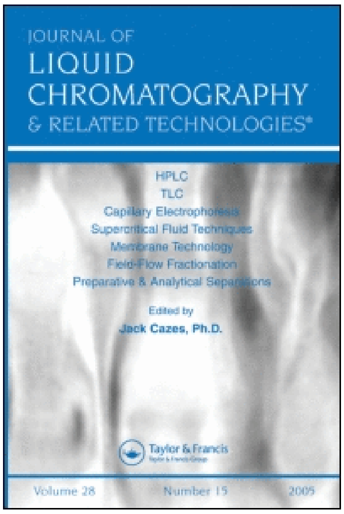

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POLYMETHYLOCTILSILOXANE ADSORBED ON POROUS SILICA AS A PACKING MATERIAL FOR REVERSED PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

Packing material having 10, 20, 30, 40 and 50% loadings of polymethyloctilsiloxane on porous silica particles have been prepared and tested. Solvent extraction tests, measurements of physical properties and determinations of chromatographic parameters show that an initial loading of 40% gives a packing material with satisfactory chromatographic properties.

INTRODUCTION

Porous silica is the support material most widely used for reversed phase HPLC packings. Usually a monomolecular layer of organosilane material is chemically bonded to the walls of the pores of this support so that this layer, the stationary phase, does not wash off into the mobile phase. Less widely used in reversed phase HPLC is an adsorbed (i.e. weakly bonded) stationary phase in which a layer of organic material, usually small (MW 50-100) molecules, is maintained on the surface by continuous replacement of desorbed molecules by similar molecules supplied from the mobile phase. The HPLC process in this case is called liquid-liquid chromatography. It is very versatile, with innumerable combinations of possible stationary phase molecular species, but tends to be inconvenient in practice because of the need to control the adsorption-desorption process [1].

In the present paper we show that large molecules (our example: polymethyloctilsiloxane, MW 6200), when adsorbed into the pores of chromatographic silica particles at sufficiently high loadings can have good chromatographics properties, even without the use of a special treatment to promote chemical bonding of the organic molecules to the silica surfaces.

EXPERIMENTAL

Reagents: methanol and dichloromethane (Lichrosolv grade, from Merck, Rio de Janeiro) were used without further purification. Carbon tetrachloride (Merck, Rio de Janeiro) was purified by distillation before use.

Davisil silica with a mean particle diameter of 10 μm was obtained from Alltech Associates, Inc.

Polymethyloctylsiloxane (PMOS) polymer was obtained from Petrarch Systems/Hüls America Inc. (product PS 140).

Method of Preparation of the Packing Materials: the silica was dried at 150°C for 24 hours prior to preparation of the packing material. Determined quantities of silica were added to solutions of polymethyloctylsiloxane dissolved in 60mL of dichloromethane to prepare packings with 10, 20, 30, 40 and 50% loadings. This mixture was slowly agitated at room temperature for three hours and then the solvent was evaporated, also at room temperature.

Columns: columns (125 x 3.4 mm id) were made from 316L grade stainless steel tubing. The internal surface was polished using a technique developed in our laboratories [2].

Columns were slurry packed using a 10% (w/v) slurry of the prepared packing material in CCl_4. A packing pressure of 38 MPa (Haskel High Pressure Packing Pump) was used, with methanol as propulsion solvent.

Columns were conditioned for five hours with mobile phase (methanol:water, 70:30, v/v) prior to testing.

Solvent extraction: the prepared packings were extracted at reflux temperature for six hours with each of three solvents (methanol, benzene and dichloromethane) using a modification of the method of Sanchez et al. [3]. Methanol was used because it is a polar solvent in wich PMOS is only slightly soluble; benzene because it is an apolar solvent in which PMOS is moderately soluble and dichloromethane because it is an even better solvent for PMOS.

Instrumentation: The chromatography was performed with a modular HPLC system equipped with a pneumatic injector (SSI model x3L), a Waters 510 pump, a UV-VIS absorbance detector (Waters Model 481) and a Waters 740 integrator. All measurements were carried out at ambient temperature. Two test mixtures were used during this study: (1) acetone, benzonitrile, benzene, toluene and naphthalene and (2) aniline and N,N-dimethylaniline both dissolved in mobile phase. Injections of 10 μL of these mixtures produced satisfactory chromatographic peaks with a x128 atenuation at 254 nm. The mobile phase was prepared volumetrically from individually measured aliquots of methanol and water, the mobile phase flow rate was set at 0.2 $mL.min^{-1}$.The column dead time, t_0, was determined using methanol as an unretained compound. Efficiency, resolution, capacity factor and peak asymmetry were determined for each chromatogram.

