1874 *Chem. Mater.* **2001,** *13,* 1874−1879

Synthesis and Solid-State NMR Investigations of Radiation-Immobilized Polysiloxanes on Bare, Titanium-Grafted, and Zirconium-Grafted Silicas

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Received September 22, 2000. Revised Manuscript Received January 8, 2001

Three different reversed-phase materials for high-performance liquid chromatography, obtained by sorption of poly(methyloctylsiloxane) (PMOS) onto bare silica, titanized silica, and zirconized silica pores, followed by immobilization with γ-radiation, were characterized by means of solid-state NMR spectroscopy. The surface properties of these stationary phases were investigated by ^{29}Si CP/MAS and ^{13}C CP/MAS NMR spectroscopy. γ-Radiation causes the formation of new bonds, either between PMOS and the different supports or between different siloxane chains, which leads, in either case, to a higher amount of polysiloxane immobilized onto the silica support material.

1. Introduction

Reversed-phase high-performance liquid chromatography (RP-HPLC) typically uses columns packed with stationary phases having the retentive groups chemically bonded to the surface of the silica support. Stationary phases with attached C_8 and C_{18} alkyl chains are most common in HPLC,[1−4] although countless variations of phases with different alkyl chain lengths are available. Recently, C_{22} and C_{30}[5,6] materials were employed to obtain an improved selectivity for the separation of vitamin-A acetates[7] and β-carotene isomers.[8] Several stationary phases contain aromatic systems such as acridine, anthracene, pyrene, or fluorene.[9−12] Even so-called mixed phases, which combine different interactions during the separation process, have been introduced.[13] But all these conventional phases are limited in two important aspects. One is related to the inhomogeneity of the surfaces because of the presence of residual silanol groups, which influence the chromatographic separations.[14,15] The second is related to the instability of the silica support, which limits the pH range of the aqueous mobile phases that are used.[16] Various approaches have been taken to reduce these limitations, including end-capping (bonding small groups to some of the residual silanols of the silica surface),[17,18] the use of voluminous groups on the initial siloxane derivatizing agent,[19,20] horizontal polymerization,[21] encapsulation,[16,22] and the insertion of polar groups into the middle of the aliphatic chain.[23]

Another approach is the use of a polymer as a “liquid” phase, which is sorbed and then immobilized in the pores of an appropriate support. Schomburg and collaborators[24,25] loaded poly(methyloctylsiloxane) (PMOS) or poly(methyloctadecylsiloxane) (PMODS) into silica support particles and then immobilized a fraction of the polymer by heating in the presence of a radical initiator.

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10.1021/cm001179f CCC: $20.00

More recent studies have shown that columns prepared from stationary phases having PMOS adsorbed or adsorbed/immobilized onto silica,[26–28] zirconized silica,[29,30] and titanized silica[31,32] exhibit chromatographic properties similar to those of conventional C_8 and C_{18} reversed-phase materials. γ-Irradiation is a good method for immobilization of liquid phases coated on silica. It increases the amount of PMOS retained on the support materials and therefore improves the chromatographic performance. Even after prolonged contact with a high pH mobile phase, the amount of γ-radiation immobilized PMOS is only slightly reduced. Thus, these materials show significant promise as a support when high pH mobile phases are required.[30,32] Since there is no direct information available about the structure of these adsorbed and immobilized phases, an overall objective of the present work is to evaluate the physical properties of these new stationary phases for RP-HPLC, using solid-state NMR spectroscopy. Indirect evidence suggests that the liquid polysiloxane phase is initially deposited in a "wall-to-wall" manner (as "plugs" in the case of partially filled pores[33]), with formation of an essentially uniform adsorbed ("self-immobilized") monolayer over time.[34] Extraction, according to this model, involves the removal, by dissolution, of the central, nonadsorbed region of the plugs or filled pores.[35] Solid-state NMR spectroscopy is a powerful method[36] that should contribute to the elucidation of the structure and to the detection of new bonds within these stationary phases.

