Langmuir **1997,** *13,* 2271−2278

Influence of the Deposition Process on the Structure of Grafted Alkylsilane Layers

J. Duchet,*,† B. Chabert,† J. P. Chapel,† J. F. Gérard,*,‡ J. M Chovelon,§ and N. Jaffrezic-Renault§

Laboratoire d'Etudes des Matériaux Plastiques et des Biomatériaux-UMR CNRS #5627, Université Claude Bernard LYON I, 43 Boulevard du 11 Novembre 1918-Bât 303, 69622 Villeurbanne Cedex, France, Laboratoire des Matériaux Macromoléculaires-UMR CNRS #5627, INSA Lyon, 20 Avenue Albert Einstein-Bât. 403 69621 Villeurbanne Cedex, France, and Laboratoire d'Ingénierie et Fonctionnalisation des Surfaces-UMR CNRS #5621, Ecole Centrale de Lyon, BP 163, 69131 Ecully Cedex, France

Received June 17, 1996. In Final Form: December 19, 1996⊗

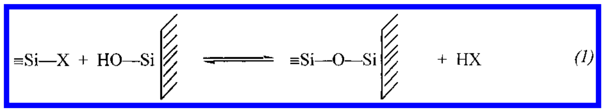
Monofunctional alkylsilanes, $CH_3(CH_2)_{n-1}Si(CH_3)_2R$ with n varying from 4 to 30 and the hydrolyzable group $R = Cl$ or $N(CH_3)_2$, were deposited on quartz slides and on nanometric silica. Due to the presence of only one hydrolyzable group for these alkylsilanes, silane monolayers result from the grafting process. Two methods for silanization were considered: deposition from a solvent (derived from Sagiv's process) and vapor phase deposition (derived from Kovats's process). In vapor phase deposition, the physisorbed water is mainly removed from the surface during the conditioning of the specimens, whereas this is not the case for the solvent method. In addition, the two deposition processes do not take place at the same temperature: the silane needs to be heated under vacuum for the vapor deposition method, whereas the reaction takes place at room temperature for the solvent method. Characterizations of the grafting efficiency and of the structure of the grafted layers were performed with different techniques including contact angle measurements, cross polarization magic angle spinning ^{29}Si NMR, and gas chromatography. The comparison between the two methods of deposition showed that the grafting process has a great influence on the resulting monolayers. By considering the wetting behavior, we can evidence that silane monolayers deposited from a toluene solution are less well-ordered than those resulting from the vapor phase method. In fact, the choice of the solvent for deposition is crucial. This effect is due to the competition between the solvent and the silane molecules to reach the silica surface. This competition, which infuences the packing density of the grafted layer, is dependent on the polarity and the shape of the solvent molecules and on the deposition process.

Introduction

Modification of hydrophilic substrates by grafting organic chains with controlled structures is of great importance in science and industry. Organosilanes, in particular functionalized molecules (e.g., amino, vinyl, epoxy, or chlorosilanes), are used extensively for generating organic layers on silica substrates. They provide a wide field of applications from biosensors for antibody immobilization[1] to lubricants.[2] Silanes also find extensive applicability in the preparation of bonded phases for liquid and gas chromatography.[3] Adhesive and mechanical properties of the glass fiber/polymer matrix interface can be improved by addition of the appropriate silane-coupling agents.[4,5] Because of their widespread applications, there is a lot of research on the underlying reaction mechanisms in the modification process involving silanes. A fundamental understanding of these mechanisms can lead to an improvement of known applications and the development of new ones.

Chemical surface modification may be defined as the chemical bonding of molecules or molecule fragments to a surface in order to change its chemical or physical properties in a controlled way. The properties imparted by the silane are closely linked to the selection of the organo group and to the nature of the bond to the surface. If a chemical modification procedure is to be selected, the desired coating morphology is of main concern. The coating morphology includes the type of interaction between the coating layer and the surface (relative balance between physisorption and chemisorption), the modification density (molecules per surface unit), the orientation of the molecules on the surface, and the layer thickness. The organic solvent and the vapor phase modification procedures are commonly used in silane technology.

In the vapor phase process, a direct reaction of the organosilane with the surface hydroxyl groups forms a strong siloxane Si−O−Si surface bond. The oxygen atom of the surface hydroxyl group attacks the silicon atom of the alkylsilane as follows:



(1)

But this reaction is generally performed at very high temperatures (>300 °C), limiting the number of silanizing agents to those which have a high thermal stability and sufficient vapor pressure.[6,7] Thus, the more common approach is to perform the silanization in a solvent at room temperature. The main drawback, in these solution

---

* To whom correspondence should be addressed.

† Laboratoire d'Etudes des Matériaux Plastiques et des Biomatériaux.

‡ Laboratoire des Matériaux Macromoléculaires.

§ Laboratoire d'Ingénierie et Fonctionnalisation des Surfaces.

⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1997.

(1) Andle, J.; Vetelino, J.; Lec, R.; Alister, D. M. *Proc. IEEE Ultrason. Symp.* **1989**, 579.

(2) Zarrad, H.; Cléchet, P.; Belin, M.; Martelet, C.; Jaffrezic-Renault, N. J. *Micromech. Microeng.* **1993**, *3*, 222.

(3) Gaget, C.; Morel, D.; Traoré, M.; Serpinet, J. *Analysis* **1984**, *12*, 386.

(4) Feller, J. F.; Guyot, A.; Spitz, R.; Chabert, B.; Gérard, J. F. *Compos. Interfaces* **1995**, *3* (2), 121.

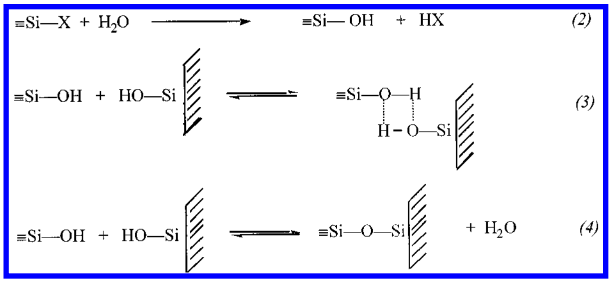
(5) Gonon, L. Ph.D. Thesis, University of Lyon I, Lyon, France, 1994.