Elemental determinations on the packings were made using a Model 2400 Perkin Elmer CHN analyzer.

The surface areas of the silica support and of the prepared packings were determined by the conventional Brunauer-Emmett-Teller (BET) method [4] using a Model 2300 Micromeritics Flow Sorb II instrument.

Mean pore diameters (D_p) and specific pore volumes (V_p) of the silica and the packings were determined by mercury intrusion using a Model 9310 Micromeritics instrument.

The infrared spectrum of the liquid stationary phase was obtained from a film of the sample in a NaCl cell. For silica and the prepared packings, the spectra were obtained in KBr pellets compressed to 103 MPa. Transmission spectra were obtained with a Model 1600 Perkin Elmer FT-IR spectrophotometer.

RESULTS

Results from the solvent extractions are presented in Table 1. They indicate that, as the amount of PMOS

TABLE 1

Percentage of the Liquid Stationary Phase Extracted by Solvents.

% PMOS on Silica	% extracted with			% total extracted	% retained
	CH_3OH	C_6H_6	CH_2Cl_2		
10	0.2	3.3	2.0	5.5	4.5
20	0.2	12.0	2.0	14.2	5.8
30	0.2	14.5	2.0	16.7	13.3
40	0.3	21.4	1.5	23.2	16.8
50	0.3	25.4	4.4	30.1	19.9

deposited on the silica increases, the quantity of PMOS remaining after extraction also increases. These retained percentages are atributed to the PMOS that stays in the pores of the silica. Note that the methanol solvent extracts only a very small amount while benzene extracts a larger quantity according to the increase in the loading.

Figure 1 shows a linear increase in carbon load with the amount of PMOS used in the preparation of the packing between 10 and 40%. However, at 50%, the increase in carbon load is no longer linear, suggesting that further liquid phase may saturate the silica support.

The specific surface area (S_{BET}, Table 2) decreases as the amount of PMOS on the silica increases, up to 40%, after which the area stays practicality constant. This decrease presumably reflects the filling of the pores of the silica with the PMOS phase. Table 3 gives the values of the

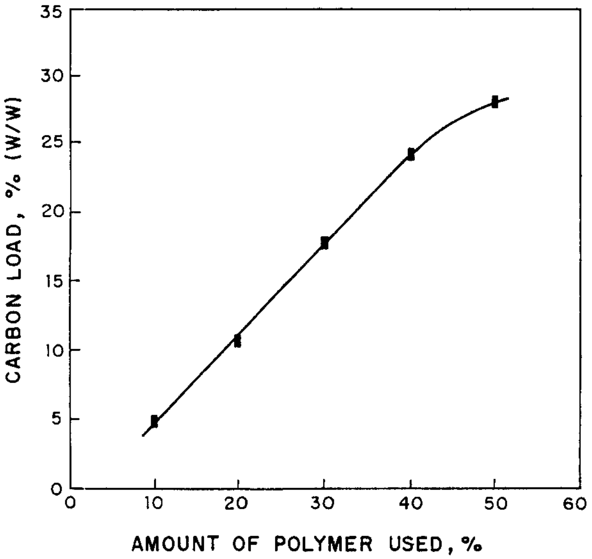

FIGURE 1 - Percentage of carbon in the prepared packings

TABLE 2

Specific Surface Area (S_{BET}) of the Silica and of the Packing Materials.

Sample	S_{BET} (m^2g^{-1})
silica	386.72
10% PMOS on silica	327.13
20% PMOS on silica	323.85
30% PMOS on silica	68.27
40% PMOS on silica	3.26
50% PMOS on silica	2.13

TABLE 3

Mean Pore Diameter (D_p) and Specific Pore Volume (V_p) Values of the Silica and Packing Materials

Sample	D_p (nm)	V_p (mL g^{-1})
Silica	9.9	1.24
10% PMOS on silica	10.2	1.08
30% PMOS on silica	10.5	0.84
40% PMOS on silica	10.8	0.56
50% PMOS on silica	12.5	0.43

mean pore diameter (D_p) and specific pore volume (V_p) of the packing materials. The increase in the percentage of the PMOS on silica results in a decrease of the specific pore volume to about 65% of its initial value as a consequence of the liquid phase loading.

The effect of carbon load on the specific surface area and specific pore volume of the prepared packing materials is illustrated in Figures 2 and 3, respectively. The pore volume decreases in a nearly linear manner with increase of the carbon load while the surface area decreases to a minimum at 40% PMOS on silica support, indicating that a layer of liquid phase has formed.