2. Experimental

2.1. Synthesis of the Zirconized and Titanized Silica Supports. For the synthesis of the silica supports, bare silica was activated at 140 °C under vacuum and then immersed in previously dried toluene. For the preparation of titanized silica, titanium tetrachloride ($TiCl_4$) was added at a ratio of 1.0 mmol of Ti/g of SiO_2,[31] while for the preparation of zirconized silica, 1.5 mmol of Zr/g of SiO_2 was added as $Zr(OBu)_4$.[29] The mixtures were refluxed for 12 h under an atmosphere of argon. The resulting materials were washed with toluene to remove any excess of $TiCl_4$ or $Zr(OBu)_4$, filtered, and heated to 140 °C under vacuum. In the case of the titanized silica, gaseous ammonia was passed through the dried material for 3 h, after which the material was washed with ethanol. Finally, the materials were hydrolyzed with 10^{-3} mol/L nitric acid, washed several times with water to remove all residual chloride or butoxy groups from the surface of the modified silica, and dried at 110 °C for 24 h before use.

2.2. Preparation of the Stationary Phases with PMOS. Bare silica (Si), zirconized silica (Si−Zr), or titanized silica (Si−Ti) were each added to a solution containing an equal mass of PMOS in excess dichloromethane solvent. After this mixture was stirred for 3 h at room temperature, the dichloromethane was removed by evaporation to obtain the stationary phases Si(PMOS), Si−Zr(PMOS), and Si−Ti(PMOS). Once the stationary phases had been prepared, portions of each of the PMOS modified phases were sealed in glass ampules under air and then irradiated to 80 kGy of an absorbed dose with an industrial ^{60}Co γ-ray source (IBRAS-CBO, Campinas, Brazil) at a dose rate of ~40 kGy h^{-1}. Portions of all samples, without and with γ-irradiation, were extracted with dichloromethane for 4 h and then dried before being submitted to further analyses.

2.3. Elemental Analyses. %C determinations were obtained on a Perkin-Elmer CHN Analyzer (Model CHN-2400). Quantification of Ti and Zr were made using a Spectrace 5000 X-ray fluorescence spectrometer.

2.4. Solid-State NMR Measurements. ^{13}C CP/MAS NMR spectra were obtained using a Bruker DSX 200 instrument. Magic-angle spinning was carried out with 4-mm double bearing rotors of ZrO_2 and spinning rates of 10 000 Hz. The proton 90° pulse length was 7 μs and the contact time and delay time were 5 ms and 3 s, respectively. The line broadening used was 10 Hz.

^{29}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 bearing ZrO_2 rotors. The spectra were obtained with a cross-polarization contact time of 5 ms. The pulse interval time was 1 s. Typically, 1.5 k 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 20 kHz.

3. Results and Discussion

The preparation of the titanized and zirconized silica supports can be described by the following equations:

titanized silica

$$n{\equiv}\mathrm{SiOH} + \mathrm{TiCl_4} \rightarrow ({\equiv}\mathrm{SiO})_n\mathrm{TiCl}_{4-n} + n\mathrm{HCl}$$

$$({\equiv}\mathrm{SiO})_n\mathrm{TiCl}_{4-n} + (4-n)\mathrm{H_2O} \rightarrow ({\equiv}\mathrm{SiO})_n\mathrm{Ti(OH)}_{4-n} + (4-n)\mathrm{HCl}$$

zirconized silica

$$n{\equiv}\mathrm{SiOH} + \mathrm{Zr(OBu)_4} \rightarrow ({\equiv}\mathrm{SiO})_n\mathrm{Zr(OBu)}_{4-n} + n\mathrm{BuOH}$$

$$({\equiv}\mathrm{SiO})_n\mathrm{Zr(OBu)}_{4-n} + (4-n)\mathrm{H_2O} \rightarrow ({\equiv}\mathrm{SiO})_n\mathrm{Zr(OH)}_{4-n} + (4-n)\mathrm{BuOH}$$

Both the specific surface area and the quantity of titratable hydroxyl groups (Si−OH, Ti−OH, Zr−OH) decreased with the titanium or zirconium modification, while the adsorption of PMOS leads to a significant decrease of the specific surface area as a result of loading the polymers into the pores of the different silica supports, as described elsewhere.[26,29,31]

