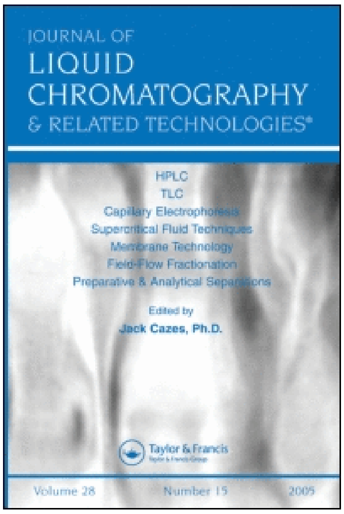


Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Experimental Study of Model Bonded Stationary Phases for Liquid Chromatography II. Silica/Polystyrene

J. Lecourtier[a b]; R. Audebert[a b]; C. Quivoron[a b]
[a] E.S.P.C.I. 10, Paris Cedex 05, France [b] Laboratoire de Physico-Chimie Macromoléculaire de l'Université, Pierre et Marie, Curie

To cite this Article Lecourtier, J. , Audebert, R. and Quivoron, C.(1978) 'Experimental Study of Model Bonded Stationary Phases for Liquid Chromatography II. Silica/Polystyrene', Journal of Liquid Chromatography & Related Technologies, 1: 4, 479 — 490
To link to this Article: DOI: 10.1080/01483917808060013
URL: http://dx.doi.org/10.1080/01483917808060013

JOURNAL OF LIQUID CHROMATOGRAPHY, 1(4), 479-490 (1978)

EXPERIMENTAL STUDY OF MODEL BONDED STATIONARY PHASES FOR LIQUID CHROMATOGRAPHY

II. SILICA/POLYSTYRENE

J. Lecourtier, R. Audebert and C. Quivoron

E.S.P.C.I. 10, rue Vauquelin 75231 - Paris Cedex 05, France.
Laboratoire de Physico-Chimie Macromoléculaire
de l'Université Pierre et Marie Curie.

ABSTRACT

Mechanisms of separations performed on bonded phases in liquid chromatography are investigated by studying model grafted phases.

These phases are prepared by reaction of chlorinated silica with living anionic polystyrene of various molecular weights. Owing to thermodynamic predictions, an expression of the elution volume of various solutes on such packings and conditions for reverse-phase chromatography are proposed.

INTRODUCTION

Several recent reviews have emphasized the increasingly important part played by chemically bonded phases in liquid chromatography(1-6). However, only few papers report the study of retention mechanisms on such bonded phases.

Recently, we studied the retention behavior(7) of a series of chemically bonded phases obtained by condensation of polyethylene-oxides of various molecular weights with porous silica. The results stressed the importance of the sizes of bonded molecules and of the solute, and the interactions between these molecules and solvent.

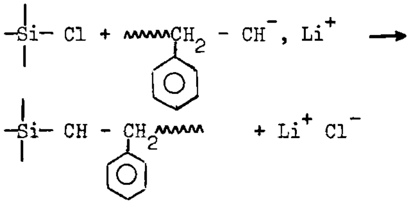
Non-polar bonded phases are frequently used in a broad range of separation problems. In order to generalize our previous results and to elucidate mechanisms involved in reverse-phase chromatography, we have studied the chromatographic behavior of silica chemically bonded with polystyrene chains.

MATERIALS

Preparation and Characterization of model bonded phases.

The silica support employed is silica gel Merck Si 60(7).

Living anionic polystyrene is deactivated on chlorinated silica, following the reaction :



A grafting method based on a similar principle was elaborated by Donnet and Al(8-10).

Silica is heat treated at 400°c under vacuum for 16h. Then it is mixed with an excess of thionyl chloride. The mixture is refluxed for 8h and free thionyl chloride is removed by distillation.

Chlorinated silica is added, at 0°c, to a benzene solution of anionically polymerized living polystyrene. Polymerization is initiated by n-butyllithium. An excess of living polymer is necessary. Usual precautions for anionic polymerization of styrene are required : solvent and glassware have to be carefully dried. Reaction between silica and polystyrene is performed under nitrogen. After several hours, the silica is extracted in a soxhlet with tetrahydrofuran.