The infrared spectra of PMOS, of silica and of the prepared packing materials are shown in Figure 4. In these spectra the intensity of the signals characteristic of the silanol groups of the support (shoulder at 973.5 cm^{-1}) decreases as the percentages of PMOS on silica increase, up to 40%, confirming that

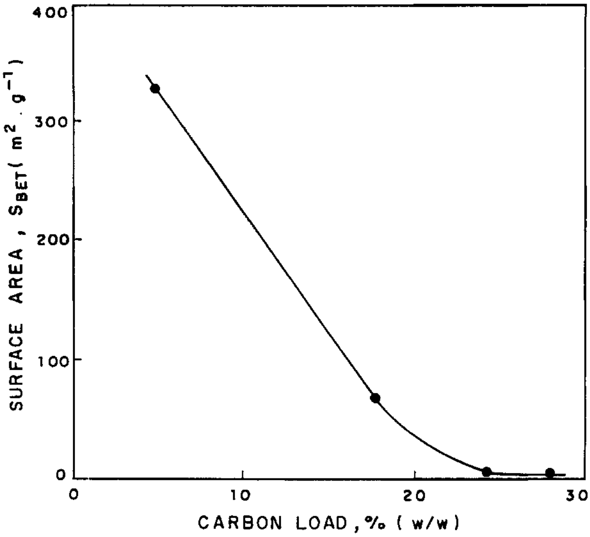

FIGURE 2 - Effect of carbon load on specific surface area of the packing materials

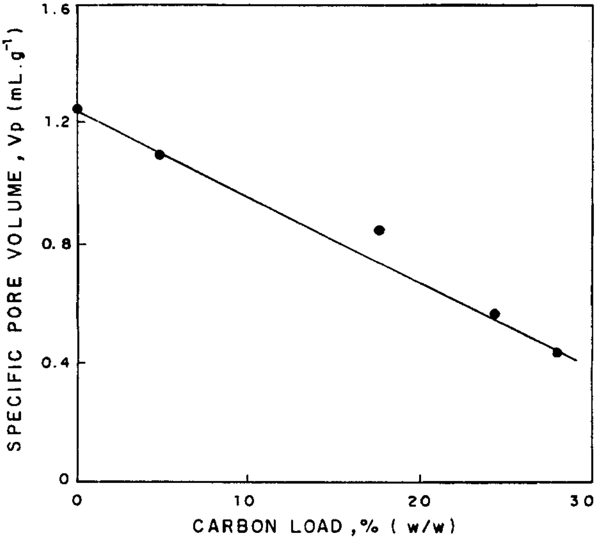

FIGURE 3 - Effect of carbon load on specific pore volume of the packing materials.