Figure 1 shows the ^{13}C CP/MAS NMR spectra of the three polysiloxane stationary phases based on PMOS adsorbed into Si, Si−Zr, or Si−Ti supports with and without γ-irradiation treatment. This technique enables a clear structure elucidation of these materials. The spectra of the PMOS-covered samples show the same resonances due to a similar structure concerning the organic parts of the molecules. The methyl group

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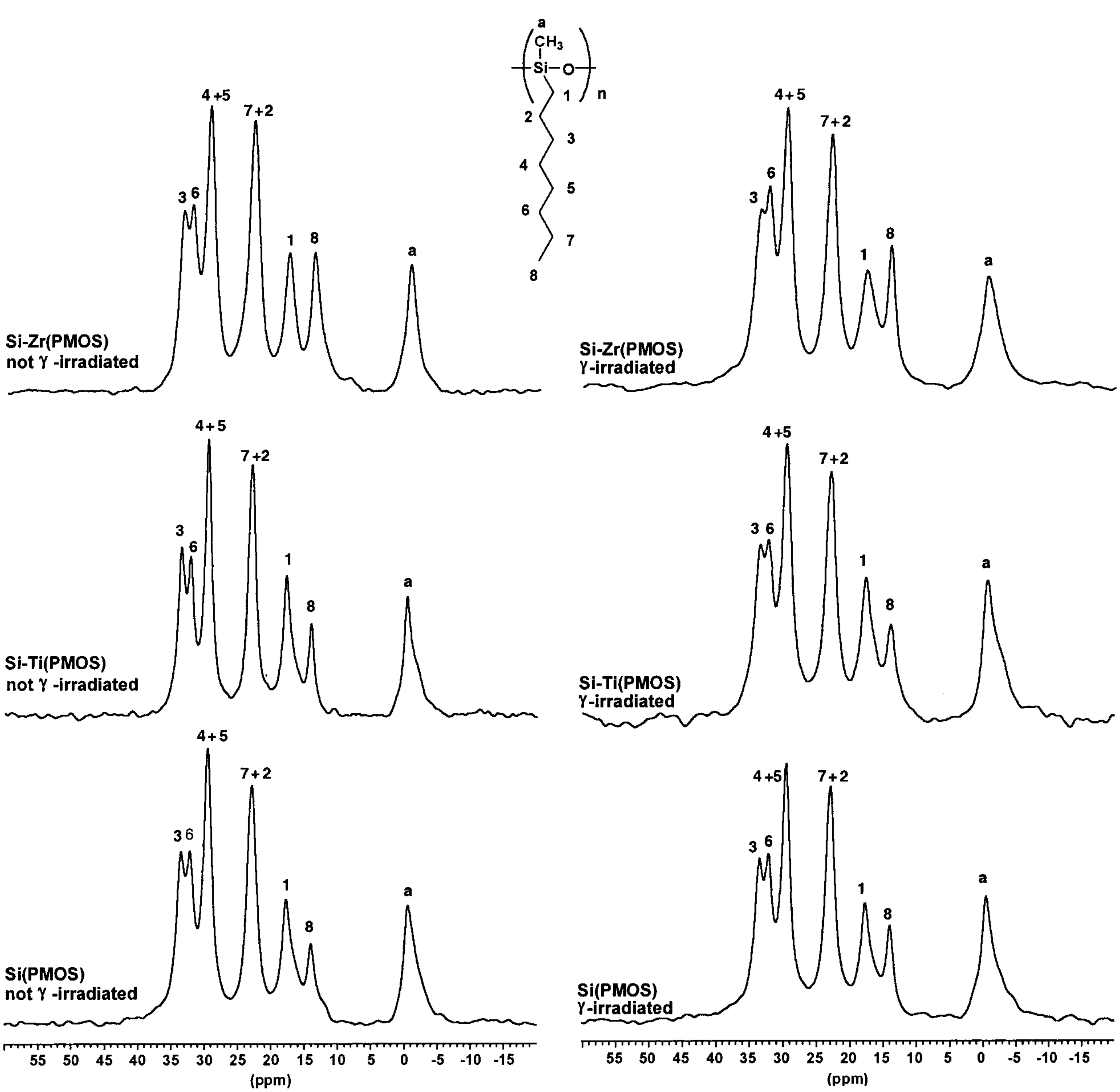

Figure 1. ^{13}C CP/MAS NMR spectra of poly(methyloctylsiloxane) (PMOS) adsorbed on bare silica, zirconized silica, and titanized silica support materials and of the immobilized phases irradiated at 80 kGy at a dose rate of ~40 kGy h^{-1}.

