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Self-immobilization and/or thermal treatment for preparing silica-poly(methyloctylsiloxane) stationary phases

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Abstract

Batches of poly(methyloctylsiloxane) (PMOS)-loaded silica were prepared by the deposition of PMOS, into the pores of HPLC silica. Portions of PMOS-loaded silica were allowed to remain at ambient temperature, without further treatment for 2, 9, 20, 31, 51, 105 and 184 days after preparation to undergo self-immobilization (irreversible adsorption of a layer of polymer on silica at ambient temperature in the absence of initiators). Other portions were subjected to a thermal treatment (100 °C for 4 h) after 1, 2, 5, 7, 9, 15, 20, 25, 70, 111 and 184 days. Self-immobilized and thermally treated samples were characterized by % C, ^{29}Si cross-polarization magic angle spinning (CP/MAS) NMR spectroscopy and reversed-phase column performance. The results show that thermal immobilization accelerates the distribution and rearrangement of the polymer on the silica surface. However, from the time that a monolayer has been formed by self-immobilization (∼100 days for PMOS on Kromasil silica), the thermal treatment does not alter this configuration and, thus, does not change the resulting chromatographic parameters.

Keywords: Stationary phases, LC; Silica-poly(methyloctylsiloxane) stationary phases; Polysiloxane

1. Introduction

Despite development of stationary phases with new supports such as titania [1–3], zirconia [4–7], porous graphitic carbon [3,8,9] and alumina [1,10,11], modified silica packings are still the most commonly used stationary phases in HPLC [12]. Porous silica is the most used support because it can be easily derivatized and is mechanically stable at high pressures. The preparation, properties and availability of silica-based chemically bonded phases have been described in numerous papers [3,13–17]. The most common procedures are those in which a functional group (alkoxy or chloro) of an organosilane reacts with a silanol group on the silica surface.

In addition to these phases, the deposition and immobilization of polymers onto silica have been explored for the preparation of packing materials for reversed-phase liquid chromatography [18,19]. The immobilization of polymers on silica is a complex process influenced by contributions from different types of adsorption interactions, from the chemical attachment of macromolecules onto the silica surface and from the insolubility of immobilized polymer in selected eluents. Microparticulate silica gel, either non-porous or with a suitable pore structure, seems to be the best support for polymer immobilization, enabling high column efficiencies and good flow properties [19]. The thickness of the polymeric film can be varied by coating from solutions having variable concentrations of the polymer and the selectivity can also be varied by appropriate choice of polymer. These characteristics make this type of stationary phase very versatile. A survey of polymers used for modification of silicas for liquid chromatography is given by Petro and Berek [19]. Some advantageous of these phases are: easy preparation, higher coverage of the active sites of the support when compared with bonded silica phases and consequently, protection of solutes from undesirable interactions with the silica matrix and protection of silica against chemical attack from aggressive mobile phases. These properties make such materials suitable for separation of drugs, pesticides or other compounds with slightly basic mobile phases, without the need for complicated ion-pairing techniques. The practical

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utility of stationary phases based on immobilization of a polymer onto silica has been demonstrated in our laboratory for the determination of diuron and linuron pesticides in human urine [20].

It has already been shown that the self-immobilization process (irreversible adsorption of a layer of polymer on silica at ambient temperature in the absence of initiators to induce the immobilization) takes considerable time to complete at room temperature. Column performance and retention factors increase as a function of the time interval between particle loading and column packing [21]. Other papers have shown that the use of higher temperatures is a reasonable procedure for more rapid immobilization of polysiloxanes onto silica [22–24]. Thus, we have shown that monolayer poly(methyloctylsiloxane) (PMOS) stationary phases prepared by thermal immobilization at up to 150 °C in the absence of cross-linking additives are good reversed-phase packing materials [23]. However, columns prepared from PMOS stationary phases immobilized at temperatures above 150 °C are not satisfactory. Subsequent studies suggested significant degradation of the polymer at these temperatures [25].

This investigation reports a comparison between stationary phases which are self-immobilized with and without a subsequent thermal treatment of 4 h at 100 °C onto HPLC silica.