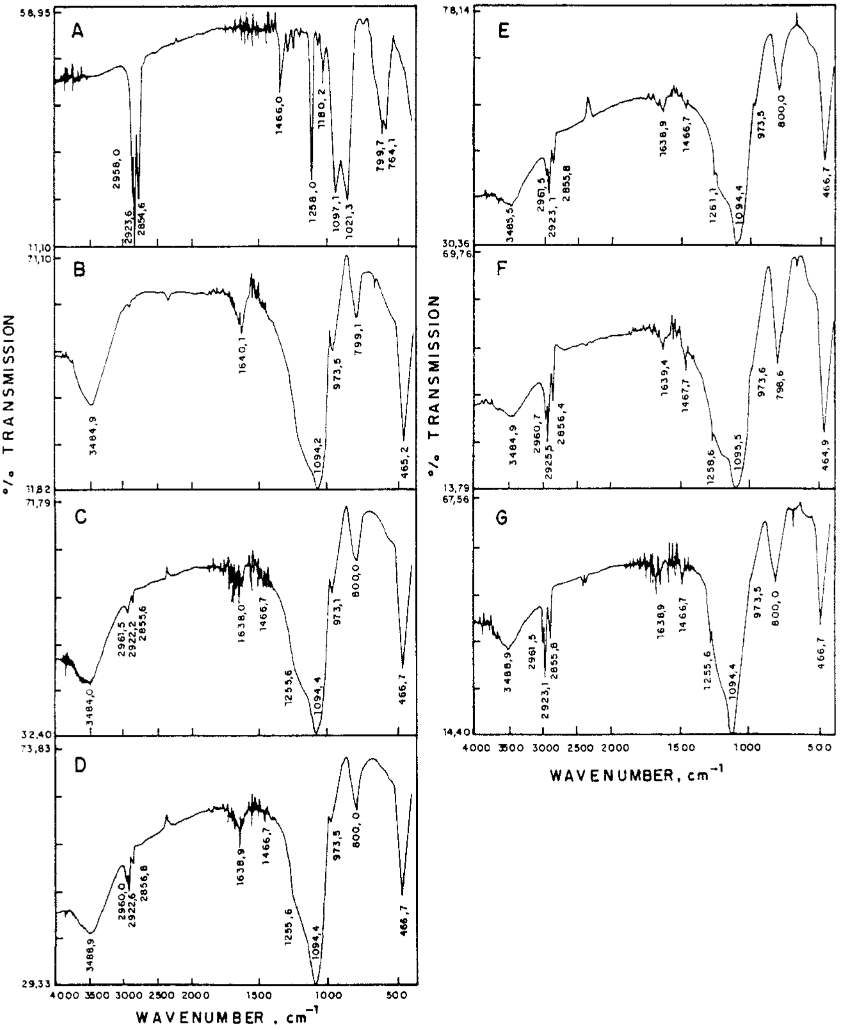

FIGURE 4 - Infrared spectra of: (A) PMOS, (B) silica, (C) 10% PMOS on silica, (D) 20% PMOS on silica, (E) 30% PMOS on silica, (F) 40% PMOS on silica and (G) 50% PMOS on silica.

TABLE 4

Chromatographic Parameters as a Function of the Amount of PMOS on Silica Using Test Mixture 1

% PMOS on silica	Chromatographic Parameters*				
	n** (x10^3)	n/meter** (x10^3, m^{-1})	k**	As**	Rs***
10	1.12	8.96	0.15	0.83	---
20	2.12	16.96	0.40	1.40	0.80
30	2.39	19.12	0.58	1.55	0.83
40	3.12	24.96	3.26	1.43	2.19
50	3.89	31.12	1.98	1.38	2.05

* Conditions of Determination: Column: 125 x 3.4mm id, mobile phase: methanol:water (70:30) at 0.2mL min^{-1}, detection: UV, 254nm

** Calculated for naphthalene

*** Calculated for toluene-naphthalene

a saturation of the porous silica has occurred, decreasing the number of exposed silanol groups.

The results obtained with test mixture 1 are given in Table 4. The amount of PMOS on silica affects all these parameters.

The retention factor (k) values show that the retention of naphthalene on columns packed with stationary phase having 10, 20 and 30% of PMOS on silica is low, limiting the resulting analysis. With 40 and 50% of PMOS the k values, for naphthalene, are

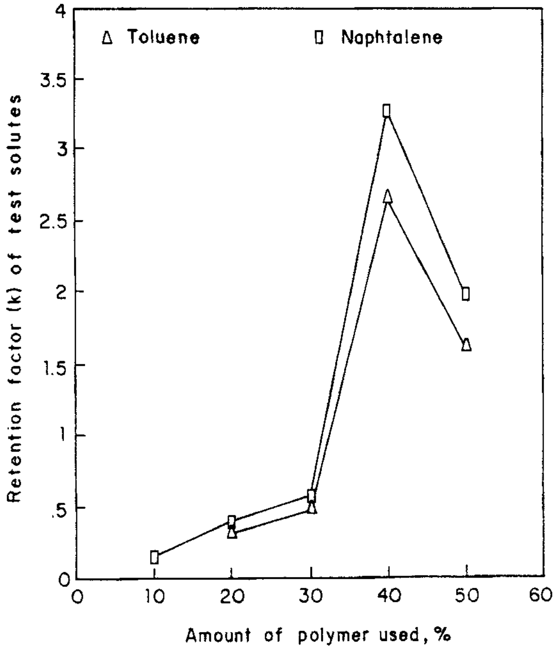

FIGURE 5 - The effect of the amount of polymer on the capacity factor of the test solutes toluene and naphthalene.

reasonable, due to the suitable interaction of the test compounds with both the mobile phase and the stationary phase ($1< k< 10$) [5].

Figure 5 shows the dependence of the retention factors of toluene and naphathalene on the loadings of the packing materials, indicating that the retention factor increases with increasing loading up to 40%, after which the solute retention decreases.

