

# Self-immobilization of poly(methyloctylsiloxane) on high-performance liquid chromatographic silica

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Received 30 September 2003; received in revised form 15 December 2003; accepted 16 December 2003

## Abstract

Poly(methyloctylsiloxane) (PMOS) was deposited on HPLC silica by a solvent evaporation procedure and this material was then extracted, using a good solvent for the PMOS, after different time periods, to remove unretained liquid polymer. Solvent extraction data reveal changes which occur at ambient temperature as a function of the time interval between particle loading and extraction. The quantity of PMOS remaining on the silica after extraction, as determined by elemental analysis for carbon, is attributed to strongly adsorbed polymer. This phenomenon is termed self-immobilization. Solid-state <sup>29</sup>Si NMR spectra indicate the formation of a silicon species with a different chemical shift than the original PMOS. These new signals are attributed to a combination of different adsorbed and chemically bonded groups.

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**Keywords:** Stationary phases, LC; Self-immobilization; Nuclear magnetic resonance spectroscopy; Poly(methyloctylsiloxane)

## 1. Introduction

Packing materials for reversed-phase high-performance liquid chromatography (RP-HPLC) usually consist of porous silica support particles having a modifying layer on their surfaces. Most stationary phases are based on silanes chemically bonded to the silica surface. Stationary phases for HPLC can also be prepared by depositing and immobilizing a polymer layer onto the pore surfaces of silica support particles. Columns prepared from these polymer-coated packing materials give chromatographic performances comparable to those of conventional bonded-phase packing materials. Various procedures have been studied for the preparation of such polymer-coated packing materials [1–6]. Most of the procedures utilize cross-linking by ionizing radiation or radical initiators (peroxides) to secure (immobilize) the polymer layer onto the support surfaces. Schomburg and others had already shown that poly(methyloctylsiloxane) (PMOS) immobilized by cross-linking gave excellent RP stationary phases [2–5].

An even simpler approach is to deposit a layer of liquid polymer onto the support surface and to use this liquid layer as a stationary phase for reversed-phase liquid–liquid chromatography. This approach is plausible, permitting an enormous range of possible selectivities, because many polymers are effectively non-soluble in typical water–organic RP mobile phases. A test of this concept was made by Jardim and coworkers [7–9] using PMOS as the liquid polymer. Indeed, columns prepared with PMOS sorbed on silica, without cross-linking agents of any kind, gave RP columns of good quality, similar to those packed with commercial C-8 bonded phases [7,8].

It soon became apparent that a significant fraction of the sorbed PMOS was not extractable from the prepared stationary phases, even when using solvents in which bulk PMOS is very soluble (toluene, dichloromethane) [7,10], an observation previously noted by Bien-Vogelsang et al. [3]. This non-soluble PMOS layer had become immobilized without cross-linking, presumably due to rearrangement of the PMOS molecules to a favorable “multi-point” adsorbed configuration. This process was subsequently labeled “self-immobilization” [11,12].

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As an adsorption process, the kinetics of self-immobilization should be readily available to laboratory study, as is commonly done in non-chromatography-related adsorption studies. The present work presents time dependence data for the (thermal) self-immobilization of PMOS in HPLC silica at ambient temperature. The possibility that covalent bonding might play a role in the self-immobilization process is also examined, using solid-state  $^{29}\text{Si}$  NMR spectra, by use of cross-polarization (CP) and magic-angle spinning (MAS), of  $\text{SiO}_2(\text{PMOS})$  samples taken at various times following preparation. NMR investigations are a powerful means for obtaining detailed structural information [13–16] and the results can be combined with HPLC investigations [17,18]. The use of the  $^{29}\text{Si}$  CP-MAS-NMR leads both to higher sensitivity, due to transfer of magnetization and reduction of the long relaxation times and to specifically monitoring the silicon atoms on the particle surface. The relatively easy handling of the  $\text{SiO}_2(\text{PMOS})$  samples makes it possible to measure the  $^{29}\text{Si}$  CP-MAS-NMR spectra in a very fast and efficient way. Due to the use of the same instrument parameters for data accumulation, a semi-quantitative comparison between silicon species of similar structure is possible. This comparison permits defining the self-immobilization process of PMOS onto the silica surface. Thus, using carefully chosen conditions, quantification of the siloxane species within an error of  $\sim 5\%$  is possible [19].