2. Experimental

2.1. Materials

HPLC-grade methanol, Mallinckrodt (Rio de Janeiro, Brazil) and Milli-Q water (Millipore, Bedford, MA, USA) were used to prepare mobile phases which were filtered (0.22 μm membrane) before use. HPLC-grade dichloromethane, EM Science (Gibbstown, NJ, USA) and analytical-reagent grade chloroform, Merck (Darmstadt, Germany) were used without further purification. Most of the compounds used for the chromatographic tests (acenaphthene, phenol, naphthalene and uracil) were analytical-reagent grade and not further purified. Analytical-reagent grade *N*,*N*-Dimethylaniline was purified by distillation. Kromasil silica, Akzo Nobel (Bohus, Sweden), with 6 μm spherical particles, a 11.1 nm mean pore size and a 320 $m^2 g^{-1}$ specific surface area and (PMOS), polymer (weight-average molar mass, M_w, of 6200) from United Chemical Technologies (Bristol, PA, USA) were used to prepare the stationary phases.

2.2. Preparation of PMOS-coated stationary phases

Batches of PMOS-loaded silica having an initial specific mass ($\bar{m}_{PMOS}$) of nearly 1.0 g_{PMOS}/g_{silica} were prepared by addition of a determined quantity of silica (dried at 150 °C for 24 h) to a solution of PMOS in dichloromethane. This mixture was slowly agitated at room temperature for 3 h, after which the dichloromethane was evaporated at room temperature. When dry, the material was stored in closed glass containers at room temperature until needed.

2.3. Thermal treatments

Portions were subjected to thermal treatments 1, 2, 5, 7, 9, 15, 20, 25, 33, 70, 111 and 184 days after the stationary phase was dried. For this, portions of the stationary phase were placed in stainless steel tubes (150 mm × 10 mm) fitted with frits and connectors and then heated for 4 h in an oven at 100 ± 1 °C.

2.4. Solvent extraction of excess polymer

Stainless steel tubes (150 mm × 10 mm) containing the stationary phase (∼3.5 g) were connected to a Waters 510 pump (Millford, MA, USA) for extraction of all the non-immobilized PMOS by passing 150 ml of chloroform followed by 150 ml of methanol at 0.8 ml min^{-1} at 25 °C. After each extraction, the sample contained in the column was removed, the residual solvent was evaporated and the solid was dried in an oven at 45 °C for 2 h.

2.5. Elemental analyses

Carbon percentages for all the stationary phases, SiO_2 (PMOS), were determined on a Perkin-Elmer Model 2400 Analyzer (Norwalk, CT, USA). At least three determinations were made for each material. From these data, the specific mass of PMOS, $\bar{m}_{PMOS}$, which represents the mass of non-extractible polymer per gram of silica, was calculated, using the formula: $\bar{m}_{PMOS}$ = % C/(62% C), where 62% refers to the percent of carbon in PMOS. With the data of specific mass the polymer layer thickness, τ, was calculated, as follows:

$$\tau = -\left(\tfrac{1}{2}\left(\sqrt{d^2 - Fd^2} - d\right)\right)$$

where $F = \bar{m}_{(immobilized)}/\bar{m}_{(fullpores)}$ is the self-immobilized or thermally immobilized fraction and d is the mean pore diameter. It is assumed for this calculation that the pores of the silica have a constant diameter and that the self-immobilized polymer is characterized by a layer of constant thickness, τ, on the pore walls [23]. The specific pore volume, v_p for the Kromasil silica is 0.88 ml per gram of SiO_2 and the density of PMOS is 0.91 g ml^{-1}. From this pore volume, the mass of polymer that fills the pore system is 0.80 g_{PMOS}/g_{silica}.

2.6. Column packing

Columns (60 mm × 4 mm) were made from type 316 stainless steel tubing. The internal surface was polished using a technique developed in our laboratory [26]. The columns were downward slurry packed using 10% (w/v) slurries of

the stationary phases in chloroform with methanol as propulsion solvent. A constant packing pressure of 34.5 MPa with a Haskel packing pump (Burbank, CA, USA) was used. After packing, columns were conditioned for 3 h with mobile phase at 0.2 ml min^{-1} prior to testing.