(6) Tripp, C. P.; Hair, M. L. *Langmuir* **1991**, *7*, 923.

(7) Hair, M. L.; Tripp, C. P. *Colloids Surf. A* **1995**, *104* (20), 95.

S0743-7463(96)00598-7 CCC: $14.00

reactions, is the poorly reliable structure of the resulting films. This variability is due to the water molecules which are physisorbed at the surface. The processes involved can be described as follows:



In the first step, the organosilane is hydrolyzed by water which is either preadsorbed on the surface or present in the solvent (reaction 2). In the second step, the hydrolyzed silane is adsorbed via hydrogen bonds and can react with the surface silanol groups at the surface to form a siloxane Si−O−Si bond (reactions 3 and 4). The HX species can also catalyze the hydrolysis and silanization of silanes. In fact, the balance between these two chemical mechanisms, i.e., the kinetics of grafting, is dependent on the pH of the solution (basic or acidic medium).[8] For example, the hydrochloric acid, which corresponds to the HX species in the case of chlorosilane, favors the hydrolysis mechanisms.[9] In the absence of water at the silica surface, it has been shown that no reaction between the alkylchlorosilane and the silica surface occurs in solution at these low temperatures.[7,10] However, as reported by McGovern, if a small amount of water is necessary for hydrolysis of the chloro moieties of the silane in the bulk solvent phase, too much water needs to be avoided to prevent the condensation between silanes located on top of the water monolayers.[11] In the latter case, the silane layer can easily be floated off.[12] As an example of the important role of water on the grafting process, Le Grange observed using FT-IR spectroscopy that silane molecules can react with a partially hydrated surface suggesting that some of the silane groups are bonded to the surface.[13]

The cleaning procedure used prior to the silanization of the substrates is another crucial parameter involved in the variability of the grafting and structure of the layers. McGovern et al. give plenty of experimental details concerning the cleaning process needed to obtain noncontaminated and reproducible surfaces.[11] They showed that (highly) reliable monolayers were produced when the solvents used were able to extract water from the glass surface and induce the hydrolysis of the chloro moieties of silane. Child et al. have also investigated the effect of the solvent (nature−polarity) on adsorption behavior.[14] Tripp showed that 70% of the trimethylsilanol reacts with the surface silanol groups to form a siloxane bond; the remaining 30%, attributed to weakly adsorbed species, was removed from the surface silanol groups by curing.[10] Silberzan et al.[12] concluded that room temperatures favor grafting, and Brzoska et al.[15] confirmed the existence of a transition temperature below which layers of a high order can be obtained.

The aim of this paper is to evidence the chemical bonding between alkylsilane molecules and a silica surface. The grafting of monofunctional organosilanes (chloro- and aminosilane) on a silica surface is investigated. As the functionality of the silanes is equal to that of the silanol groups, the silane−silica interactions are simplified and the interface interactions can be modeled since monolayers are formed. This paper is devoted to a comparative investigation of some basic structural features for grafting silane monolayers using a solvent or vapor phase method. The solvent modification allows us to investigate the effect of the solvent on the silanization of glass substrates. The effect of activation before grafting the substrates is also considered because the silica surfaces were treated at 140 °C under vacuum during the vapor phase process in order to remove physisorbed water, whereas that was not the case for solvent process.

Contact angle measurements were performed in order to characterize the hydrophobicity, the structure, and the continuity of the grafted monolayers onto silica. The chemical bonding between the alkylsilanes and the silica surface was checked by ^{29}Si cross-polarization at the magic angle (CP/MAS) NMR spectroscopy. Furthermore, the grafting density was determined on quartz by chromatography and was correlated with the grafting ratio measured by elemental analysis on nanosize silica.

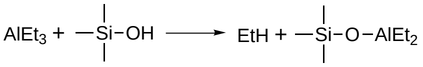
Experimental Section

Chemical Reagents. The alkylchlorosilanes used have the structure $CH_3{-}(CH_2)_{n-1}(CH_3)_2Si{-}Cl$ with $n = 4, 8, 18$, and 30 (denoted C4, C8, C18, and C30, respectively) (from Roth Sochiel) and were used without any further purification (purity > 97%). The aminosilane $CH_3{-}(CH_2)_{17}{-}Si(CH_3)_2N{-}(CH_3)_2$ was used as received from Chemical Ueticon (Switzerland, purity > 97%)

All of the used solvents were of analytical grade and obtained from Aldrich. Toluene and carbon tetrachloride were dried before use.

Silica Surfaces. Depending on the characterization technique used organosilanes were deposited on quartz slides ($50 \times 15 \times 2$ mm^3; from Verres & Sciences Technol.; R_a roughness estimated at 7 Å) and pyrogenic silica particles (Aerosil 200 from Degussa) having a diameter of 7 to 12 nm and a specific area (measured by nitrogen adsorption) of 200 ± 25 m^2·g^{-1}. According to the high value of the specific area, the grafting density can not be easily compared to that obtained on quartz slides, especially for the largest molecules. This type of silica was considered in order to verify the ability of the silanes to be grafted.

The cleaning and the hydroxylation of the silica surface are of importance in the grafting process. Quartz was degreased under ultrasonic stirring with acetone first and in methanol thereafter. The sample was dipped in a hot sulfochromic solution (120 °C) for 15 min, and the substrates were then rinsed with purified water and blown with dry nitrogen. For silica particles, a long dipping time (160 h) in an aqueous solution (pH = 6) leads to hydrolysis of the surface siloxane groups. Thus, in order to determine the number of silanol groups per unit surface (area), the silica was first treated with a solution of triethylaluminum in heptane according to the following reaction scheme:



$$AlEt_3 + {-}\overset{|}{\underset{|}{Si}}{-}OH \longrightarrow EtH + {-}\overset{|}{\underset{|}{Si}}{-}O{-}AlEt_2 \qquad (5)$$

The volume of released ethane was then measured. A blank measurement with pure heptane was performed to eliminate the contribution of heptane vapor (solvent of triethylaluminum).[16] The results are given in Table 1.