Bonded polystyrenes are assumed to have the same molecular weight as polystyrene which did not react with silica. For our three bonded phase samples, molecular weight of polystyrene was measured by gel permeation chromatography : $\bar{M}$ = 1000, 8000 and 50 000.

A thermogravimetric study, confirmed by an elemental analysis, gives bonded silica loading τ, ratio of the weight of bonded polystyrene to the weight of grafted silica.

Specific surface, s, and porous volume, V_p, of each prepared support, were measured by nitrogen adsorption(11). Results are given in table 1.

Unexpectedly, grafting of 1g of polymer (i.e. 0,9 cm^3), led to a 5 cm^3 decrease in porous volume. The chemical nature of the

Table 1: Specific surface and porous volume of silicas bonded with polystyrene.

Nature of support	s m^2/g	V_p cm^3/g	τ
SI 60	345	0,58	0
SI 60-(PS 1000)	60	0,15	8 %
SI 60-(PS 8000)	50	0,09	10 %
SI 60-(PS 50 000)	145	0,37	5 %

bonded phases does not account for such behavior. (For instance, specific surface and porous volume of styrene-divinylbenzene supports can be measured by the technique of nitrogen adsorption (12-13)). Therefore,this unexpected decrease of porous volume and specific surface with τ is readily explained by assuming that the polystyrene chains are mainly bonded outside the silica pores. In this way, at-195°c, the grafted chains prevent nitrogen molecules from penetrating into the pores.

Apparatus and experimental conditions.

A liquid chromatograph, Waters Associates model 201, was used throughout these experiments(7).

For polystyrene grafts of molecular weight $\bar{M}$ > 8000, swelling of bonded silica is observed in good solvents such as tetrahydrofuran or chloroform. Therefore, chromatographic columns (1'x1/4"O.D.) were slurry packed.

EXPERIMENTAL

As for pure silica and silica bonded with polyethyleneoxide(7), adsorption occurs for macromolecular solutes in poor solvents. Conversely, in good solvents solutes are eluted in decreasing order of molecular weight.

Systems leading to adsorption on pure silica.

Polystyrene solutes are adsorbed on pure silica in decalin (fig. 1). For silica bonded with polystyrene $\bar{M}$ = 1000, retention volumes of polystyrene solutes slightly decrease with their size. If the molecular