2.7. Chromatographic evaluation

The chromatographic mixture used in this study consisted of uracil, phenol, *N*,*N*-dimethylaniline, naphthalene and acenaphthene. HPLC separations were performed with a Waters 510 pump, a Rheodyne (Cotati, CA, USA) model 7125i injection valve (5 μl) and a Waters 486 UV-Vis detector (at 254 nm). The mobile phase was methanol–water (50:50, v/v) at 0.2 ml min^{-1}, the optimal flow-rate as determined by a Van Deemter plot. The column dead time, t_M, was determined using uracil as an unretained compound. Data collection and treatment was carried out by Chrom Perfect for Windows, version 3.52, and Report Write Plus from Justice Innovations (Mountain View, CA, USA). Chromatographic performance was evaluated by means of efficiency [plates per meter ($N\,m^{-1}$) and reduced plate height (h)], retention factor (k), resolution (R_s) and asymmetry (A_s) measured at 10% of the peak height.

2.8. Solid-state NMR measurements

^{29}Si Cross-polarization magic angle spinning (CP-MAS) NMR spectra were collected on a Bruker ASX 300 NMR spectrometer. Representative samples of 200–250 mg were spun at 3500 Hz using 7 mm double bearing ZrO_2 rotors. The spectra were obtained with a cross-polarization contact time of 5 ms. The pulse interval time was 1.5 s. The transmitter frequencies of ^{29}Si and ^{1}H were 59.59 MHz and 300.13, respectively. Typically, 1.5 k FIDs with an acquisition time of 30 ms were accumulated in 1 kilobytes (kb) data points and zero-filling to 8 kb prior to Fourier transformation. The line broadening used was 30 Hz and the spectral width for all spectra was about 25 kHz. Each spectrum was deconvoluted using the Bruker WINNMR 6.0 program.

3. Results and discussion

These experiments involved tests on stationary phases from batches of PMOS-loaded Kromasil particles where the mass of PMOS exceeded that necessary to fill the pores. One batch was allowed to stand at room temperature, without any further treatment, for 2, 9, 20, 31, 51, 105 and 184 days to undergo self-immobilization. After this time, small portions were solvent-extracted to remove PMOS that had not self-immobilized at room temperature. Other portions were allowed to stand at room temperature for 1, 2, 5, 7, 9, 15, 20, 25, 30, 70, 111 and 184 days but, before extraction, these portions were subjected to a thermal treatment at 100 °C for 4 h, to learn if the thermal treatment modifies the immobilized layer. After extraction, columns were packed with these stationary phases. Portions of all samples were also subjected to elemental analysis to permit calculation of the specific mass of PMOS present in each stationary phase (Table 1). As can be seen, the amount of PMOS retained (self-immobilized) increases with time, although with this very pure silica (Kromasil) the self-immobilization process takes considerable time to

Table 1
Percent carbon, specific mass, $\bar{m}_{PMOS}$, and layer thickness, τ, from extraction experiments, for the self-immobilized and thermally immobilized stationary phases

Conditions	Time before extraction (days)	% C after extraction	% C after packing columns	$\bar{m}_{PMOS_{retained}}$ (g_{PMOS}/g_{silica})	τ[a] (nm)
Only standing at room temperature	2	2.40	1.75	0.105	0.14
	9	5.54	2.04	0.098	0.35
	20	5.79	4.76	0.103	0.37
	31	6.12	6.39	0.109	0.39
	51	8.90	7.92	0.167	0.61
	105	12.99	12.52	0.265	1.01
	184	15.86	16.16	0.344	1.36
Standing at room temperature with subsequent thermal treatment	1	2.93	–	0.049	0.17
	2	5.32	–	0.094	0.34
	5	3.57	–	0.061	0.22
	7	3.43	–	0.058	0.20
	9	4.36	–	0.075	0.26
	15	5.25	–	0.092	0.33
	20	9.48	–	0.180	0.66
	25	10.82	–	0.211	0.79
	70	11.72	–	0.233	0.69
	111	14.95	–	0.318	1.24
	184	16.86	–	0.374	1.50

[a] Calculated from % C after extraction.

complete. This should be compared to self-immobilized PMOS monolayers which are complete in 40 and 5 days for Davisil [21] and Rainin [27] silicas, both of which have significant contaminations with metallic species. With Kromasil, a complete self-immobilized monolayer, that is, 1.1 nm, is reached only after 100 days.