## 2. Experimental

### 2.1. Materials

Irregular porous chromatographic silica gel (Davisil 630 having  $13\ \mu\text{m}$  particle size and  $8.7\ \text{nm}$  pore size) was obtained from Alltech (Deerfield, USA). PMOS (number-average molar mass ( $M_n$ ), 6200; and weight-average molar mass ( $M_w$ ), 14 000; viscosity 600–900 mPa s at  $25^\circ\text{C}$ ) was obtained from United Chemical Technologies (Bristol, USA). Dichloromethane was from Merck (Rio de Janeiro, Brazil and Darmstadt, Germany).

### 2.2. Preparation of the stationary phase $\text{SiO}_2(\text{PMOS})$

Silica particles were dried at  $150^\circ\text{C}$  for 24 h. Then a weighed amount of the silica was added to a solution of PMOS in dichloromethane in a ratio of 0.35 g PMOS/g  $\text{SiO}_2$ . The mixture was gently stirred for 3 h at room temperature and then the solvent was allowed to evaporate, without stirring, at room temperature, giving silica with PMOS deposited in the pore system.

### 2.3. Extraction procedure

Small stainless steel tubes containing  $\sim 0.8\ \text{g}$  of the phase were placed in an Eldex model CH-150 column oven ( $50^\circ\text{C}$ ) and connected to a Waters 510 pump for extraction

Table 1  
%C and specific mass data from extraction experiments

Time (days)	%C after extraction	$\bar{m}_{\text{PMOS}}$ (final) ( $\bar{m}_{\text{PMOS}} = g_{\text{PMOS}}/g_{\text{SiO}_2}$ )	Percent retained (percent extracted)
1	2.45	0.041	12.1 (87.9)
2	4.05	0.069	20.6 (79.4)
3	4.30	0.074	22.0 (78.0)
4	4.93	0.086	25.5 (74.5)
7	5.02	0.088	26.0 (74.0)
10	6.01	0.107	31.7 (68.3)
17	6.70	0.121	35.6 (64.4)
24	7.43	0.136	40.2 (59.8)
31	6.98	0.127	37.4 (62.6)
60	7.93	0.146	43.3 (56.7)
119	8.64	0.162	47.8 (52.2)
149	8.33	0.155	45.8 (54.2)

Initial specific mass: 0.35 g PMOS/g  $\text{SiO}_2$ .

of all non-immobilized PMOS by passing hexane for 3 h at  $0.2\ \text{ml}\ \text{min}^{-1}$ .

### 2.4. Determination of %C

Elemental analyses for carbon (%C) were obtained on a Perkin-Elmer model 2400 analyzer (Norwalk, CT, USA). From these data, the specific mass of PMOS,  $\bar{m}_{\text{PMOS}}$ , which represents the mass of PMOS/g of  $\text{SiO}_2$ , was calculated using the formula:

$$\bar{m}_{\text{PMOS}} = \frac{\%C}{62 - \%C} \quad (1)$$

where 62% refers to the percent carbon in PMOS.