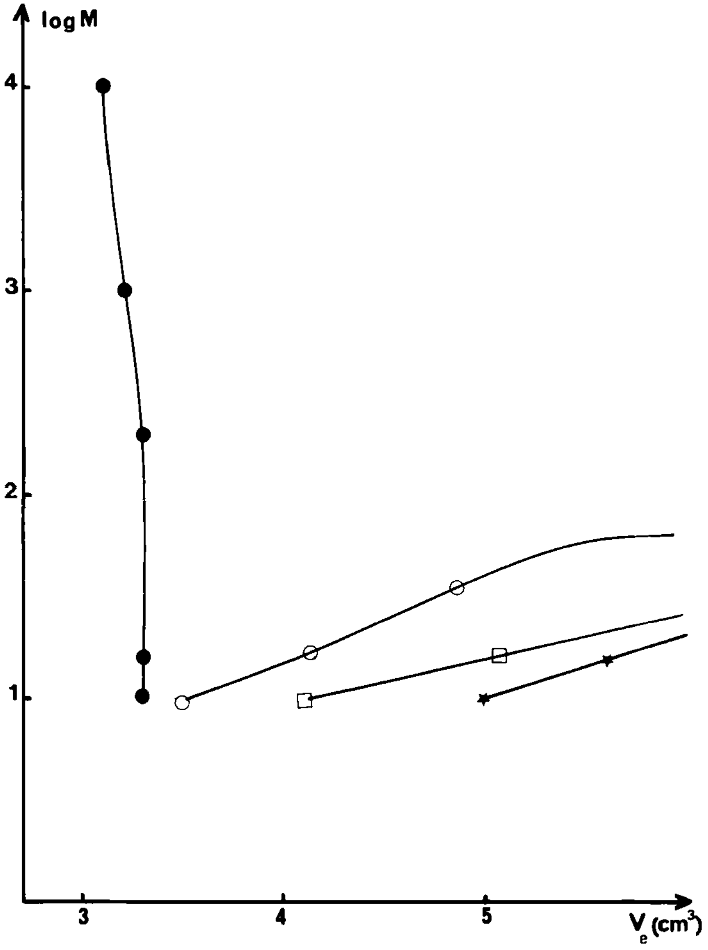


FIGURE 1

Elution volume (V_e) of polystyrenes (molecular weight M) by decalin on pure silica Si - 60 (○) and silicas bonded with polystyrene. (Molecular weight of the graft : 1000 (●), 8000 (□) and 50 000 (✱)).

weight of grafts is 8000 or 50 000, elution volumes of polystyrene solutes increase with their molecular weights. As depicted in figure 1, retention is stronger on silica bonded with polystyrene $\bar{M} = 50\ 000$ than on pure silica.

Similar results are obtained by eluting polyethyleneoxides with methanol but retentions are lower.

Adsorption on silica, steric exclusion effect in silica pores and selective dissolution into the grafted phase(14) are simultaneously occuring.

For this last mechanism, a theoretical expression of the K_D partition coefficient of a solute between a macromolecular grafted phase and a solvent was proposed from our thermodynamical study(7,14).

$$\text{Log}\ K_D \simeq -r_2\left(\frac{1}{r_1}-\frac{1}{r_3}\right)\phi_3 - \frac{(\phi_3^{1/3}-\phi_3)}{2}\frac{r_2}{r_3} + \text{Log}\left(1-\frac{r_1}{r_3}\phi_3\right)r_2 + \chi_{12}\frac{r_2}{r_1}\phi_3$$

$$+\ \chi_{13}\frac{r_2}{r_1}\phi_1\phi_3 - \chi_{23}r_2\phi_3 - \frac{\phi_3^{4/3}\sqrt{\frac{2}{3\pi}\frac{r_1\,r_2^2}{r_3^3}}}{\text{erf}\sqrt{\frac{3}{2}\frac{r_1}{r_3}\phi_3^{2/3}}}\,e^{-(\frac{3}{2}\frac{r_1}{r_3}\phi_3^{2/3})} + \qquad [1]$$

$$\text{Log}\left[\text{erf}\left(\phi_3^{-1/3}\sqrt{\frac{r_3}{r_2}\frac{3}{2}}\right)+\sqrt{\frac{2}{3\pi}\frac{r_2}{r_3}}\,\phi_3^{1/3}\left(e^{-(\frac{3}{2}\frac{r_3}{r_2}\phi_3^{-2/3})}-1\right)\right]$$

and : [2]

$$\text{Log}\ (1-\phi_3) + \phi_3\left(1-\frac{r_1}{r_3}\right) - \text{Log}\left(1-\phi_3\frac{r_1}{r_3}\right) + \frac{r_1}{2r_3}\left(\phi_3^{1/3}-\phi_3\right)$$

$$+\left(\text{erf}\sqrt{\frac{3}{2}\frac{r_1}{r_3}\phi_3^{2/3}}\right)^{-1} e^{-\frac{3}{2}\frac{r_1}{r_3}\phi_3^{2/3}}\sqrt{\frac{2}{3\pi}\left(\frac{r_1}{r_3}\right)^3}\,\phi_3^{4/3} + \chi_{13}\phi_3^{2} = 0$$

r_1, r_2, r_3 are the segment numbers of identical volume constituting respectively, a solvent, a solute and a grafted polymer molecule. ϕ_3 is the volume fraction of grafted molecules in the stationary phase. χ_{ij} are the Flory's interaction parameters which can be expressed in terms of solubility parameters(15).

For usual values of these parameters, K_D is smaller than 1 and it increases as the molecular weights of solutes decrease. However, for solutes having stronger affinity for grafted polymer than for solvent (i.e. $\chi_{23} - \chi_{12} \ll 0$), the relationships we proposed (14) show that K_D can be greater than 1. Then, it increases with solute molecular weights (solvophobic effect). Such an evolution can be observed for graft-solute interactions, and is found to be especially strong as molecular weight of bonded molecules is decreased.