Grafting Processes. *Vapor Phase Method (Figure 1).* After the cleaning procedure, the silica surfaces were dried at 140 °C under vacuum (0.2 Pa) for 2 h to remove the physisorbed water.

---

[8] Pope, E. J. A.; McKenzie, J. D. J. *Non-Cryst. Solids* **1986**, *87*, 185

[9] Keefer, K. D. *Mater. Res. Soc. Symp. Proc.* **1984**, *32*, 15

[10] Tripp, C. P.; Hair, M. L. *Langmuir* **1995**, *11*, 149.

[11] Mc Govern, M. E.; Kallury, K. M. R.; Thompson, M. *Langmuir* **1994**, *10*, 3607.

[12] Silberzan, P.; Léger, L.; Ausserré, D.; Benattar, J. J. *Langmuir* **1991**, *7*, 1647.

[13] Le Grange, J. D.; Markham, J. L.; Kurkjian, C. R. *Langmuir* **1993**, *9*, 1749.

[14] Child, M. J.; Heywood, M. J.; Pulton, S. K.; Vicary, G. A.; Yong, G. H.; Rochesier, C. *J. Colloid Interface Sci.* **1982**, *89*, 1202.

[15] Brzoska, J. B.; Ben Azouz, I.; Rondelez, F. *Langmuir* **1994**, *10*, 4367.

[16] Pasquet, V.; Spitz, R. *Makromol. Chem.* **1990**, *191*, 3087.

Table 1. Determination of Hydroxyl Groups on Bare Silica by Reaction with Triethylaluminum

silica treatment	Σ^{OH}_{silica} (nm^2)
nonhydroxylated silica	1.90
hydroxylated silica	4.45
hydroxylated and thermally treated silica[a]	3.43

[a] Thermal treatment: at 140 °C for 2 h under vacuum (0.2 Pa).

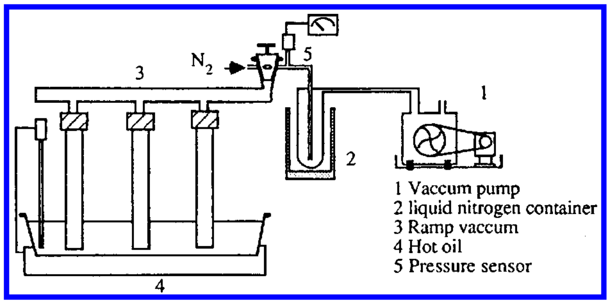


Figure 1. Vapor phase deposition device.

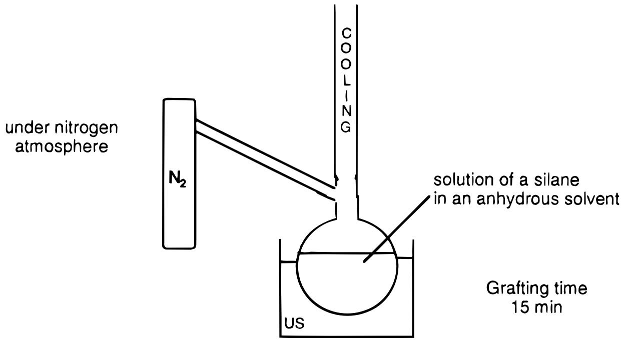


Figure 2. Solvent deposition device.

For planar substrates, both pure silanes with short alkyl chains (from C4 to C8) and pure aminosilane were introduced in a nitrogen atmosphere, whereas the long chain silanes (from C18 to C30) were dissolved in a dry toluene solution before introduction under nitrogen atmosphere.

For silica particles, all the silanes were used in isopentane solution which ensured a good wetting of the silica surface.

In all the cases where a solvent was used, it was removed under vacuum. The condensation reaction on the silica sample was performed in sealed vessels under vacuum for 48 h at 70 °C for the short silanes, at 100 °C for the octadimethylchlorosilane, and at 140 °C for the longest alkyl chains.

For planar substrates, the excess of silane was eliminated by washing with THF, followed by a further extraction using xylene at 150 °C for 20 min. The substrates were then blown with dry nitrogen. For the silica nanoparticles, the stability of the silane bonded to the surface was ascertained by Soxhlet extraction of the modified supports in THF for 2 h. The treated particles were then filtered and dried in air.

Solvent Method. Clean silica substrates were immersed in a solution of *n*-alkyldimethylchlorosilane (0.02 M) in dried toluene for 15 min (Figure 2). The reaction took place at room temperature under ultrasonic stirring and under dry nitrogen. Due to the poor solubility of C30 in toluene at room temperature, the reaction was carried out in dry toluene at 60 °C.

The weakly adsorbed silane molecules and/or the dimers (from the self-condensation of two silanes molecules) were removed by a Soxhlet extraction for 2 h using methanol. This extraction was followed by drying under nitrogen and storage under dry air to remove the solvent.

Contact Angle Measurements on Planar Substrates. Due to the hydrophobicity of the silanized surface in comparison to the untreated ones, the contact angles were measured at room temperature using the sessile drop method. A video camera equipped with a homemade image analysis device visualized the shape of the drop and gave the contact angle between a given liquid and the silica surface. The reported contact angles, θ, are the average value of at least 10 drops for each surface treatment of the silica substrate for a given liquid. The standard deviation gives an estimation of the macroscopic homogeneity of the surface structure for each sample.

The measurements were performed with distilled water in order to underline the hydrophobic character of grafted layers. The relationships between the contact angle θ and the surface energy of grafted silica was obtained by applying Fowkes theory.[17] For this purpose, a dispersive test liquid, the diiodomethane, was used.

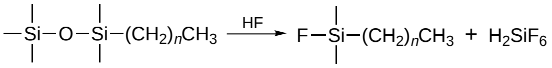
^{29}Si NMR CP/MAS. Solid state ^{29}Si NMR spectra were obtained using a Brucker AC-200 NMR spectrometer operating at 39.73 MHz. All the spectra were obtained with a contact time of 12 ms. The NMR allowed us to semiquantitatively determined the number of grafted molecules per surface unit, τ (i.e., the grafting density), defined as[18]

$$\tau = \frac{[g]}{[g] + [SiOH]}$$

where [*g*] is silane concentration and [SiOH] the silanol concentration after grafting.