### 2.5. Solid-state NMR measurements

$^{29}\text{Si}$  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

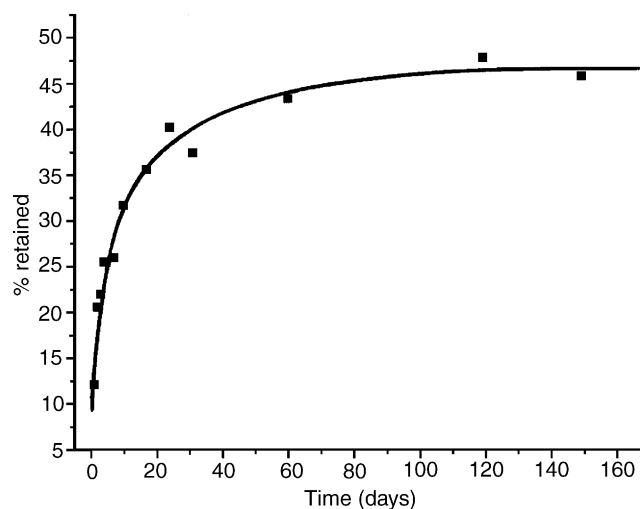


Fig. 1. Percent of PMOS retained in extracted  $\text{SiO}_2(\text{PMOS})$ , as a function of time before extraction, determined by elemental analysis.

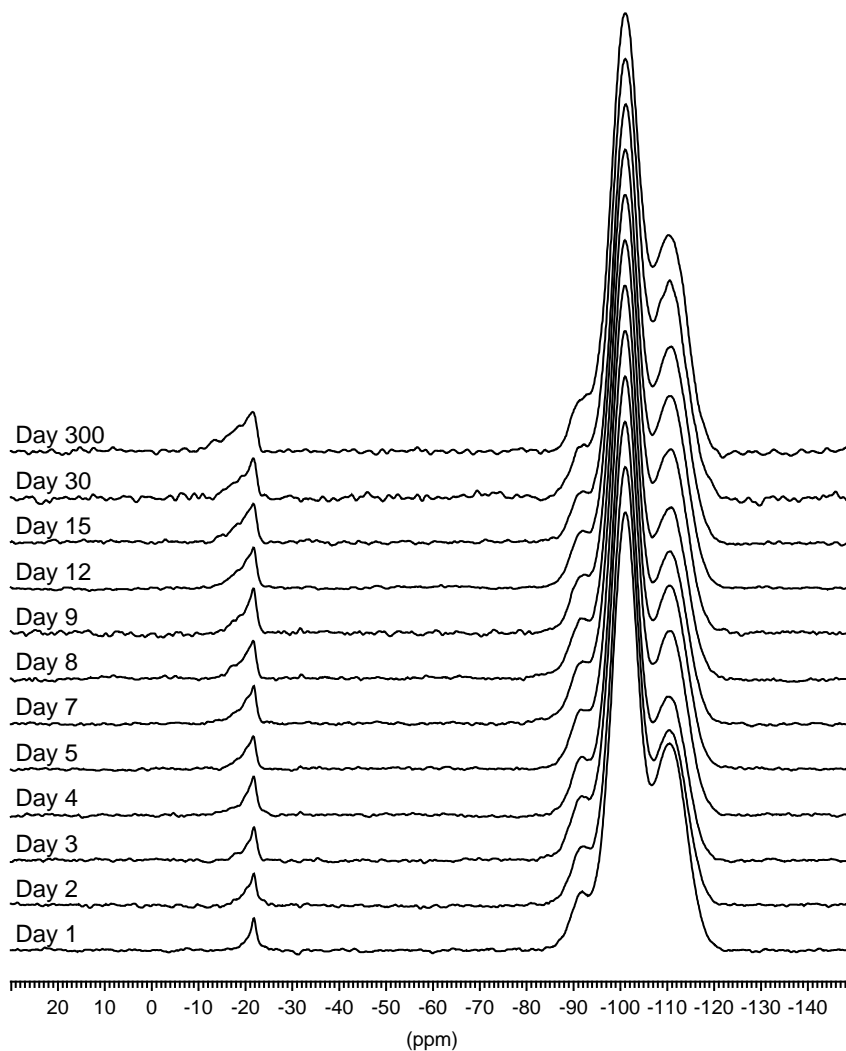


Fig. 2.  $^{29}\text{Si}$  CP-MAS-NMR spectra of non-extracted  $\text{SiO}_2(\text{PMOS})$  as a function of time.

bearing  $\text{ZrO}_2$  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  $^{29}\text{Si}$  and  $^1\text{H}$  were 59.59 MHz and 300.13, respectively. Typically, 1500 FIDs with an acquisition time of 30 ms were accumulated in 1 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