Comparing the % C after the extraction (before column packing) of self-immobilized stationary phases having a thermal treatment with the phases which were only self-immobilized (Table 1), it can be seen that there is not a significant increase in % C due to the thermal treatment. Clearly, the polymer layer thickness has the same behavior, since the calculation of this parameter uses the fraction of polymer retained on the silica. Thus, a monolayer of PMOS on Kromasil silica is reached after 100 days, without thermal treatment. After this time no additional immobilization occurs with the thermal treatment. It is important emphasize that this result has been observed

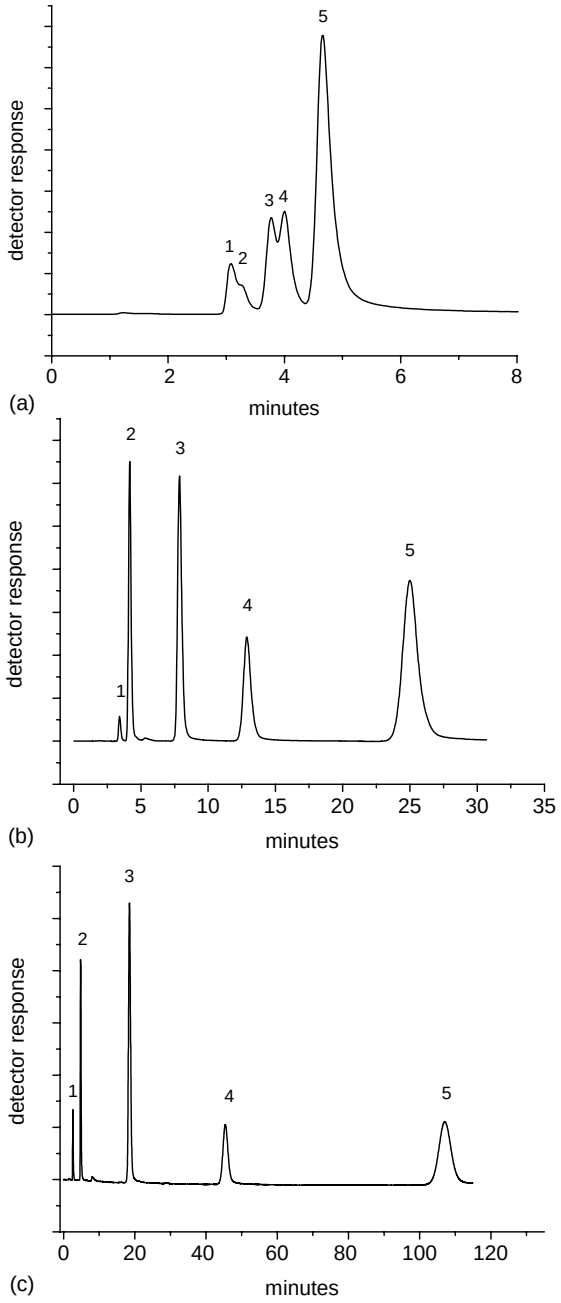

Fig. 1. Chromatograms obtained from self-immobilized SiO_2(PMOS) SP as a function of time since sorption: (a) 2 days; (b) 20 days; and (c) 184 days. Chromatographic mixture: (1) uracil; (2) phenol; (3) *N*,*N*-dimethylaniline; (4) naphthalene; and (5) acenaphthene. Chromatographic conditions—mobile phase:methanol–water (50:50, v/v); flow-rate: 0.2 ml min^{-1}; volume of injected sample: 5 μl; detector: UV at 254 nm.