Table 1. ^{13}C Chemical Shift Values of Si(PMOS), Si−Ti(PMOS), and Si−Zr(PMOS) with and without γ-Irradiation

chemical shift values (ppm)	33.6	32.1	29.6	23.0	17.8	14.1	−0.3
structural components	CH_2	CH_2	CH_2	CH_2	$SiCH_2$	CH_3	$SiCH_3$
peak assignment no.	3	6	4+5	7 + 2	1	8	*a*
reference				38			

directly attached to the siloxane backbone (C-*a*) causes a signal at 0 ppm and the carbon atoms of the C_8 chain (C-1 to C-8) show resonances in the range from 15 to 36 ppm. The ^{13}C NMR spectrum of PMOS dissolved in $CDCl_3$ shows the same resonances for all carbon atoms, even though the resolution in the solid state is not as high as that in the liquid. The ^{13}C CP/MAS NMR spectra of the PMOS adsorbed and γ-irradiation-immobilized solid phases are also very similar to those of the nonirradiated phases. Table 1 gives the chemical shift values together with structural components and the peak assignment numbers as well as reference data from the literature. Only slight differences in the intensity of the C-8 signal (methyl group) are seen. The zirconized sample shows, in both cases, the highest intensity of the C-8 signal. But the mobility of the different structural elements plays an important role in the signal intensity. A change in the contact time used for cross polarization from 5 to 3 ms leads to a strong intensity decline of the C-8 signal whereas the other resonances maintain their intensities. Taking this into account, the changes observed in the ^{13}C CP/MAS NMR spectra between irradiated and nonirradiated samples are insignificant. It only can be concluded that the Si−Zr(PMOS) phase shows a slightly higher mobility for the C_8 chains compared to the other samples. This result is confirmed by the elemental analysis data (Table 2). Only 16.6% PMOS are adsorbed on the zirconized silica, which leads to a higher mobility of the C_8 chains. Summarizing the results of the ^{13}C CP/MAS NMR measurements, it is believed that γ-irradiation has only a minor influence on the bonding of the organic groups of the siloxanes.

Table 2. Elemental Analysis and X-ray Fluorescence Data for Si(PMOS), Si−Ti(PMOS), and Si−Zr(PMOS) with and without γ-Irradiation

sample	results of analysis
Si(PMOS) (nonirradiated)	16.8% C (27.1% PMOS)
Si(PMOS) (γ-irradiated)	20.7% C (33.4% PMOS)
Si−Ti	5.1% Ti (3.3 μmol of Ti/m^2 of SiO$_2$)
Si−Ti(PMOS) (nonirradiated)	15.5% C (25.0% PMOS)
Si−Ti(PMOS) (γ-irradiated)	20.5% C (33.1% PMOS)
Si−Zr	16.7% Zr (5.2 μmol of Zr/m^2 of SiO$_2$)
Si−Zr(PMOS) (nonirradiated)	10.3% C (16.6% PMOS)
Si−Zr(PMOS) (γ-irradiated)	20.2% C (32.6% PMOS)