It should be noted that only silane molecules covalently bonded to the surface (chemisorbed) are considered when using NMR. The physisorbed species solely immobilized by van der Waals interactions or hydrogen bonds are not taken into account. Such molecules can be removed from the surface by washing. According to the literature, the Q_3 and Q_2 resonances are associated with the silicon atoms carrying hydroxyl groups (monosilanols and the disilanols, respectively). These silanol groups can interact with the unreacted silane molecules adsorbed on the silica surface. The resonance Q_4 at 110 ppm is associated with the silicon atoms in the silica network (−Si−O−Si−). According to the NMR procedure used in this work, the resulting grafting density cannot be considered as quantitative, and the accuracy of the measurements is estimated to be about 4−5%.

Gas Chromatography (GC). This method[3] is based on the opening of the siloxane bond under acidic conditions (hydrofluoric acid, HF, was used in the present case) according to the reaction scheme:



$$-\mathrm{Si}-\mathrm{O}-\mathrm{Si}-(\mathrm{CH_2})_n\mathrm{CH_3} \xrightarrow{\mathrm{HF}} \mathrm{F}-\mathrm{Si}-(\mathrm{CH_2})_n\mathrm{CH_3} + \mathrm{H_2SiF_6}$$

This reaction was performed with 2.5 mL of a 40% HF solution and 0.2 mL of concentrated H_2SO_4 in a Teflon beaker; 3 mL of an organic phase was added to extract the fluorosilane. This phase was used as an internal standard.

After extraction, the fluorosilane was analyzed by gas chromatography using a GC6000 Vega series 2, with an on-column injection system from Carlo Erba Instruments. This system was equipped with a capillary column filled with an SE 30 stationary phase and a flame ionization detector. The results were recorded using a Spectra Physics SP 4400 integrator.

For quantitative determinations, a reference solution of the grafted reagent and an internal standard which is an alkane with a molar mass close to that of the fluorosilane are required. The mass of fluorosilane is calculated according to the expression

$$w_F = (A_F w_e A'_e w'_F)/(A_e A'_F w'_e)$$

where w_F is the total mass of fluorosilane, A_F the area under the peak of the fluorosilane, w_e the internal standard mass, and A_e the area under the peak of the internal standard. w'_F, A'_F, and w_e' are the corresponding values for the reference solution. The coverage density, Σ_c, of grafted alkyl chains is defined as

$$\Sigma_c = w_F/(S w_w) \text{ (silane molecules nm}^{-2}\text{)}$$

where S is the quartz area and w_w is the molar mass of the fluorosilane. The real area (including roughness) was considered instead of the geometric one.

---

(17) Fowkes, F. M. *Ind. Eng. Chem.* **1964**, *56* (12), 40.
(18) Pétiaud, R. *J. Chim. Phys.* **1994**, *91*, 895.

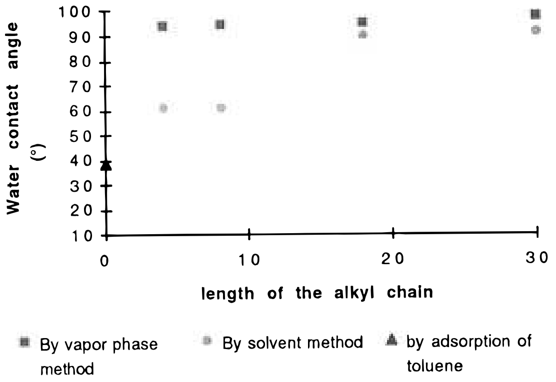


Figure 3. Contact angle with water as a function of the chain length (number of carbons) for silica surfaces grafted by different methods: (■) vapor phase process; (●) solvent process, toluene as solvent; (▲) toluene adsorbed on the silica surface.

Elemental Atomic Analysis Measurements. From the atomic percentage of carbon, the grafting density can be calculated using the following equation

$$\Sigma_c = \frac{1}{A}\,\frac{10^6\ \mathrm{Pc}}{(1200 n_c) - \mathrm{Pc}(M_w - 1)}\ (\text{silane molecules}\cdot\text{nm}^{-2})$$

where A is the specific area of the bare silica, n_c the number of carbon atoms, M_w the molar mass of the bonded moiety, and Pc the percentage of carbon for the grafted silica. These measurements also take into account the traces of carbon from the physisorbed solvent molecules. As a consequence, the grafting density could be overestimated.

Results and Discussion

Influence of Silane Structure on Grafting Efficiency. Influence of Chain Length. As reported in Figure 3, the contact angle for the silica surface modified by the solvent method varied as the length of the alkyl chains increased. Inversely, the wettability of the monolayers obtained by the vapor phase method was quite independent of the chain length, in agreement with the results reported in the literature.[19] For the longer alkyl chains, the contact angles with water were constant regardless of the grafting process, whereas the wettability was very different for the shorter chains deposited from both methods. This effect can be explained by the presence of solvent molecules which can be further adsorbed onto the silica surface during grafting. As a consequence, they hinder the silane molecules and reduce their number of accessible sites (hydroxyl groups). When the alkyl chain is long enough (about 18 carbon atoms long) to cover the whole surface (solvent molecules could be trapped in between the chains), the contact angles are characteristic of a hydrophobic surface (similar to those of polyolefin) since the wettability is an extreme surface measurement. These contact angles with water and the coverage densities were similar to those measured on monolayers deposited in the vapor phase (Table 2). The similar results for both vapor phase and solvent processes show that the temperature of the reaction has no effect on the efficiency of the grafting. On the other hand, for shorter chains, the solvent molecules are easily extracted during the washing process, creating a disordered layer containing holes. In this case, due to the chemical nature of the grafted layers, interchain van der Waals interactions are very weak, and the physisorbed silanes are more easily removed during washing than the long alkyl chain, associated by van der Waals interactions.[21] In this latter case, a lower contact angle and grafting density are observed in comparison to the monolayers obtained by the vapor phase method. Wetting measurements showed a contact angle hysteresis, reflecting the heterogeneous nature of the grafted monolayers obtained by the solvent method (Figure 4). This effect is more pronounced for the long chains because of the interactions between chains. Indeed, in this case, the physisorbed species are more tightly bound to the surface than those for the shorter chains. These are therefore less easily removable by washing and lead to a 3D disordered structure (multilayers). Inversely, for the monolayers deposited by the vapor phase method, a low hysteresis is the signature of a dense and well-ordered organic layer. The relative efficiency of the vapor deposition technique compared to that of the solvent one can be explained by the way used for the silane molecules to reach the surface. In the vapor deposition method, the silane molecules reach the silica surface individually, whereas in the solvent deposition process, they reach the surface in a collective way depending on the concentration of the solution and the affinity with the silica surface relative to the solvent molecules. According to this hypothesis, the difference will be larger for short silanes, whereas the effect will not be pronouced for the longest silanes. In fact, the first longest silanes deposited by a vapor process will hinder the surface for futher graftings more efficiently than the shortest ones.