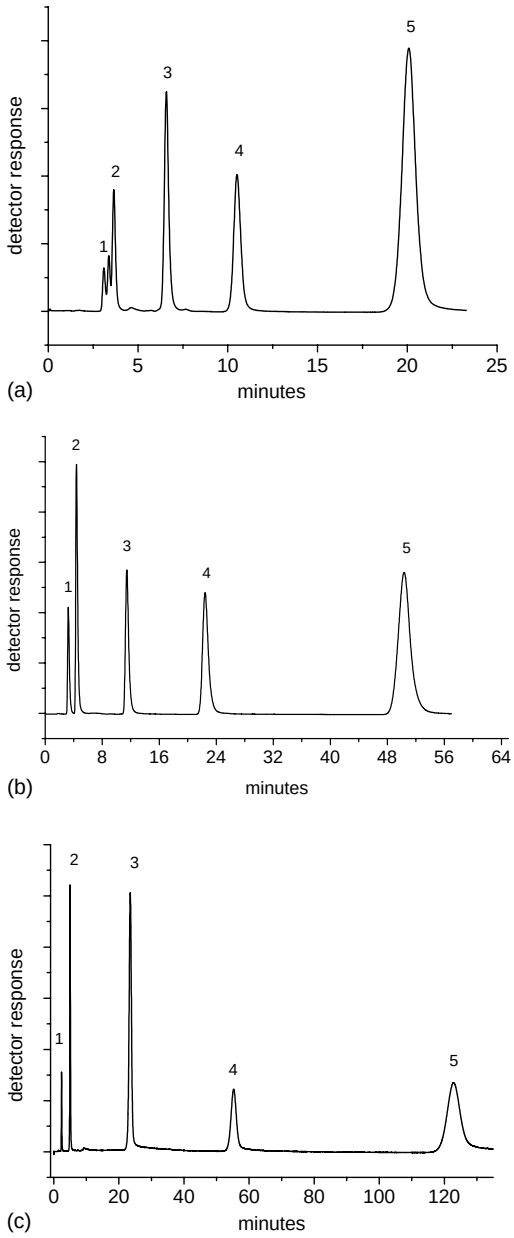

Fig. 2. Chromatograms obtained from SiO_2(PMOS) SP which was self-immobilized and then subjected to a thermal treatment before extraction, as a function of time of self-immobilization: (a) 2 days; (b) 20 days; and (c) 184 days. Chromatographic mixture: (1) uracil; (2) phenol; (3) *N*,*N*-dimethylaniline; (4) naphthalene; and (5) acenaphthene. Chromatographic conditions: see Fig. 1.

Table 2
Chromatographic parameters obtained from self-immobilized and thermally immobilized stationary phases[a]

Conditions	Time before extraction (days)	N/L[b]	h[b,c]	A_s				k[b,g]
				2[d]	3[e]	4[f]	5[b]	
Only standing at room temperature	2[h]	–	–	–	–	–	–	–
	9	52 870	3.1	1.5	1.8	1.6	1.3	2.5
	20	38 630	4.3	1.4	1.5	1.4	1.3	6.3
	31	44 260	3.7	1.1	0.9	0.7	0.6	9.4
	51	53 630	3.1	1.6	1.9	1.8	3.1	13.3
	105	70 680	2.3	1.3	1.1	1.3	1.0	24.2
	184	62 630	2.6	1.4	0.9	1.0	1.1	36.9
Standing at room temperature with subsequent thermal treatment	1	54 470	3.0	1.7	1.9	2.1	1.5	4.2
	2	54 780	3.0	1.4	1.3	1.2	1.1	5.5
	5	54 150	3.1	1.4	1.6	1.7	1.3	5.0
	7	58 020	2.9	1.4	1.8	1.8	1.2	5.3
	9	58 280	2.8	1.6	1.9	1.7	1.3	5.6
	15	62 660	2.6	1.8	2.0	1.9	1.5	8.6
	20	71 850	2.3	1.9	1.6	1.6	1.2	14.5
	25	73 300	2.3	2.0	1.8	1.7	1.2	11.5
	70	60 416	2.7	1.8	1.5	1.3	1.2	36.4
	111	77 650	2.1	1.2	1.1	1.0	1.2	40.8
	184	73 620	2.3	1.3	1.1	1.1	1.2	50.2

[a] Values are average of three different chromatographic runs with each of two different columns for each stationary phase.
[b] Calculated for the acenaphthene peak.
[c] Calculated: $h = L/(Nd_{part})$.
[d] Calculated for the phenol peak.
[e] Calculated for the *N*,*N*-dimethylaniline peak.
[f] Calculated for the naphthalene peak.
[g] Column dead time was measured with uracil.
[h] Calculation was not possible.

with a number of different batches of PMOS on Kromasil silica.

The chromatograms obtained using columns packed with self-immobilized stationary phases are shown in Fig. 1 and those obtained with columns packed with thermally immobilized stationary phases are shown in Fig. 2. The plate number per meter, $N\,m^{-1}$, reduced plate height, h, asymmetry measured at 10%, A_s, and retention factor, k, were calculated from the chromatograms and the results are summarized in Table 2.