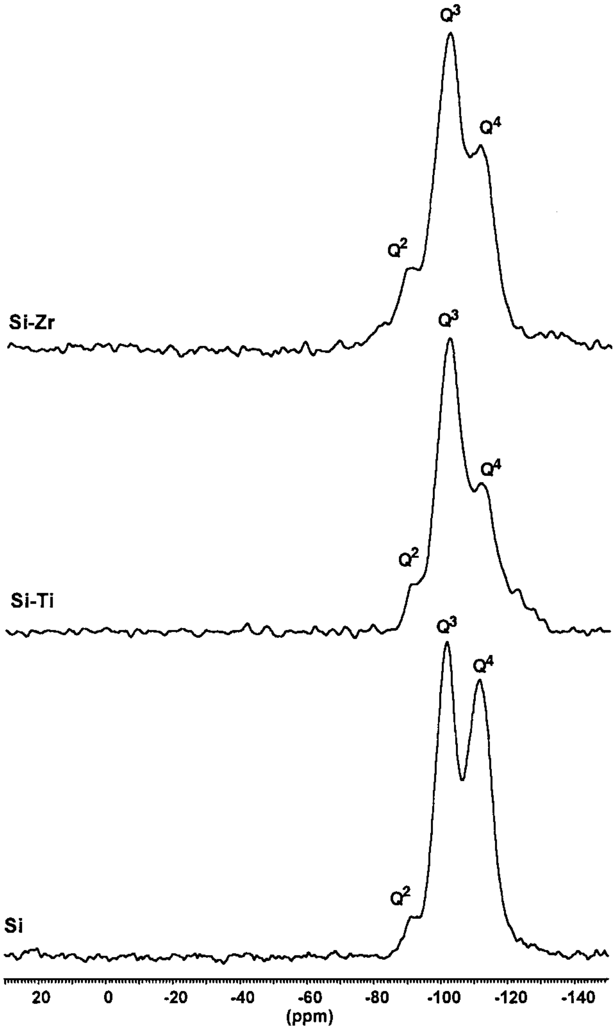

Figure 2. ^{29}Si CP/MAS NMR spectra of bare silica, zironized silica, and titanized silica support materials before adsorption of PMOS.

The ^{29}Si CP/MAS NMR spectra of the Si, Si−Zr, or Si−Ti supports are shown in Figure 2. The bare silica, and the materials modified with ZrO$_2$ and TiO$_2$, show the well-known resonances of Q^2 (dihydroxysiloxane), Q^3 (hydroxysiloxane), and Q^4 (tetrasiloxane) groups (Figure 3). Although all spectra were measured with the same instrument parameters, the zirconized and titanized supports show lower amounts of Q^4 groups than the bare silica. Contact time measurements with similar materials showed that the cross-polarization efficiencies for Q^3 and Q^4 groups are quite similar. Therefore, it is possible to compare these structural units qualitatively but not quantitatively.

After PMOS deposition, different silicon species (Figure 3) are seen in the ^{29}Si CP/MAS NMR spectra (Figure 4). At −22 ppm a strong signal shows the resonances of the polysiloxane backbone (D$^{2''}$). With Si(PMOS), signals of D^1, D$^1_{\mathrm{H}}$, D$^{2'}$, and M groups can be detected, whereas with the titanized and zirconized support materials, there are hardly any resonances of D^1 groups. Furthermore, the comparable small shoulder at −20 ppm indicates only a small amount of D$^1_{\mathrm{H}}$ and possibly D$^{2'}$ groups in all three materials. All these samples show a lower amount of free silanol groups (Q^2; Q^3), probably because of the interaction of some of the silanol groups with the adsorbed polysiloxane.

After the γ-irradiation, additional signals occur in the ^{29}Si CP/MAS NMR spectra of PMOS immobilized into Si, Si−Zr, or Si−Ti supports (Figure 5). Table 3 gives the chemical shift values of the different materials along with reference data from the literature used for the peak assignments.

A similar cross-polarization efficiency of the same structural elements in the three different phases permits a qualitative comparison. In addition to the D$^{2''}$ groups (−22 ppm) of the PMOS chain, there are signals at −32 ppm and around −20 ppm, which are assumed to belong to D$^2_{\mathrm{H}}$ and D$^1_{\mathrm{H}}$ groups and signals of D^1 groups at −9 ppm. These signals may be explained as due to the breaking of some Si−O−Si bonds of the polysiloxane chain by the γ-irradiation. Signals in the range of −20 ppm (D$^{2'}$ groups) can be attributed to the formation of short loops.[37] Some of the PMOS chains are only loosely attached or physically adsorbed (D$^{2''}$ groups) while others are chemically bonded (D$^{2'}$ groups). The signals of T^3 groups occurring at −65 ppm and of T^2 groups at −55 ppm support this interpretation. For bare and titanized support materials, these groups indicate an increase of cross linking. Therefore, it can be concluded that either a reaction between the polysiloxane backbone and the support material or a reaction within the polysiloxane chain itself has taken place as a result of the γ-irradiation, although we believe the first reaction to be more likely.

