and 110,000 MW polystyrene and benzene to estimate the interstitial volume and the total liquid volume in the column, respectively. No correction was calculated for the dead volume of the system. Table 1 shows that the 800 MW molecular weight polystyrene was excluded to a significant extent by the 100 Å material and to a lesser extent by the 300 Å material. Although the exclusion effect was qualitatively in the correction direction, the internal volumes calculated from Table 1 (0.74, 0.67, and 0.35 mL) did not agree well with the pore volumes provided by the manufacturer (1.2, 1.0 and 0.8 mL/g) for the 100, 300, and 1000 Å silica. Derivatization of the surfaces of the pores undoubtedly accounted for a large fraction of the discrepancy in each case (*6*, *7*).

Effect of Rate of Gradient Change

The expected result, a smaller hump for a slower change, was observed as shown in Fig. 6. However, it should be noted that the longer elution time required for the slower gradient resulted in the disappearance of oligomer 14 in Fig. 6(a).

Effect of Eluent Composition

The effect of a change in solvent was examined by adding acetonitrile to the THF used as the eluent. In each case the starting solvent strength was calculated to be same as in the preceding chromatograms. However, no attempt was made to keep the rate of change the same during the elutions.

TABLE 1

Retention Times and Volumes in Size Exclusion

Column	Polystyrene 110,000 MW	Polystyrene 800 MW	Benzene
C_{18}-Si-100 Å	3.8 min 0.63 mL	7.4 min 1.23 mL	8.2 min 1.37 mL
C_{18}-Si-300 Å	4.8 min 0.80 mL	8.4 min 1.39 mL	8.8 min 1.47 mL
C_{18}-Si-1000 Å	6.7 min 1.12 mL	8.8 min 1.47 mL	8.8 min 1.47 mL

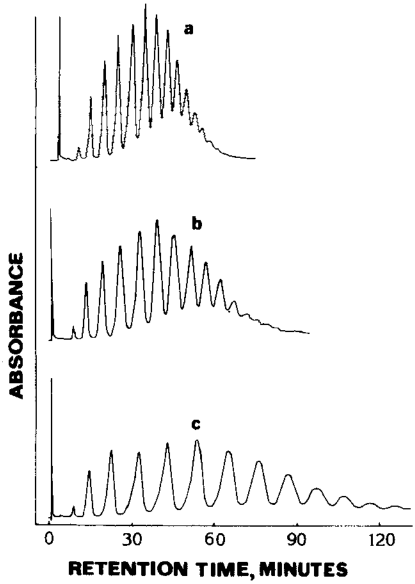

FIG. 6. Effect of the THF gradient on the fractionation of 800 MW polystyrene using a 25-μL sample of 25 mg/mL polystyrene, a starting solvent of 1:1 THF/water, and derivatized Lichrospher-100 Å. (a) 0.3% THF/min; (b) 0.2% THF/min; (c) 0.1% THF/min.

The curves in Fig. 7 have been selected from a larger series that showed the following behavior. The hump first shifted to lower molecular weights and then it started as a whole to decrease. Furthermore, as shown in Fig. 8, acetonitrile, in the absence of the THF, clearly produced shoulders due to the early stages of isomer fractionation.

DISCUSSION

An increase in pore diameter had the expected effect in steric exclusion experiments. However, the surface area, which decreased as pore size increased, appeared to be the overriding factor that influenced the relative height and width of the underlying hump. This implies that, when the molecular weight of the sample is larger, the pore size should be larger so as to minimize exclusion effects (*8*). However, because of the concomitant decrease in specific surface area, the amount of solute should be smaller so as to minimize the possibility of overloading the column. Unfortunately, the use of smaller samples makes the detection problem more difficult.

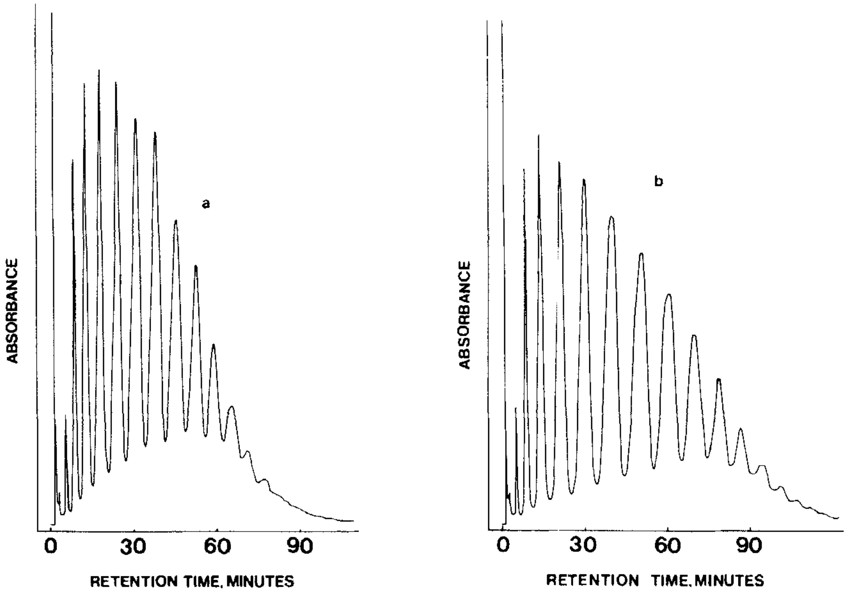

FIG. 7. Effect of substituting acetonitrile for some THF and water while using the fractionation at the same initial solvent strength and using a 25-μL sample of 100 mg/mL of polystyrene and a derivatized Lichrospher-100 Å packing. (a) 37.8% THF/16.2% acetonitrile/46% water and a gradient of 0.2%/min of 70% THF/30% acetonitrile. (b) 29% THF/29% acetonitrile/42% water and a gradient of 0.2%/min of 1:1 THF/acetonitrile.

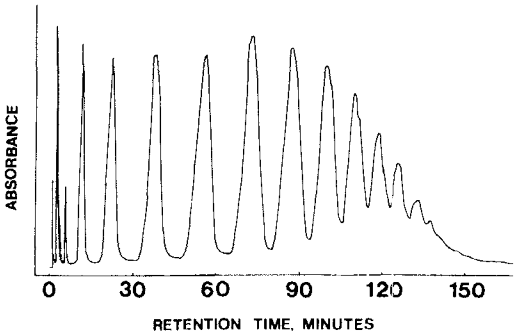

FIG. 8. Effect on the fractionation of substituting acetonitrile for THF using the same initial solvent strength of 7:3 acetonitrile/water and a gradient of 0.2% acetonitrile/min; other conditions were the same as in Fig. 7.

The effects of other more widely recognized factors were also clearly evident. Clearly, the best conditions for a fractionation would include a small sample volume and as low a concentration as permitted by one's ability to detect the oligomers. A slower change in gradient while providing a better fractionation also increases the detection problem as confirmed in Fig. 6(a).

Another factor that needs to be mentioned is the column length. If one compares curves from an earlier study (*1*) made under the same conditions as those reported here, the earlier separation will be seen to be better. In that case, a 25-cm rather than a 10-cm column was used. (A length of 10 cm was chosen for the present study so as to conserve silica.) Hence a shorter column length decreases the resolution in a way that contributes to the hump near the high molecular weight end rather than producing a uniformly high baseline under the oligomers.

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