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## SWELLING PROPENSITY (SP FACTOR) OF SEMI-RIGID CHROMATOGRAPHIC PACKING MATERIALS

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### SUMMARY

The rigidity of chromatographic packing materials has been evaluated by measuring the swelling during a solvent gradient and plotting the pressure drop across the column. The procedure requires an ordinary liquid chromatograph and can be used routinely for the quality control of packing materials. A derivatization technique is proposed for improving the rigidity of porous polystyrene packing materials.

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### INTRODUCTION

The poor stability of chromatographic columns is very often a problem, rapidly causing reduced efficiency and loss of resolution. The reproducibility of the retention times may also be effected, which makes automated analysis difficult. For silica gel-based packing materials, the instability can arise from the solubility of the silica gel skeleton in aqueous eluents. Polymer-based packing materials do not suffer from this disadvantage and are generally very stable against chemical degradation, but they are more or less sensitive to solvent changes. In size exclusion chromatography (SEC), commercial columns filled with porous polystyrene particles can be eluted only with good solvents for polystyrene like toluene, methylene chloride, tetrahydrofuran, etc.<sup>1-3</sup>. Flushing the column with more polar eluents like methanol or acetonitrile considerably reduces the plate number and results in deterioration of the packing through irreversible shrinking of the packing bed. All polymeric packing materials are more or less sensitive to solvent changes. Recently, however, reversed-phase columns filled with more rigid porous polystyrene beads have become available. These columns are stable over a wide range of eluents from non-polar to polar. The packing material seems to be less sensitive to swelling and shrinking than the previously available polystyrenes. This swelling behaviour is however difficult to evaluate. Until now a quantitative comparison had not been reported. In this work a convenient method to compare the swelling or rigidity of chromatographic packing materials is presented.

## EXPERIMENTAL

The solvent gradient chromatographic runs were performed on a Model 5000 liquid chromatograph (Varian, Walnut Creek, CA, U.S.A.). Any other chromatographic system capable of producing a gradient and giving an analogous signal related to the pressure drop across the column can be used.

*Materials*

Two commercially available polymeric packing materials were tested: PRP-1, which is a 10- $\mu\text{m}$  polystyrene reversed-phase material (Hamilton, Reno, NV, U.S.A.), and G 3000 (Toyo Soda, Japan) which is a 10- $\mu\text{m}$  polystyrene material suitable for SEC analysis. The other packing materials mentioned in this paper are porous polystyrenes made in our laboratory. They were prepared by suspension polymerization of styrene and divinylbenzene, with subsequent derivatization to improve their rigidity (Table I).

*Methods*

The 10  $\times$  0.41 cm stainless-steel columns were packed with a suspension of polystyrene particles in acetone-water (50:50) at 12 ml/min with distilled water as eluent. The packing pressure ranged from 5 to 30 MPa depending on the particle size, the particle size distribution and the rigidity of the particles. The column was then equilibrated at a constant flow-rate with distilled water. The solvent gradient was started after the pressure drop across the column had stabilized. During the gradient the solvent composition changes linearly from 100% water to 100% tetrahydrofuran (THF) in 10 min. A direct change from water to THF is also possible, but we prefer the gradient because this allows easy evaluation of the pressure increase during the swelling process. The pressure is continuously recorded during this gradient. Water and THF were chosen because the former produces least swelling and the latter strong swelling of polystyrene materials.

TABLE I  
PACKING CHARACTERISTICS<sup>a</sup>

PS 1, 2, 3 and 4 are polystyrenes, underivatized and home-made (see Materials). PS 1.a is obtained by derivatization of PS 1 via chloromethylation. PS 4 is prepared with decaline-heptane (50:50) as diluent during polymerization. PS 5 is the commercially available PRP-1 packing for which the supplier's data are given. PS 6 is the commercially available TSK G3000 packing for which the nominal porosity is given by the supplier.