As previously shown [21], self-immobilization significantly affects all the chromatographic parameters of the column (see Table 2). The retention factor increases considerably with the self-immobilization time, as can be seen in Fig. 1, and the peak asymmetry for *N*,*N*-dimethylaniline decreases from $A_s = 1.8$ to ~1.0 for the self-immobilized stationary phase which has a complete monolayer, demonstrating significant coverage of the superficial silanol groups of the support. On the other hand, the phase self-immobilized for only 2 days shows very poor resolution, related to the small amount of PMOS retained on the surface of the silica, as confirmed by the % C, which is not capable of retaining the probe solutes (Table 1). However, when the stationary phase self-immobilized for 2 days is subjected to a thermal treatment, it was possible to obtain good resolution and to calculate the chromatographic parameters for this phase, as a result of the thermally-induced redistribution of the polymer on the surface.

As the time of self-immobilization before the thermal treatment is increased, the efficiency and the retention factor increase significantly, showing that the time for self-immobilization is the determining factor to obtain good chromatographic efficiencies. Without relatively long times for self-immobilization, the efficiency and asymmetry were not so good, even with a posterior thermal treatment. Further trials relating to the optimization of a monolayer by a sequence of thermal treatments will be reported in a future communication.

The ^{29}Si (CP-MAS) NMR spectra (Fig. 3) obtained from portions of the stationary phases at 2 days after preparation, both with and without thermal treatment, used the cross-polarization technique to enhance sensitivity and reduce the long relaxation times, to allowing monitoring the silicon atoms on the silica surfaces. The principal peaks exhibited in the spectra refer to the siloxane group Q_4 at −110 ppm, free silanols Q_3 at −101 ppm and geminal silanols Q_2 at −92 ppm [28,29]. For the stationary phase subjected to thermal treatment after 2 days, there is a signal in the range from −22 to −15 ppm indicating adsorbed and bonded PMOS [30,31]. The phase without thermal treatment does not show this peak, suggesting that the PMOS did not adsorb well, such as is expected when large loops,