These predictions are confirmed by our experimental results : K_D is greater than 1 for silica bonded with polystyrene $\bar{M}$ = 50 000. It follows that retention of polystyrene in decalin is stronger on this packing than on pure silica (figure 1). For grafted polystyrenes $\bar{M}$ = 8000 or $\bar{M}$ = 1000, the variation log M = f(V_e) arises from the superposition of an adsorption curve and a dissolution curve(K_D < 1).

Systems leading to any adsorption on pure silica.

The retention characteristics of polystyrenes and n-alkanes of various molecular weights on our model bonded phases, were first studied.

As shown in figure 2, exclusion limit and retention of solutes increase as the molecular weights of grafted molecules increase. The same holds true for elution of polyisobutenes by chloroform or polyethyleneoxides by dimethylformamide.

Conversely, for solvents having weak affinity for both solute and graft, the influence of the bonded-molecule size is reversed. Thus, the retention of alkanes and polystyrenes in dimethylformamide increases as the molecular weight of grafted polystyrene varies from 1000 to 50 000 (figure 3).

The influence of the nature of the solvent depends upon the length of grafted molecules. Thus, elution volumes of alkanes and polystyrenes on silica bonded with polystyrene $\bar{M}$ = 1000, are larger in dimethylformamide (poor solvent) than in tetrahydrofuran or chloroform (good solvent). The elution order is inverted for grafted polystyrene $\bar{M}$ = 50 000.(Compare figure 2 and 3).

Swelling of polystyrene-bonded silica by a good solvent for this polymer, and measurements of apparent porous volumes by liquid nitrogen adsorption show that polystyrene is mainly grafted outside the

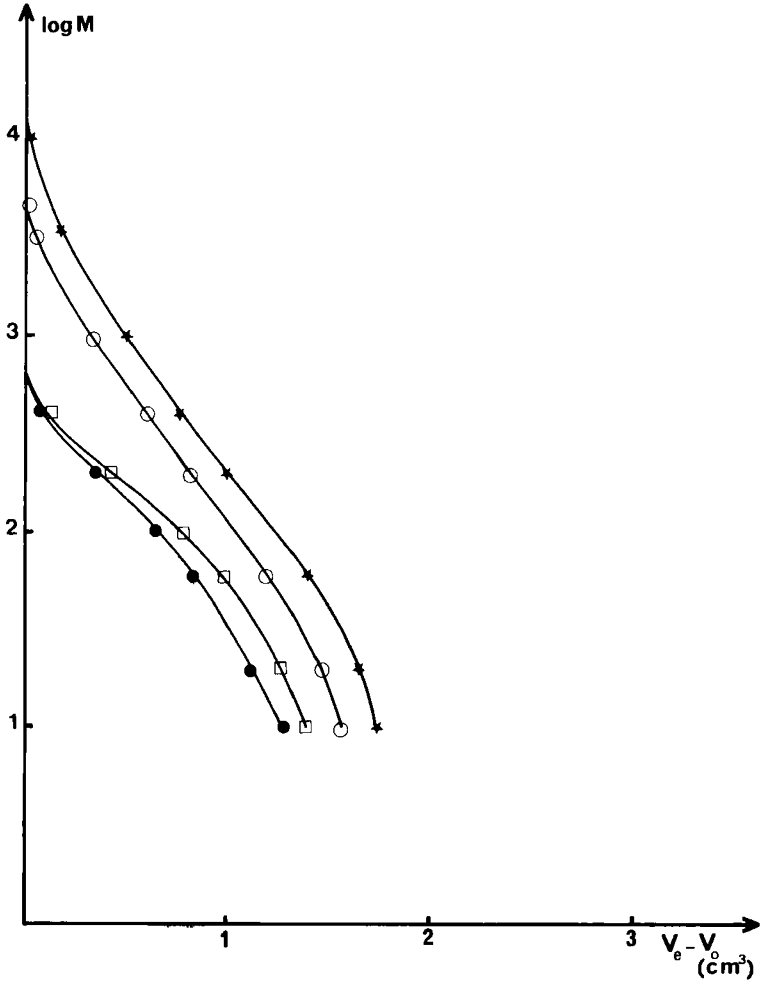


FIGURE 2

Elution volume (V_e) of polystyrenes (molecular weight M) by chloroform on pure silica Si - 60 (○) and silicas bonded with polystyrene. (Molecular weight of graft : 1000 (●), 8000 (☐) and 50 000 (✱). (V_o : dead volume of the column).