The ^{29}Si CP/MAS NMR spectrum of the γ-irradiated Si−Zr(PMOS) sample does not show the formation of T groups. The spectrum of this sample shows resonances at −22 ppm due to D$^{2''}$ groups of the intact polysiloxane. Signals in the range of −20 ppm may be caused by D$^1_{\mathrm{H}}$ and D$^{2'}$ groups. Furthermore, there are signals of D^1 groups. But in comparison to PMOS on bare and titanized silica, the PMOS on the zirconized support does not show resonances due to D$^2_{\mathrm{H}}$ or T groups. Therefore, the quantity of linkages between the Si−Zr support and PMOS is considered to be lower. A strong resonance at −20 ppm supports this interpretation. The amount of D$^{2'}$ groups is higher than that in the other two cases, which could mean that more loops of the polysiloxane backbone are formed as a result of the γ-irradiation.

Elemental analysis data help to clarify the different behaviors of the zirconized and titanized support materials. The relatively high amount of Zr in the zirconized support material (16.7% Zr) compared to the

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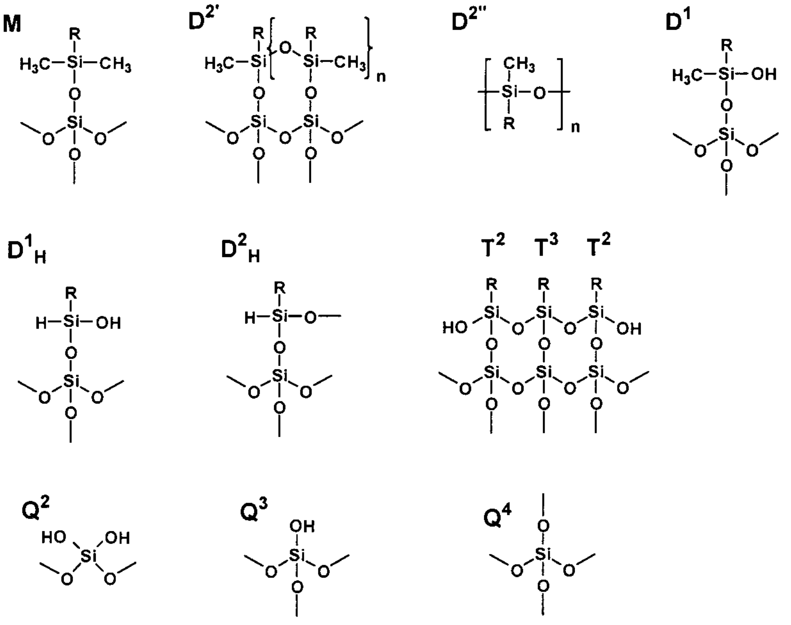

Figure 3. Different silicon elements occurring in the stationary phases (R = C_8).