In a preliminary study of polymer extraction from  $\text{SiO}_2(\text{PMOS})$  considerable variations were observed between the values of retained PMOS, even from the same batch of PMOS-loaded silica particles and using the same extraction procedure. We hypothesized that an alteration in the configuration of polymer molecules within the pore

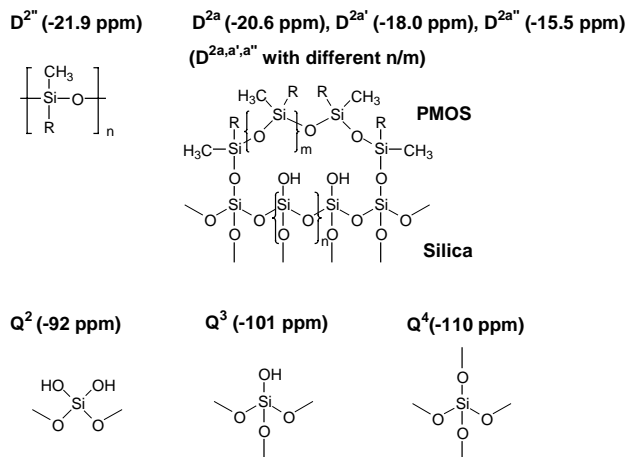


Fig. 3. Structures of the species  $\text{D}^{2a}$  ( $\text{D}^{2a'}$ ,  $\text{D}^{2a''}$ ) and  $\text{D}^{2''}$  and  $^{29}\text{Si}$  NMR chemical shifts for non-extracted and extracted  $\text{SiO}_2(\text{PMOS})$ :  $\text{R} = \text{C}_8\text{H}_{15}$ .