The observed resolutions show that columns packed with 10% PMOS on silica do not separate toluene and naphthalene. The same happens for acetone, benzonitrile and benzene. As the percentage of PMOS on silica

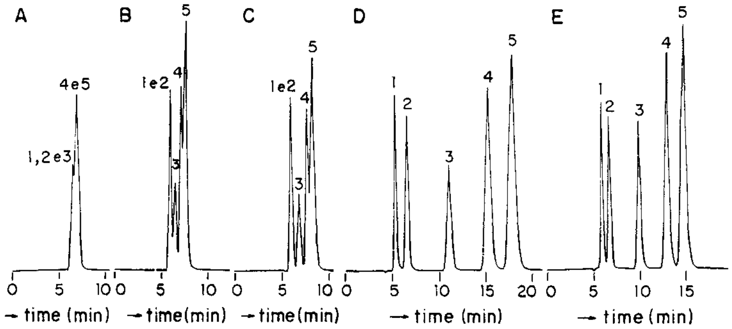

FIGURE 6 - Chromatograms obtained with the prepared packing materials: % PMOS on silica, (A) 10, (B) 20, (C) 30, (D) 40 and (E) 50. Test solutes : 1 = acetone , 2 = benzonitrile, 3 = benzene, 4 = toluene and 5 = naphthalene. Column: 125 x 3.4mm id, mobile phase: methanol: water (70:30, v/v), flow-rate: 0.2mL min^{-1}, pressure: 0 MPa, detection: UV, 254nm.

increases a better resolution of these compounds is observed, reaching acceptable separations at 40 and 50% PMOS. This can be visualized in the Figure 6 which shows the separation of the compounds of the test mixture 1.

The peak asymmetry, A_s, has been calculated for naphthalene. As can be seen in Figure 6, the toluene and naphthalene peaks in chromatograms A, B and C, corresponding to 10, 20 and 30% PMOS on silica, respectively, are not totally separated; therefore, the asymmetry values have been estimated. It should be noted that the asymmetry tends to decrease with increasing carbon load. At high loadings the asymmetry is acceptible for most purposes although it is still somewhat higher than the value (1.2) recommended by Snyder and kirkland [5] and by Poole and Poole [6].

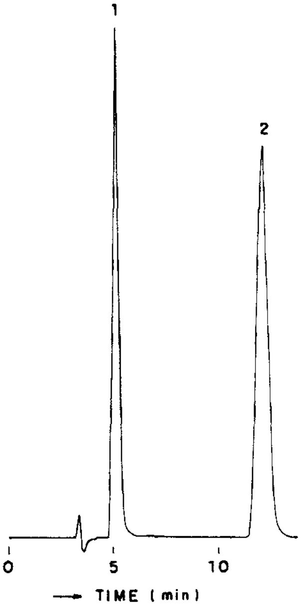

FIGURE 7 - Chromatogram obtained with the 40% PMOS on silica packing material.Test solutes: 1 = aniline and 2 = N,N-dimethylaniline. Column: 125 x 3.4mm id, mobile phase: methanol:water (70:30, v/v), flow-rate: 0.2mL.min^{-1}, pressure: 0MPa, detection: UV,254nm.

According to increase the loading, the peak became more symmetrical because of the increase of carbon load. Then, high loading helps to reduce peak asymmetry, but still present an asymmetry above that usually accepted ($A_s \leq 1.2$) [5].

Figure 7 shows the chromatogram obtained with basic solutes (test mixture 2) using a column packed with 40% PMOS packing material. The peaks for aniline and N,N-dimethylaniline are surprisingly symmetrical (with A_s values of 1.5 and 1.4, respectively) and similar to that naphthalene (Table 4). This demonstrates that the silanol group activity in these packings is quite low, even though no immobilization or endcapping was included in their preparation.

DISCUSSION

Tests of porous silica particles having heavy loads of PMOS (up to 50%) show that, although the surface area of the particles decreases to near zero at 40% loading, the pore volume decreases linearly with the loading and is still at 65% its initial value with a 50% load. This suggests that the BET measurements of surface area are in some way obscured by the nature of the organic loading.

Below 40%, there is not an effective shielding of the silanol groups of the silica, thus prejudicing resolution. Above 40% a decrease of solute retention occurs, which can be interpreted in terms of the model presented by Lork and Unger [7], where the solute molecules are able to penetrate the stationary phase created by the n-alkyl groups only when the n-alkyl groups are sufficiently flexible and the possibility exists for lateral evasion. The n-alkyl groups that are very closely packed lose this degree of freedom; i.e., above a certain ligand loading the ability of a solute to penetrate into the stationary phase is strongly reduced.

The columns reported here give good chromatographic behavior for the 40 and 50% loaded packings which are economical and easy to prepare.

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