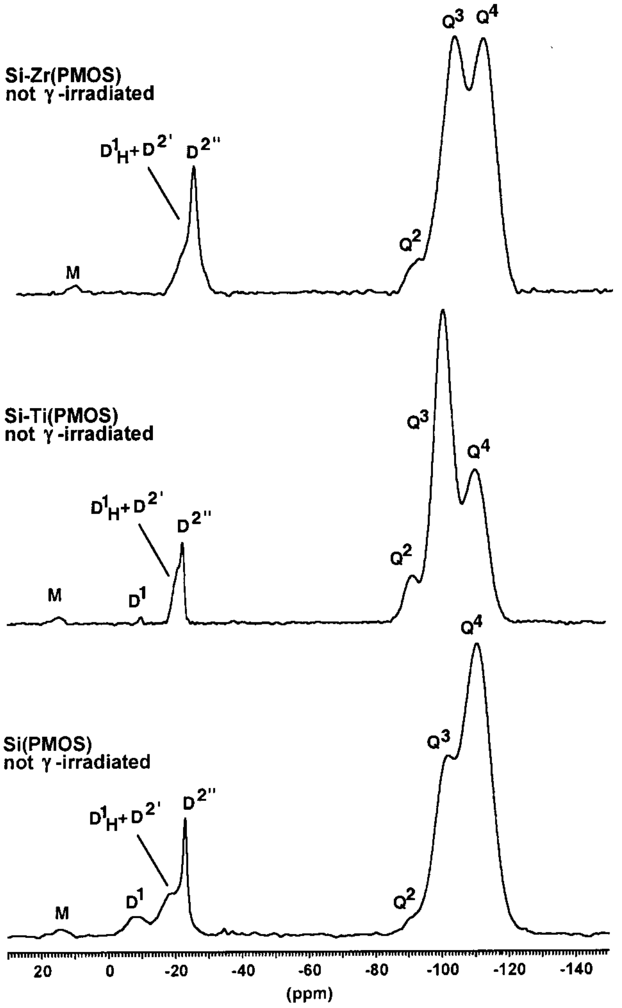

Figure 4. ^{29}Si CP/MAS NMR after PMOS deposition on the support materials, using similar cross-polarization efficencies as in Figure 2.

lower amount of Ti in the titanized sample (5.1% Ti) influences the formation of T groups. In the case of the titanized sample (Si−Ti) the surface seems to have

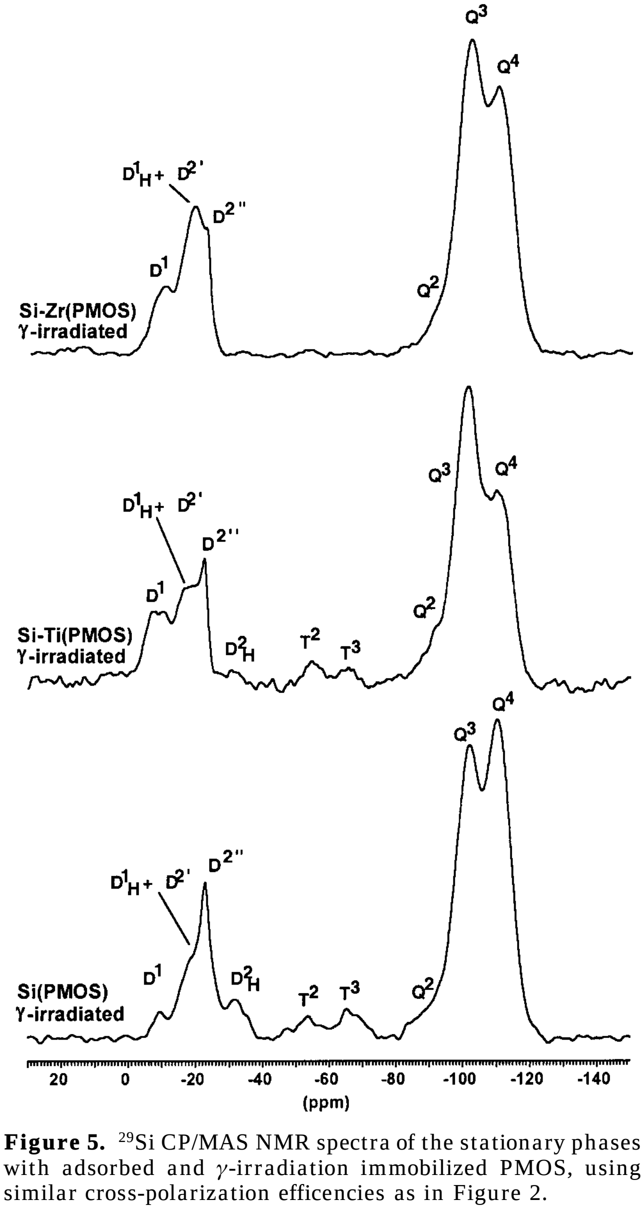

Figure 5. ^{29}Si CP/MAS NMR spectra of the stationary phases with adsorbed and γ-irradiation immobilized PMOS, using similar cross-polarization efficencies as in Figure 2.