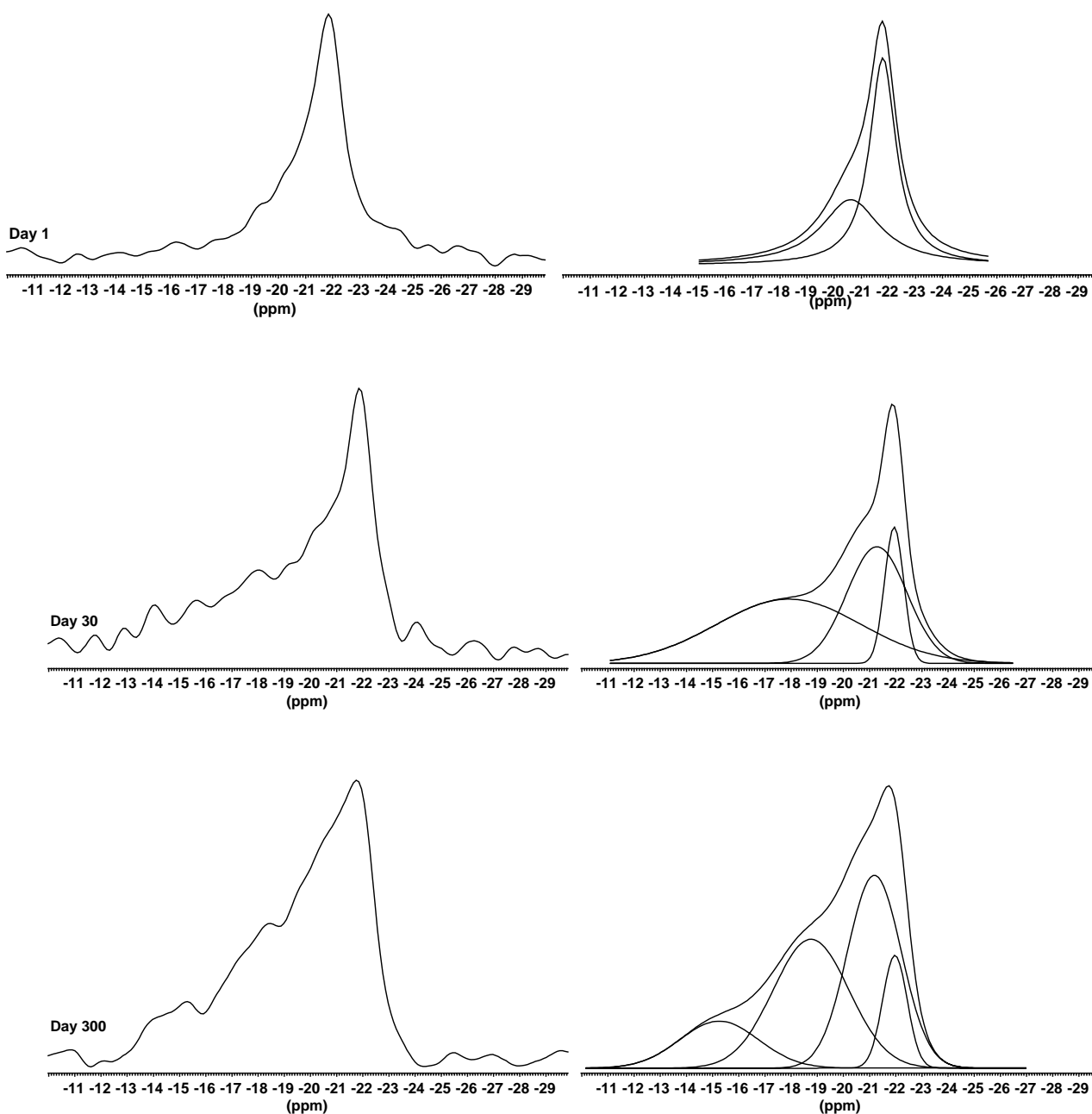


Fig. 4. Peak deconvolution of non-extracted  $\text{SiO}_2(\text{PMOS})$  at 1, 30 and 300 days after preparation.

system was occurring. Accordingly, in order to monitor the amount of polymer extracted from the same batch after different periods of time, portions of the same batch were extracted 1 day after preparation and after various other time periods, to permit an evaluation of the amount of non-extracted PMOS as function of time. These results are shown in Table 1 and the specific masses are plotted in Fig. 1.

Since the specific pore volume,  $v_p$ , for the silica used in this work is  $0.75 \text{ ml g}^{-1}$  of  $\text{SiO}_2$  and the density of PMOS at ambient temperature is  $0.91 \text{ g ml}^{-1}$ , we calculate that  $0.69 \text{ g}$  of PMOS/g of  $\text{SiO}_2$  will fill the pore system. Thus, a specific mass of PMOS ( $\bar{m}_{\text{PMOS}}$ ) equal to  $0.35 \text{ g PMOS/g SiO}_2$  corresponds to about half of the mass of PMOS necessary

to fill the pores of the silica used in this work. As shown in Fig. 1, initially  $\sim 90\%$  of the PMOS is extracted from the  $\text{SiO}_2(\text{PMOS})$  while  $\sim 60\%$  is extracted after 20 days. The samples of  $\text{SiO}_2(\text{PMOS})$  that were allowed to stand at ambient temperature, without any further treatment, for time periods of days or weeks show a slow further decrease in the amount of polysiloxane removed by extraction. This suggests that, over time, a redistribution of the liquid polymer occurs within the pore system, to give “self-immobilized” PMOS on the pore walls. As a consequence of the initial “plug” distribution of the PMOS in the pore system [8], only the plug regions will be filled (from wall-to-wall) with liquid PMOS, independent of the initial loading of liquid PMOS.

Table 2  
Relative amounts (%) of  $D^{2a}$ ,  $D^{2a'}$ ,  $D^{2a''}$  and  $D^{2''}$  determined by peak deconvolution

Time (days)	$D^{2''}$ (−21.9 ppm)	$D^{2a}$ (−20.6 ppm)	$D^{2a'}$ (−18.0 ppm)	$D^{2a''}$ (−15.5 ppm)
1	58	42	–	–
2	36	61	3	–
3	32	50	18	–
4	30	46	24	–
5	28	44	28	–
7	23	41	36	–
8	27	50	23	–
9	18	40	42	–
12	18	35	47	–
15	14	42	44	–
30	14	37	49	–
300	13	38	36	13

Non-plug regions will have no PMOS. Thus the molecular rearrangements which occur during self-immobilization must occur within the “plugs”. As a consequence, a layer coverage having  $\bar{m}_{\text{PMOS}} = 0.155$  g PMOS/g  $\text{SiO}_2$ , about 45% of the PMOS in a given plug can be immobilized, the

remaining 55% represents the central region of the plug that maintains liquid properties and can thus be extracted by an appropriate solvent (for PMOS), as shown in Fig. 1.