pores of the silica. The bonded chains prevent the direct access to the pores and solutes have to become dissolved into the grafted phase before penetrating into these pores (figure 4).

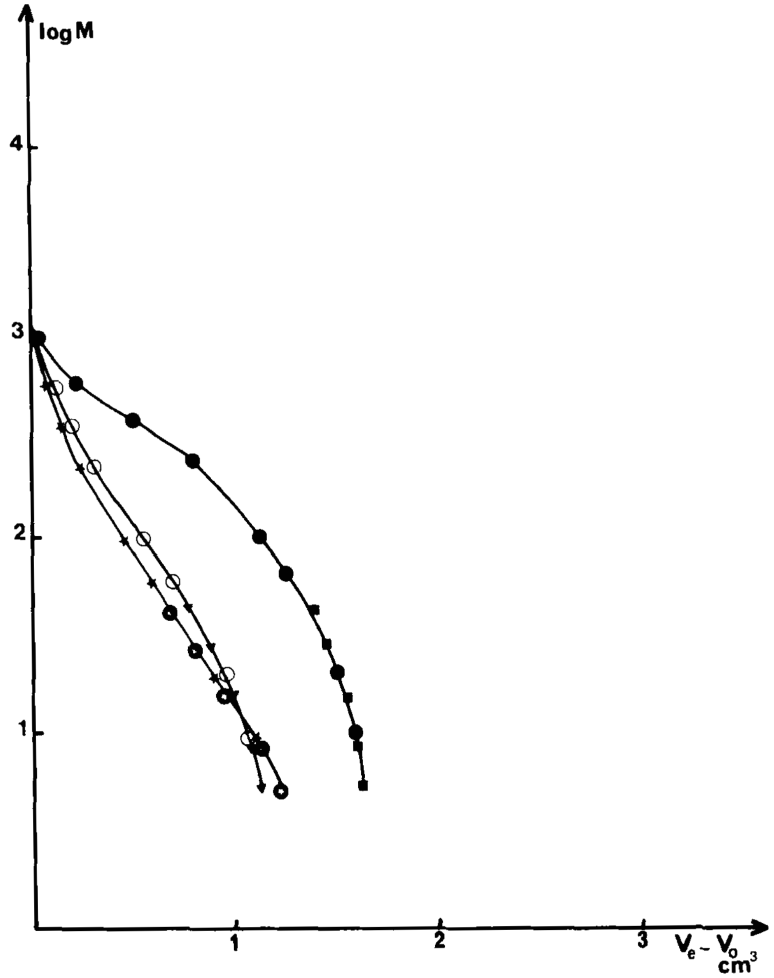


FIGURE 3

Elution of polystyrenes (PS) and alkanes (Alk) by dimethylformamide on silica bonded with polystyrene $\bar{M}$ = 1000 (PS (●), Alk (■)), $\bar{M}$ = 8000 (PS (○), Alk (▼)) and $\bar{M}$ = 50 000 (PS (✶), Alk (✪)).

As a result, a double equilibrium occurs :

$$\text{solution in mobile phase} \;\underset{\longleftarrow}{\overset{K_D}{\longrightarrow}}\; \text{solute in grafted phase} \;\underset{\longleftarrow}{\overset{K^1_{GPC}}{\longrightarrow}}\; \text{solute inside the pores}$$

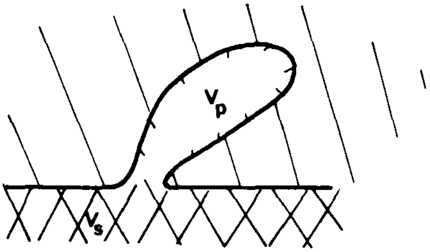


FIGURE 4

Scheme of a silica-polystyrene support.