Table 3. ^{29}Si Chemical Shift Values for Si(PMOS), Si−Ti(PMOS), and Si−Zr(PMOS), with and without γ-Irradiation[a]

	chemical shift values (ppm)						
	not γ-irradiated			γ-irradiated			
structural components	Si(PMOS)	Si−Ti(PMOS)	Si−Zr(PMOS)	Si(PMOS)	Si−Ti(PMOS)	Si−Zr(PMOS)	ref
M	+14.3	+14.4	+14.1			(+14.1)	4, 38, 39
D^1	−8.9	−9.2		−9.2	−8.9	−9.2	4, 39
$D^1_H + D^{2'}$	∼ −20	∼ −20	∼ −20	∼ −20	∼ −20	∼ −20	37
$D^{2''}$	−22.1	−22.3	−22.2	−22.2	−22.3	−22.0	37
D^2_H				−31.6	−31.4		38, 39
T^2				−55.2	−55.3		4, 38, 39
T^3				−65.1	−65.2		4, 38, 39

[a] The quarternary Q^2 and Q^3 as well as the Q^4 groups show the typical chemical shifts of −91, −101, and −110 ppm, respectively, and are not shown in this table.

similar properties to bare silica, which leads to the formation of comparable species after γ-irradiation. On the other hand, the titanized or zirconized silicas, which have been coated with PMOS and γ-irradiated, show relatively high amounts of D^1 and D^1_H groups compared to γ-irradiated Si(PMOS). Therefore, it can be concluded that during γ-irradiation the presence of the metal (Ti or Zr) on the silica surface leads to the formation of the D groups, which means that the metal may catalyze the breaking of Si−O−Si bonds of the polysiloxane chain.

γ-Irradiation is very important for increasing the amount of polymer immobilized onto the silica supports.[26,29−32] Although suggested by other physical tests, solid-state NMR spectroscopy now strongly indicates that an increase in cross linking leads to a more stable matrix and therefore to an increased amount of PMOS in the stationary phase. The fact that hardly any M groups occur in the ^{29}Si CP/MAS NMR spectra of the irradiated support materials is another hint that more cross linking is taking place. After γ-irradiation it appears that some of the polysiloxane backbone is directly attached to the support surface. This improves the chromatographic performance and significantly increases the stability of the γ-irradiated stationary phases.[30,32]

4. Conclusions

Bare silica, titanium-grafted, and zirconium-grafted silica supports, modified with PMOS, were investigated by solid-state NMR spectroscopy. The measurements of ^{29}Si CP/MAS and ^{13}C CP/MAS NMR spectra confirmed the presence of PMOS adsorbed onto the different supports and enabled a clear structure elucidation. γ-Irradiation of the PMOS adsorbed on the different support materials leads to both bond breaking and an increase in cross linking. Therefore, the packing material retains a higher amount of PMOS than the nonirradiated material, which improves chromatographic performance and stationary phase stability. Although γ-irradiation affects the PMOS adsorbed onto bare, zirconized, or titanized silica supports differently, little influence of γ-irradiation on the organic chain of the polysiloxane was detected. After γ-irradiation, PMOS on zirconized silica apparently possesses a high amount of polysiloxane loops, whereas γ-irradiation of PMOS on bare or titanized silica appears to produce T groups. Without γ-irradiation the different phases show primarily the resonances of the polysiloxane backbone, which allows clarification of the effects of γ-irradiation on the different silicon species.

Acknowledgment. Financial support from the Deutsche Forschungsgemeinschaft [FOR 184/3-1], the Fonds der Chemischen Industrie and the Fundação de Amparo à Pesquisa do Estado de São Paulo [94/3580-5] is gratefully acknowledged. S.B. also gratefully acknowledges financial support from the Graduiertenkolleg “Chemie in Interphasen” and wishes to thank LABCROM for the opportunity to work at the Instituto de Química, Universidade Estadual de Campinas.

CM001179F