PS	Diluent	Pore diameter (nm)		Pore volume (ml/g)		Surface area (m <sup>2</sup> /g)	
		BET	SEC	BET	SEC	BET	SEC
1	Decalin		3	0	0.9	1.4	1200
1.a	Decalin	4	3	0.53	0.9	512.0	1200
2	Heptane	19	25	0.57	1.4	118.9	224
3	Heptane	9	3	0.21	0.6	97.1	778
4	Heptane + decalin	15	7	1.68	1.3	454.1	714
5		7.5	7	0.79	1.2	415	686
6			150				

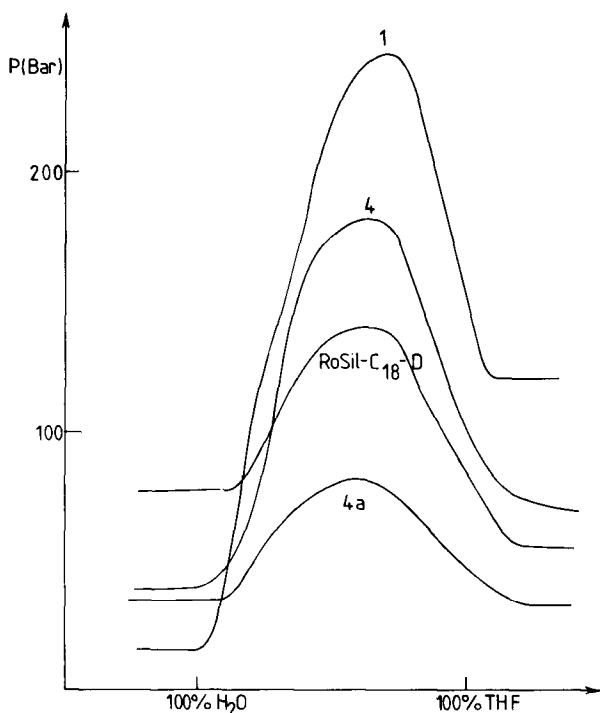


Fig. 1. The pressure versus solvent composition for four different packing materials, designated as in Table II.

## RESULTS AND DISCUSSION

Fig. 1 shows the kind of curves that are obtained for four different polystyrene packing materials. All the curves show a maximum pressure at an intermediate solvent composition. This is normal because of the maximum viscosity of a mixture of THF and water of intermediate composition. This maximum pressure is thus not related to the maximum swelling of the packing material.

Bristow and Knox<sup>4</sup> suggested the use of the column resistance factor,  $\varphi$ , to express the quality of the column in terms of permeability

$$\varphi = d_p^2 P T_0 / L^2 \eta \quad (1)$$

where  $L$  = length of the column in mm,  $\eta$  = eluent viscosity in  $10^{-3}$  Pa · s or cP,  $d_p$  = particle size in  $\mu\text{m}$ ,  $T_0$  = retention time of an unretained compound in s and  $P$  = pressure drop in bar. The pressure drop is therefore expressed as:

$$P = L^2 \eta \varphi / d_p^2 T_0 \quad (2)$$

When the packing swells, the particle size,  $d_p$ , increases and so does  $\varphi$ . This will result in an increase in the backpressure over the column. For most semi-rigid packings the

TABLE II

PRESSURE, RELATIVE PRESSURE AND SWELLING FOR CHROMATOGRAPHIC PACKING MATERIALS, OBTAINED FROM PRESSURE MEASUREMENTS DURING A SOLVENT GRADIENT

The numbers 1–6 correspond with the polystyrene packing materials described in Table I. PS 1.a, 2.a and 4.a are obtained by derivatization of PS 1, PS 2 and PS 4 respectively. ROSil-C<sub>18</sub>-D is a spherical octadecylated silica gel from Alltech-RSL (Eke, Belgium).  $P$  in bar and  $p = P/\eta$ .