These interpretations are reinforced by  $^{29}\text{Si}$  CP-MAS-NMR experiments run on similar samples, also having an initial specific mass ( $\bar{m}_{\text{PMOS}}$ ) of 0.35 g PMOS/g  $\text{SiO}_2$ . The NMR spectra (Fig. 2) obtained at specific time periods after preparation, for non-extracted portions of the  $\text{SiO}_2(\text{PMOS})$ , show an increase of the peak area in the range from −22 to −15 ppm. A growing shoulder indicates the formation of a silicon species with a different chemical shift than pure PMOS, which shows resonance at −21.9 ppm ( $D^{2''}$ ). These new signals can be attributed to a combination of different adsorbed and chemically bonded  $D^{2a}$  groups.

Fig. 3 depicts the structures of the adsorbed and attached silicon species, along with the chemical shift values. Therefore, the adsorption process includes the formation of a strong attraction between the PMOS and the silica support. This has already been reported in the literature [6] but has not been described for the time dependent adsorption process of PMOS on silica. The new bonds can be explained by the formation of short loops which can be assigned to

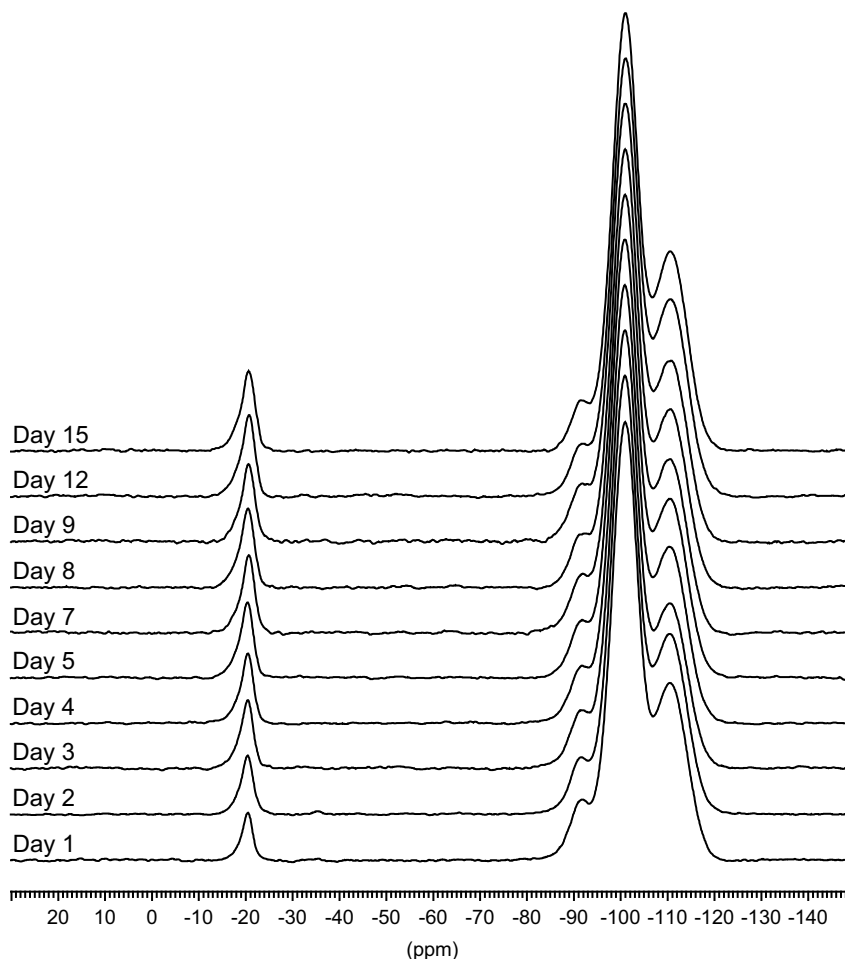


Fig. 5.  $^{29}\text{Si}$  CP-MAS-NMR spectra of extracted  $\text{SiO}_2(\text{PMOS})$  as a function of time before extraction.