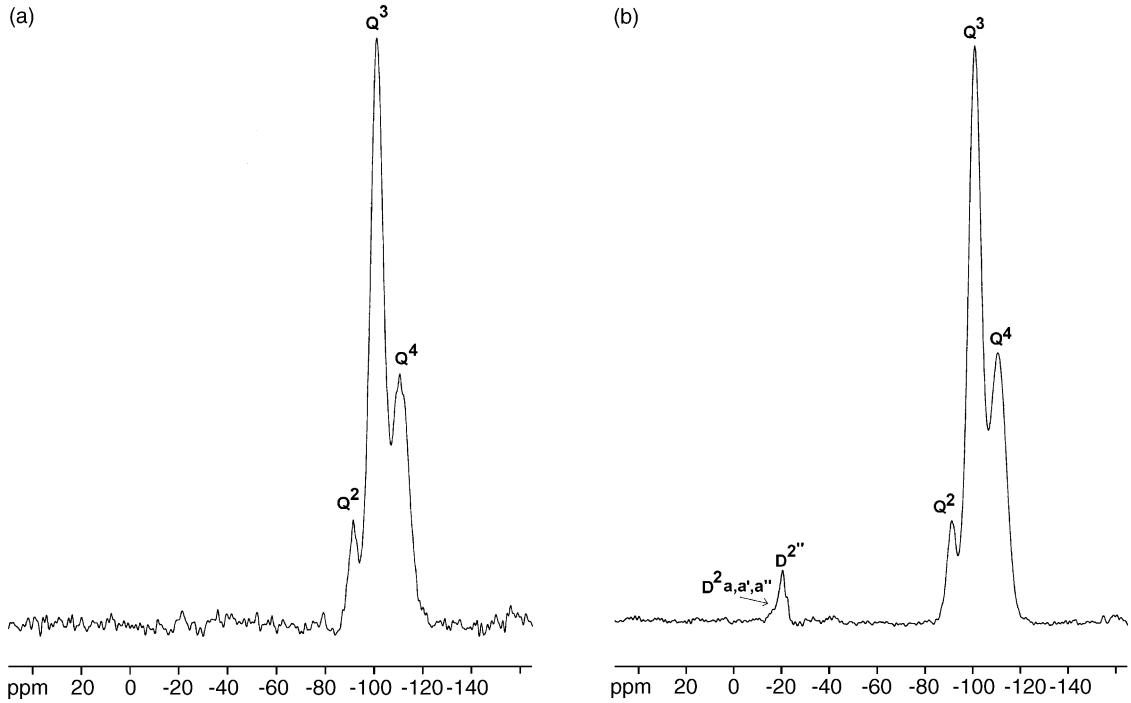

Fig. 3. ^{29}Si CP-MAS-NMR spectra of SiO_2(PMOS): (a) self-immobilized for 2 days, extracted, packed and used; (b) SP which was self-immobilized for 2 days and then thermally treated before extracting, packing and use. Structures are in Fig. 4.

trains and tails are present [32,33]. As these spectra were obtained on stationary phase removed from the column after packing and testing a small loss of polymer of the phases resulted in a reduction of the % C. The NMR spectrum confirms that stationary phase self-immobilized for only 2 days does not retain sufficient PMOS to be chromatographically useful (Fig. 4).

When the data of Table 1 are compared with the corresponding data of Table 2, it can be seen that, although the % C of the stationary phases were not significantly changed by the post-self-immobilization thermal treatment, heating was important to promote alterations in the chromatographic behavior, suggesting that the thermal treatment causes rearrangement of the polymer on the silica surface. PMOS is initially present as a pore-filling liquid or as liquid "plugs" [34]. Through self-immobilization by physisorption contact with the silica surface, over time a redistribution of the polymer occurs over time and the polymer becomes

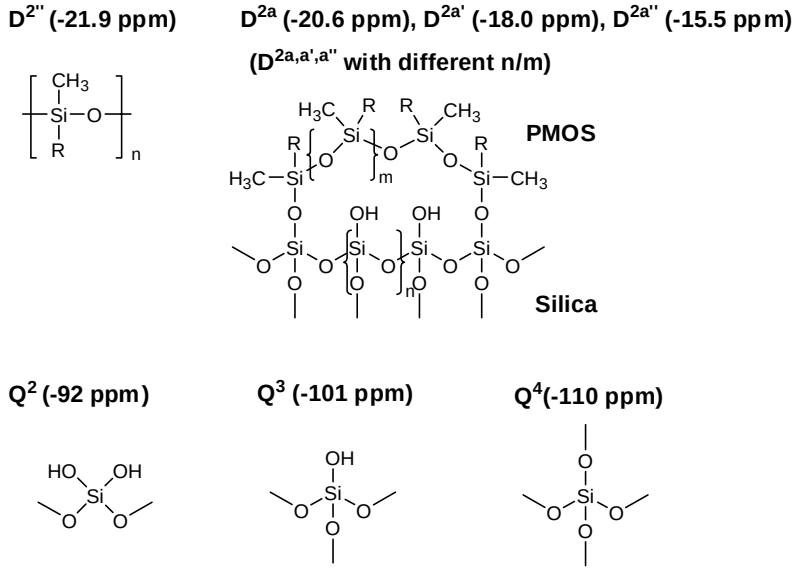

Fig. 4. Structures of the species D^{2a}, $D^{2a'}$, $D^{2a''}$ and $D^{2''}$ and ^{29}Si NMR chemical shifts for spectra of Fig. 3. R = C_8H_{15}.

distributed more uniformly until a monolayer of the PMOS is obtained. If the redistribution of polymer has not been completed (fresh phases), the thermal treatment can assist in the rearrangement of the PMOS, resulting in enhanced resolutions of the compounds of the test mixture. When the self-immobilization reaches an uniform adsorbed monolayer of PMOS, the thermal treatment does not alter this configuration and the chromatographic parameters are the same, with or without the thermal treatment.

4. Conclusions

Thermal treatment of stationary phases freshly prepared by polymer sorption onto HPLC silica particles showed the same % C as in stationary phases self-immobilized for 100 days. On the other hand, thermal treatments at 100 °C produce a stable monolayer more rapidly and, when applied following self-immobilization, result in a better stationary phase. Thus, it can be concluded that a thermal treatment produces good polysiloxane/silica stationary phases when the phase is freshly prepared. However, if the stationary phase has been at room temperature for a time sufficient to reach a monolayer, the thermal treatment does not make any difference in its chromatographic performance.

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