Table 2. Grafting Density, Σ_c, Determined by Chromatography on Silica Quartz as a Function of the Grafting Process and the Chain Length

sample	Σ_c (silane molecules nm^{-2}) by vapor phase method	Σ_c (silane molecules nm^{-2}) by solvent method[a]
for a long alkyl chain: C18	1.50	1.43
for a short alkyl chain: C8	1.70	0.40

[a] Solvent used: toluene.

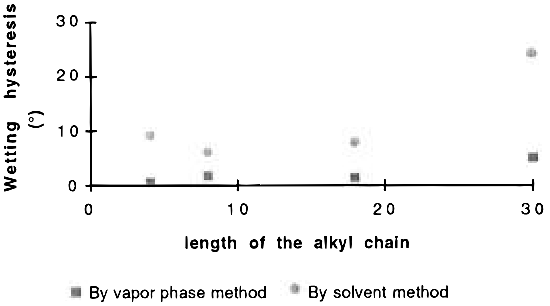


Figure 4. Hysteresis of wetting (water as probe liquid) for the silica surfaces treated with alkychlorosilanes by the vapor phase method (■) and the solvent method, toluene as solvent (●), as a function of the alkyl chain length (number of carbons).

Regardless of the deposition method, the results obtained by GC analysis with silanes having alkyl chains containing 30 carbon atoms, were nonrepeatable and displayed unexpected behavior. In fact, the resulting grafting density was too high, while its value became extremely low after an extraction using tetrahydrofuran (THF). Long enough chains (above 18 carbon atoms) can indeed interdigitate, forming a net strongly bounded to the surface by hydrogen bonds and by dispersive interactions between themselves and with solvent molecules.[21]

---

(19) Wasserman, S. R.; Tao, Y.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074.

(20) Ben Ouada, H.; Hommel, H.; Legrand, A. P.; Balard, H.; Papirer, E. J. *Colloid Interface Sci.* **1988**, *122*, 441.

(21) Ulman, A. *An Introduction to Ultrathin Organic* Films-From Langmuir-*Blodgett to Self-Assembled Monolayers*; Academic Press: London, U.K. 1991.

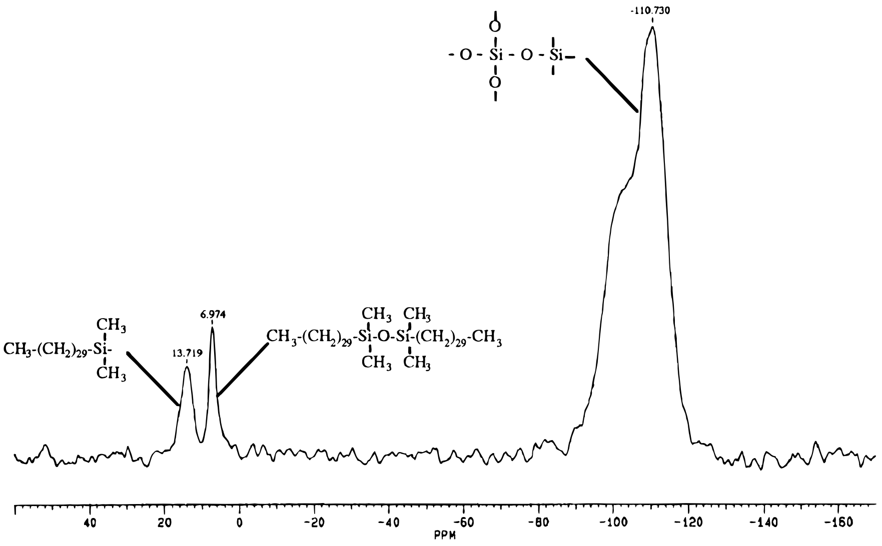


Figure 5. NMR spectrum of the C30-chlorosilane grafted by the solvent method.

Table 3. Contact Angle, Hysteresis of Wetting with Water, and Grafting Ratio Determined by Chromatography for C30-Grafted Silica as a Function of the Treatment after Grafting on Samples

treatment after grafting	θ^{w}_{water} (deg)	$\Delta\theta$ (deg)	Σ_c (silane molecules·nm^{-2})
washing under ultrasonic stirring with THF and xylene	97.8 ± 0.5	1.1 ± 0.6	$>\Sigma^{OH}_{silica}$
extraction in soxhlet with THF for 2 h	96.6 ± 1.2	12.4 ± 2.0	$>\Sigma^{OH}_{silica}$
extraction in soxhlet with THF for 5 h	99.0 ± 1.0	7.9 ± 1.4	$>\Sigma^{OH}_{silica}$
extraction in soxhlet with THF for 10 h	97.0 ± 1.3	32.0 ± 5.7	$>\Sigma^{OH}_{silica}$
extraction in soxhlet with THF for 20 h	94.7 ± 2.7	38.5 ± 0.5	0.05