chemical shifts of  $-20.6$  ppm ( $D^{2a}$ ). The increasing shift to lower field over time may be due to silicon species of the PMOS chains having more points of contact with the surface and/or forming a more uniform layer. It is believed that the loops move closer to the surface of the silica and, therefore, present a slightly higher chemical shift, as already described for the interaction of polysiloxanes on silica [20,21].

This proposal is supported by a peak deconvolution and simulation of the line shapes of the D groups. Since the resonances on the particle surface are closed, the self-immobilization process can be followed by signal deconvolution (Fig. 4). A good fit is obtained by employing various chemical shifts. Thus, the signal at  $-21.9$  ppm is assigned to pure liquid PMOS ( $D^{2'}$ ) whereas signals at  $-20.6$  ppm, as well as  $-18.0$  and  $-15.5$  ppm, may be attributed to “self-immobilized” PMOS (Fig. 3). The signal at  $-15.5$  ppm ( $D^{2a''}$ ) only appears after 300 days and may indicate that the rearrangement process continues very slowly to give an even more uniform PMOS layer. On the other hand, the signal at  $-20.6$  ppm, due to initially formed loops ( $D^{2a}$ ) appears quite rapidly. This indicates that the first step of self-immobilization is a relatively fast process. Table 2 gives the relative amounts of different silicon structural elements of the D group signals after deconvolution of the original signals. As the time before NMR evaluation increases, an increasing low field shift indicates the formation of a growing amount of self-immobilized silicon species ( $D^{2a}$ ,  $D^{2a'}$  and  $D^{2a''}$ ). Higher amounts of  $D^{2a'}$  and  $D^{2a''}$  groups are only formed after more than 8 days, which shows the more time consuming structuring process involved in completing a well formed self-immobilized PMOS layer, whereas the  $D^{2a}$  groups are formed quite rapidly. After only 1 day, nearly half of the peak area can be attributed to these  $D^{2a}$  groups.

Measurement of  $^{29}\text{Si}$  CP-MAS-NMR spectra of extracted  $\text{SiO}_2$ (PMOS) reinforces the interpretation of the self-immobilization process. Fig. 5 illustrates the spectra of extracted samples as a function of time before extraction. Thus, after extraction, no signals at  $-21.9$  ppm are detected, which means that all liquid PMOS has been removed from the sample and only the self-immobilized PMOS remains. In peak deconvolution, the chemical shifts of this adsorbed PMOS are assigned to  $-20.6$  ( $D^{2a}$ ) and  $-18.0$  ppm ( $D^{2a'}$ ), respectively. These are the same chemical shift values as obtained for the self-immobilized PMOS in the non-extracted samples.

Chromatographic evaluation of the self-immobilization process was investigated and are reported in [12]. Chromatograms obtained at specific times after preparation of the stationary phase showed that the time after polymer deposition significantly affects all the chromatographic parameters of the columns.

## 4. Conclusions

We conclude that the phenomenon of self-immobilization that occurs between PMOS and HPLC silica surfaces at ambient temperature results from a reconfiguration of the liquid polymer on the silica surface and results in a mobile-phase resistant (self-immobilized) stationary phase having good chromatographic properties.

## Acknowledgements

Financial support and fellowships from the Fundação de Amparo à Pesquisa do Estado de São Paulo, the Conselho Nacional de Desenvolvimento Científico e Tecnológico (Brazil), the Deutsche Forschungsgemeinschaft (FOR 184/3-1) and the Fonds der Chemischen Industrie (Germany) are gratefully acknowledged.

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