Packing	$P(\text{H}_2\text{O})$	$P(\text{THF})$	$p(\text{H}_2\text{O})$	$p(\text{THF})$	SP
ROSil-C <sub>18</sub> D	76	44	76	80	0.05
1	14	116	14	211	14.1
1.a	24	42	24	76	2.2
2	26	120	26	218	7.4
2.a	32	34	32	62	0.9
3	10	26	10	47	3.7
4	30	70	30	127	4.2
4.a	28	26	28	47	0.7
5	30	38	30	69	1.3
6	16	> 350	16	> 636	> 39

increase in size is negligible. If  $d_p$  is assumed to be constant we can formulate the swelling propensity, SP, as

$$\text{SP} = \frac{(\varphi) \text{ THF} - (\varphi) \text{ H}_2\text{O}}{(\varphi) \text{ H}_2\text{O}} = \frac{p(\text{THF}) - p(\text{H}_2\text{O})}{p(\text{H}_2\text{O})} \quad (3)$$

where  $p$  is the pressure relative to the viscosity,  $p = P/\eta$ . This SP factor could be expressed in several ways. In the way chosen above a non-swelling material will have an SP value of 0.

Table II lists the SP factors of some polystyrene packing materials and of one reversed-phase octadecylated silica gel. It follows that only the octadecylated silica gel does not swell in water or THF. Most polymeric packings, however, tend to swell significantly in THF. Even for the relatively highly cross-linked polystyrene (PS) packings 1–4 the rigidity is insufficient to allow applications other than SEC. These materials are useless for reversed-phase chromatography because the permeability changes too much during a solvent gradient and the column efficiency rapidly decreases.

One example of the recent improvements in polymeric packing materials is PRP-1 (PS 5 in Table II) which consists of 10- $\mu\text{m}$  porous polystyrene spheres. The composition of this packing is not completely defined but it certainly has a very high and effective degree of cross-linking. A high degree of cross-linking is necessary but not sufficient; the links should be evenly distributed in the polymeric structure. This is not always the case as can be concluded from the work of several authors<sup>5–7</sup>. The swelling propensity of only 1.3 for PRP-1 is compared with 14 for PS 1, 7.4 for PS 2 and about 4 for PS 3 and 4 which are 30% cross-linked packing materials<sup>8</sup>.

It must be emphasized that the reproducibility of the measurements is not very high (typically, relative standard deviation 20–25%) and depends on the compactness of the packing. This is normal because the pressure increase must be greatest for the

most compact packing bed. Therefore all the columns, except the silica gel column, were packed under the same conditions. Further improvements in the rigidity with the monomers styrene and divinylbenzene could not be obtained by us. Therefore several other cross-linking methods were examined. One of the most successful approaches is to cross-link the polymeric beads after their preparation.

Chloromethylation has been studied as a first step in the transformation of polystyrenes into anion exchangers. The chloromethyl group on the polystyrene surface can react further with another aromatic ring. This reaction is in fact a cross-linking step and is a well known side reaction in the chloromethylation of polystyrene<sup>9,10</sup>. Normally this reaction is unwanted because it decreases the yield of the chloromethylation reaction. Thus the reaction time is kept short and the temperature low, *i.e.*, room temperature. If the reaction proceeds further, the chlorine content in the polymer decreases and some cross-linking occurs. This is frequently observed<sup>10</sup> with initially low cross-linked polystyrenes which tend to take up a smaller quantity of solvent after the reaction.

In our case it is the side reaction that is wanted. It is promoted by using more extreme reaction conditions. The first step of the reaction is the introduction of the chloromethyl groups at room temperature. Under these conditions the chloromethylation is complete and the chloromethylmethyl ether, which is a dangerous and harmful compound, is not allowed to evaporate from the reaction vessel. After 24 h the temperature is raised to 80°C and the reaction allowed to proceed for several days if necessary. Depending on the initially added quantity of chloromethylmethyl ether, the final chlorine content in the resin is very low.

The swelling propensity, determined according to the previously described method, is always lower than for the starting material. It seems to be somewhat dependent on the nature of the diluent during the preparation (PS 1 *versus* PS 2), but for each of these samples the swelling diminishes considerably upon cross-linking. For PS 1.a, which is a cross-linked polystyrene derived from small pore size polystyrene PS 1, the swelling is much smaller than for the parent material, but very low values for the cross-linked polystyrene PS 2.a or PS 4.a, derived from large pore size polystyrene PS 2 and PS 4, could not be determined. Porous polystyrene packings that could not be used in high-performance liquid chromatography because of the excessive swelling due to low cross-linking are improved (PS 2.a and 4.a) and finally attain the same level of rigidity as the PRP-1 packing.

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