- K_D is the partition coefficient between the swelled grafted phase and the solvent.
- K^1_{GPC} is the partition coefficient by steric exclusion effect in silica pores.

The volume involved in the separations is $(V_p + V_s)$ and elution volume V_e can be expressed as :

$$V_e = V_o + \bar{K}\,(V_p + V_s) = V_o + \frac{\bar{C}_2^{\,s+p}}{C_2^m}\,(V_p + V_s)$$

$\bar{C}_2^{\,s+p}$ is the average concentration of solute in the volume $(V_p + V_s)$ and C_2^m, the solute concentration in the mobile phase. $\bar{K}$ is the average coefficient.

Hence :

$$V_e = V_o + \frac{C_2^s\,V_s + C_2^p\,V_p}{C_2^m} = V_o + K_D\,V_s + K_D\,K^1_{GPC}\,V_p \qquad [3]$$

According to equations [1] and [2], K_D can be calculated for grafted molecules of molecular weight 1000, 8000 and 50 000. With good solvents for both solute and stationary phase $(\chi_{12}=\chi_{13}=\chi_{23}=0)$ curves log M = f(V_e) with M = 100.r_2 are plotted in figure 5, for a weight of support corresponding to our experimental conditions.

Comparison of figures 2 and 5 shows that theoretical and experimental curves are in good agreement. Solutes with molecular weight higher than 4000 are completely excluded of silica and $K^1_{GPC} = 0$. Equation [3] leads to $V_e - V_o = K_D\,V_s$. Hence, the exclusion limit of bonded silicas only depends on a dissolution phenomenon. It is especially high as the graft size increases.

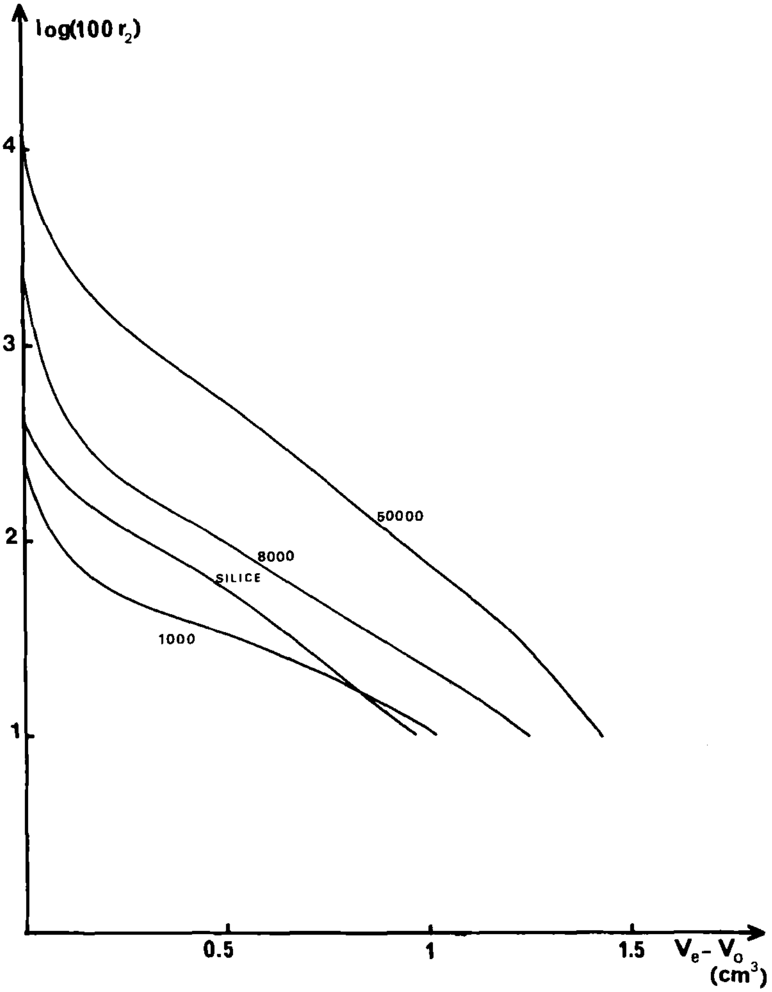


FIGURE 5

Theoretical curves log M = f(V_e - V_o) for silicas bonded with polystyrenes of various molecular weight ($\chi_{12}=\chi_{13}=\chi_{23}=0$).