Dimerization between silane molecules is also possible. In the spectrum reported in Figure 5, the additional peak at 7 ppm is associated with the dimer form. According to these results, a multilayered structure can be used to describe the grafted layer. The assumed flat conformations of C30 chains were in agreement with ellipsometry measurements.[22] Thus, the coverage density determined by chromatography on such structures can possibly be higher than the equivalent number of OH groups available on the silica surface because HF can react with the physisorbed silane and dimer as well. Washing with THF and xylene under ultrasonic stirring is not sufficient to remove the excess of physisorbed silane. As a result, extractions in a Soxhlet with THF are necessary (Table 3). After a 20 h long THF extraction, a large part of the physisorbed silane is removed, creating a very heterogeneous structure. The contact angle with water decreases and the hysteresis increases strongly, highlighting the removal of adsorbed molecules. Moreover, since all the physisorbed species are removed from the silica surface, the real grafting ratio becomes extremely low. This effect illustrates the limits of GC analysis in the determination of the grafting ratio for silanes having long alkyl chains. The extent to which silanes react with the silica surfaces depends on the density of the surface silanol groups and on the accessibility of these surface sites. The reaction may stop as the previously bonded molecules sterically hinder the reaction of the remaining unreacted surface functions. Because the C30 silane seems to adopt a flat conformation when attached to the surface, the real grafting density remains very low. As previously reported from the elemental analysis results (Table 4), the surface coverage increases when decreasing the number of methylene units in the alkyl chain. As a matter of fact, the bonded molecules sterically hinder the reaction of additional molecules. Moreover, the long chain molecules show a tilted orientation on the silica surface. The inferences on chain conformations are confirmed by ellipsometry measurements as described in another paper.[22]

Table 4. Grafting Ratio, τ, Determined by Elemental Analysis for Silica Grafted by the Vapor Phase Method as a Function of Alkyl Chain Length

alkyl chain	τ (silane molecules·nm^{-2})
$C_{30}Cl$	0.97
$C_{18}Cl$	0.95
C_8Cl	1.37
C_4Cl	1.43

Table 5. Contact Angle with Water and Grafting Densities Ratio, *R*, Measured on C18-Amino- and C18-Chlorosilane-Grafted Silica

	solvent method		vapor phase method	
	$C_{18}Cl$	$C_{18}N$	$C_{18}Cl$	$C_{18}N$
θ_{water}	89.9 ± 0.3	101.8 ± 1.4	95.0 ± 1.1	103.6 ± 1.9
$R = \tau_{C_{18}N}/\tau_{C_{18}Cl}$[a]	2		3	

[a] Determined by ^{29}Si NMR.

Effect of the Chemical Nature of Silane. Aminosilane ($C_{18}N$) and chlorosilane ($C_{18}Cl$) lead to a grafting of the silica surface with the same chain length. It was already shown that aminosilane shows a higher reactivity than that of chlorosilanes.[23] Regardless of the grafting process, the wettability of the grafted surface is better for the aminosilane-treated surface, and the grafting ratio is two to three times higher than those for the chlorosilane ones (Table 5). Moreover, as reported on the NMR spectrum (Figure 6) of the silica grafted by the vapor phase method, the free OH signal almost vanished, indicating that most of the reactive groups on the surface reacted with the alkylsilane molecules.[24] The electron rich amine can develop interactions by hydrogen bonds with hydrogen-donating groups, such as silanols. Because of its basic

---

(22) Duchet, J.; Chabert, B.; Chapel, J. P.; Gérard, J. F. to be published in *J. Colloid Interface Sci.*

(23) Allian, M.; Borello, E.; Ugliengo, P.; Spano, G.; Garrone, E. *Langmuir* **1995**, *11*, 4811.

(24) Bierbaum, K.; Grunze, M. *Prepr—Adhesion Soc.* **1994**, 213.

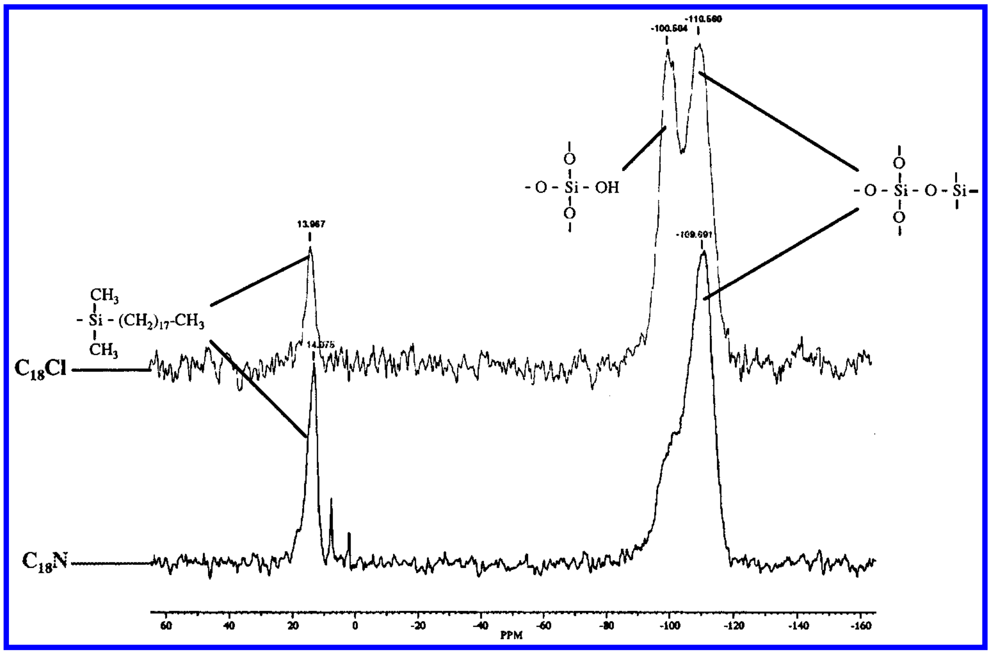


Figure 6. ^{29}Si NMR CP/MAS spectra of C18-chlorosilane- (top) and C18-aminosilane- (bottom) grafted Aerosil silica (vapor phase deposition method).