Equations [1] and [2] indicate that, as solutes' affinity towards solvent decreases, retention volumes also decrease for high molecular weight grafts and, conversely, they increase for low molecular weight grafts.

The K_D expression predicts an amplitude of V_e variations especially high as the molecular weight of grafts increases (14). This is experimentally observed for chloroform/polystyrene and dimethylformamide/polystyrene systems, in the case of grafted polystyrene $\bar{M}$ = 50 000 and $\bar{M}$ = 1000 (figure 2 and 3). However the observed evolution is less important than theoretically presumed. This is not surprising, because our theory assumes interaction parameters to be independent of polymer sizes (14). In fact, dimethylformamide is certainly a better solvent for polystyrene $\bar{M}$ = 1000 than for polystyrene $\bar{M}$ = 50 000. Thus, retention volumes may be very small on a grafted polystyrene $\bar{M}$ = 50 000, smaller than on a grafted polystyrene $\bar{M}$ = 1000.

CONCLUSION

Comparison between silicas bonded with polystyrene and previously studied (7) silicas bonded with polyethyleneoxide, shows the importance of the grafting method. With melt polymer (polyethyleneoxide), regardless of their molecular weights, grafts are largely located inside the silica pores. On the other hand, with solution polymers (polystyrene) grafts are mainly outside the silica pores.

The chromatographic behavior of the packings cannot be elucidated if this difference is neglected. Significantly, grafted supports are more efficient than silica for the separation of high molecular weight compounds, only when grafts are outside the silica pores.

Grafting of low polarity molecules on silica does not always lead to decreasing adsorption on the mineral support. This result, which we theoretically predicted (14), was verified in the case of grafted polystyrene $\bar{M}$ = 50 000.

Dissolution into a grafted phase largely depends on the difference between solute affinity towards the grafted molecules and the solvent. In the case of solutes having strong affinity towards the stationary phase, reverse-phase chromatography occurs. Then, in accordance with thermodynamic predictions, retention volumes of solutes increase with their size.

REFERENCES

1. Grushka, E., Bonded stationary phases in chromatography, Ann. Arbor. Sci., Mick., 1974.

2. Locke, D.C., J. Chrom. Sci., 11, 120, 1973.
3. Majors, R., Analusis, 10, 549, 1975.
4. Pryde, R., J. Chrom. Sci., 12, 486, 1974.
5. Rehak, V., and Smolkova, E., Chromatogr., 9 (5), 219, 1976.
6. Rosset, R., Caude, M., and Jardy, A., Manuel pratique de chromatographie en phase liquide, Varian, Orsay, 1975.
7. a) Lecourtier, J., Audebert, R., and Quivoron, C., J. Liquid Chrom. in press. (1978).

   b) Lecourtier, J., Thesis, Paris, University P. and M. Curie, 19/12/1977.
8. Donnet, J.B., Papirer, E., N Guyen, V.T., J. Polym. Sci., part B, 9, 195, 1971.
9. Papirer, E., and N Guyen, V.T., Polym. lett., 28, 31, 1973.
10. Papirer, E., and N Guyen, V.T., Polym. lett., 10, 167, 1972.
11. Gregg, S.J., and Swing, K., Adsorption surface area and porosity, Acad. Press., London, 1967.
12. Sederel, W.L., and Dejong, G.L., J. Appl. Polym. Sci., 17, 2835, 1973.
13. Dawkins, J., and Hemming, M., Die Makr. Chem., 176, 1795, 1975.
14. Lecourtier, J., Audebert, R., and Quivoron, C., To be published.
15. Flory, P.J., Principle of polymer chemistry, Cornell University Press., Ithaca, 1953.