Table 6. Grafting Density, Σ_c, Measured on Silica by Chromatography on Grafted Silica Plates and by Elemental Analysis on Treated Aerosil Particles

	Σ_c vapor phase method (silane molecules·nm^{-2})				Σ_c solvent method (silane molecules·nm^{-2})			
determination	$C_{30}Cl$	$C_{18}Cl$	C_8Cl	C_4Cl	$C_{30}Cl$	$C_{18}Cl$	C_8Cl	C_4Cl
gas chromatography	$>\Sigma^{OH}_{silica}$	1.50	1.70		$>\Sigma^{OH}_{silica}$	1.43	0.40	
elemental analysis	0.97	0.95	1.37	1.43	5.02	5.05	1.41	0.88

character, the amine is easily protonated. After adsorption, the amine group can catalyze the silanization of the silicon side of the molecule with a surface silanol.[25]

Effect and Role of the Solvent on the Silanization. Toluene is frequently used as a solvent in the grafting method because of its ability to extract significant amounts of water from the surface of the substrate. This moisture leads to the hydrolysis of the chlorosilane in the bulk solvent phase.[11] Indeed, toluene, which is rather polar, can also be adsorbed on the silica surface and then prevents the silanol groups on the surface from reacting. As a consequence, it results in a lower grafting density. In addition, the solvent molecules strongly adsorbed on the surface will increase the carbon percentage determined by elemental analysis. This phenomenon can explain the higher grafting density found for the long chain silane on the silica particle by the solvent process than the density found for those grafted by the vapor phase method. In this latter case, the high values obtained result from the toluene insertion between chains (Table 6). By comparing the grafting densities measured on quartz and on nanosize particles, we can underline that the substrate nature plays an important role in the resulting grafted structure. The grafting density measured on C30-grafted Aerosil by the vapor phase method and determined by elemental analysis is close to the value reported in the literature[26] (Table 6).

Table 7. Grafting Density Obtained by Solvent Method, Σ_c, as a Function of the Solvent Used and the Length of the Alkyl Chain

	Σ_c (molecules·nm^{-2})			
treatment	$C_{30}Cl$	$C_{18}Cl$	C_8Cl	C_4Cl
1	5.02	5.05	1.41	0.88
2	3.92	4.48	3.88	1.73
3	3.80	4.57	3.65	1.94
4	15.76	2.82		4.03
5	2.21	1.25	1.29	1.43

[a] Treatment 1: Grafting realized with toluene, extraction with methanol, drying under vacuum. Treatment 2: Grafting realized with toluene, extraction under vacuum, extraction with methanol, drying under vacuum. Treatment 3: Treatment 2 followed by an additional extraction with methanol. Treatment 4: Grafting realized with CCl_4, extraction with methanol, drying under vacuum. Treatment 5: Treatment 4 followed by an additional extraction with THF.

Several experiments were realized in order to remove the solvent from the grafted monolayer and to get a more efficient grafting density (Table 7). The extraction of toluene under vacuum after grafting tends to decrease the coverage density, but it still remains high. An additional washing with methanol does not modify the structure of the grafted layer. As reported by several authors,[11,27] the nature of the solvent used for the silanization is an important factor. By using carbon tetrachloride (instead of toluene) followed by an extraction with tetrahydrofuran, the resulting grafting densities were rather similar to those determined on silica powder grafted by the vapor phase method (Table 7). Child already reported that the grafting was more efficient in solution with carbon tetrachloride than with toluene.[14] From these experiments, the extraction with methanol is not sufficient, and washing with THF is necessary. The solvent used for extraction seems to play an essential role in the structure of the resulting grafted layers.

---

(25) Iler, R. K. The Chemistry of Silica; J. Wiley & Sons: New York, 1979.

(26) Vansant, E. F.; Van der Voort, P.; Vrancken, K. C. *Characterization and Chemical Modification of the Silica Surface*; Elsevier Sci.: Amsterdam, The Netherlands, 1995; 93.

(27) Gun, J.; Sagiv, J. J. *Colloid Interface Sci.* **1986**, *112*, 457.

(28) Van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier Sci.: New York, 1991.

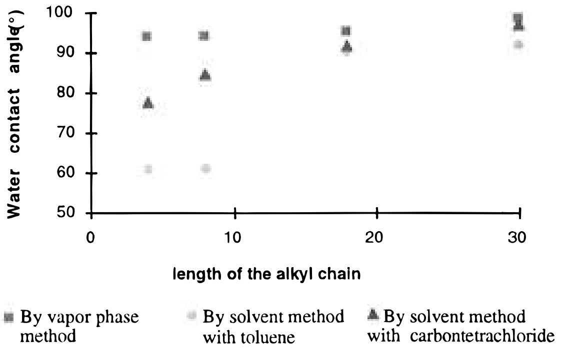


Figure 7. Water contact angles of silica surfaces treated with alkyl chlorosilanes as a function of the length of the alkyl chain and deposition method: vapor phase process (■); solvent process, toluene (●); solvent process, carbon tetrachloride (▲).

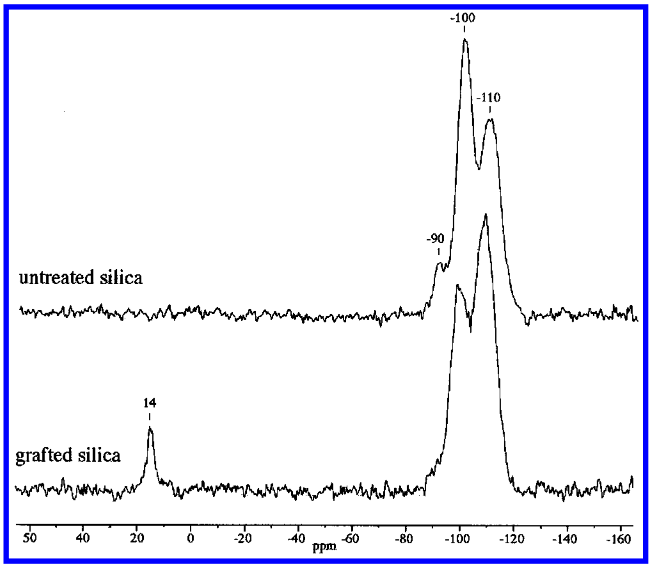


Figure 8. ^{29}Si NMR CP/MAS spectra of untreated and C_{30}-Cl-grafted Aerosil silica (grafted by a vapor phase deposition method).

The contact angle measurements show that the wettability of the grafted structure can be controlled by choosing an appropriate solvent for the silanization reaction (Figure 7). Carbon tetrachloride, which is less polar than toluene ($\delta_p^{CCl_4} = 0$ and $\delta_p^{toluene} = 1.4$),[27] is less adsorbed on the silica surface, and as a consequence, higher contact angles and grafting densities can be observed.

Nature of Bonds at the Silica Surface. Further information on the chemical bonding of the silanes to the surface is obtained from ^{29}Si CP/MAS NMR. By comparing the NMR spectra before and after silanization, presented in Figure 8, an additional peak at 14 ppm can be observed which is assigned to the silicon attached to the alkyl chain groups of the bonded chain ($\underline{Si}-CH_2-$). The occurrence of this resonance is balanced by the disappearance of the silanol resonances (hydrolyzed and surface $\underline{Si}$-OH). In addition, the siloxane resonance ($-O-\underline{Si}-O-Si-CH_2-$) increases since the silanols on the silica surface have reacted with the hydrolyzed silanes. As a consequence, ^{29}Si NMR spectroscopy is the best technique to determine the grafting density, since it is possible to quantify the rate of the siloxane bonds by measuring the amount of $Si-O-\underline{Si}-CH_2-$ bonds. On the other hand, the adsorbed species via hydrogen bonds are not taken into account by NMR spectroscopy.

The grafting densities measured for monolayers grafted by means of a vapor phase process were higher than those measured for monolayers by the solvent method (Table 4). Both grafting processes (phase vapor and solvent methods) led to the formation of siloxane bonds, but the grafting performed in a solvent is less dense.

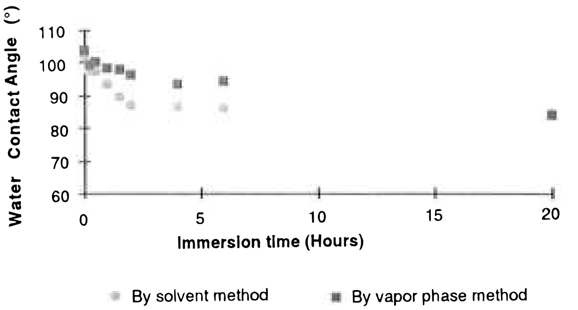


Figure 9. Dependence of the water contact angle with time of dipping in a 0.1 N KOH solution for the C18N-grafted silica surface: (●) solvent method; (■) vapor phase deposition process.

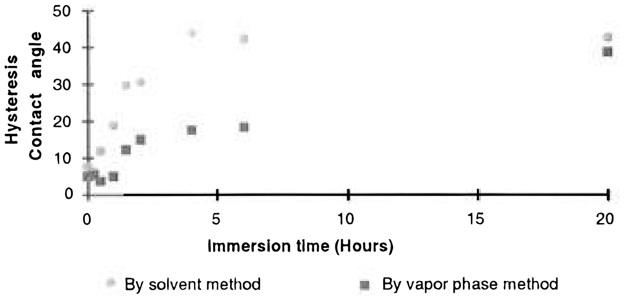


Figure 10. Dependence of the hysteresis of wetting with water with the time of dipping in a 0.1 N KOH solution for the C18N-grafted silica surface: (●) solvent method; (■) vapor phase deposition process.

In order to quantify the stability of the formed bonds, chemical attack was done by dipping (from 15 min to 12 days at room temperature) the aminosilane monolayers grafted by both methods in a 0.1 N KOH solution. The water contact angles and hysteresis of wetting are given in Figures 9 and 10, respectively. From this point, the monolayers grafted by the solvent method are degraded faster than the monolayers resulting from the vapor phase method. An increased contact angle hysteresis is an obvious indication of layer degradation. This rapid degradation is due to the extraction of the remaining physisorbed molecules. These results are similar to those reported on TTS monolayers by Wasserman et al.[29] They noticed after 80 min in the same type of solution that 50% of the film was removed from the silica surface. The vapor phase monolayers were less affected by hydrolysis than the monolayers deposited from a toluene solution. This phenomenon can be explained by the fact that the monolayers deposited by the vapor phase method have more dense and stable structures. However, after a dipping time of 20 h, both monolayers grafted by the vapor phase and solvent methods presented the same degradation. These results are not surprising since a Si−O bond is known to undergo hydrolysis in basic media.[6]

Conclusion

In this work, the influence of the silanization process on the quality of grafted monolayers was studied in the case of alkylchlorosilanes having different chain lengths (from 4 to 30 carbons long) deposited onto quartz slides and silica particles. Both methods lead to a chemical grafting via siloxane bonds. However, two different structures of silane monolayers are obtained: (i) By using a vapor phase deposition method, the low-wetting hys-

---

(29) Wasserman, S. R. *J. Am. Chem. Soc.* **1989**, *111*, 5852.

teresis shows that the monolayers are well-structured and dense. The removal of the physisorbed water from the surface during the conditioning of the specimens allows us to get a very repeatable grafted surface. Even if this technique is particularly reliable, it cannot be used to graft longer chains such as polymers.[4] (ii) Consequently, a solvent process for grafting alkylsilanes was developed and optimized in order to obtain denser and more ordered layers. The nature of the solvent plays an important role for obtaining well-ordered monolayers. Well-ordered monolayers are obtained by using carbon tetrachloride as a solvent because it is apolar and consequently less adsorbed onto the silica surface than toluene. The resulting monolayers are characterized by higher contact angles with water and grafting densities close to those determined on layers deposited by the vapor phase method. However, by using a solvent method, the samples are not dried and part of the physisorbed water remains. Thus, the resulting grafting ratio is lower, and the monolayer is less dense than that obtained from the vapor phase deposition process. The hydrolysis kinetics may also be faster for these monolayers than that for the monolayers resulting from the vapor phase method. The difference between the layers resulting from the solvent and the vapor deposition methods can be explained by (i) the way used by the silane molecules to reach the surface—individually or collectively for the vapor and the solvent methods, respectively—and (ii) by the competition between the solvent and the silane molecules to reach the silica surface for the solvent process. This competition, which infuences the packing density of the grafted layer, is dependent on the polarity and the shape of the solvent molecules.

The study of this model interface finally allows us to predict some of the possible problems arrising when grafting longer chains (longer than 29 methylene units) on silica surfaces. In particular, it will be especially difficult to build well-ordered and homogeneous monolayers from silane-grafted polymers.

LA960598H