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Influence of the nature of the organic precursor on the textural and chemical properties of silsesquioxane materials

Geneviève Cerveau, Robert J. P. Corriu,* Cédric Lepeytre and P. Hubert Mutin

Laboratoire de Chimie Moléculaire et Organisation du Solide, UMR 5637, Université Montpellier II, Case Courrier 007–34095 Montpellier Cédex 5, France

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The hydrolytic sol–gel polymerization of molecular organosilicon precursors with a rigid geometry $C_6H_4[Si(OMe)_3]_2$-1,4 and $C_6H_3[Si(OMe)_3]_3$-1,3,5 **2** was investigated and compared to the results obtained with precursors having a more flexible structure C_6H_4RR'-1,4 [$R = R' = CH_2Si(OMe)_3$ **3**; $R = R' = CH_2CH_2Si(OMe)_3$ **4**]. Compounds **1–4** have been studied in the same conditions. They were hydrolyzed under nucleophilic catalysis (TBAF: tetrabutylammonium fluoride) in MeOH and in THF. The structure of the organic group was found to be a determining parameter for both the physical and chemical properties of the resulting silsesquioxane materials. The molecular precursors **1** and **2** containing a 'rigid' organic group led to hydrophilic solids with similar degrees of condensation. In all cases, high specific surface area (370–1018 $m^2\ g^{-1}$) and poor chemical reactivity towards $Cr(CO)_6$ (11–33%) were observed. By contrast, the precursors containing a 'flexible' organic group (**3** and **4**) led to hydrophobic solids; the texture, the degree of condensation and the reactivity towards $Cr(CO)_6$ of these solids strongly depended on the solvent. For instance the solids prepared in MeOH had no significant specific surface area. The solids derived from the most flexible precursor (**4**) exhibited the highest chemical reactivity. The short range organization of the solid is a function of the geometry of the precursor and the experimental conditions.

Introduction

Organic–inorganic hybrid materials are a wide field of growing interest.[1,2] Sol–gel chemistry, which corresponds to an inorganic polymerization, offers an access to a wide variety of silica-like structures.[3] The mild reaction conditions allow the incorporation of organic moieties into inorganic oxide networks. The preparation of monocomponent hybrid materials in which organic molecules are covalently bound to silica is opening interesting perspectives for chemists. The incorporation of an organic unit in the core of an inorganic matrix can be achieved when at least two covalent bonds are formed between the organic molecule and the solid. A large variety of nanostructured hybrid materials has been reported[4–13] and it has been shown that changing the nature of the organic group induces changes in the macroscopic properties of the hybrid solid. For instance, linear rigid rod structures with *p*-phenylene groups[4,5] and flexible structures due to methylene groups[6,7] influence properties such as the microporosity. Microporous bridged polysilsesquioxanes have been used as a confinement matrix for nanosized particles.[9] Short range organization in the amorphous solids arising from the molecular structure of the precursor has been detected using the chemical reactivity of organic spacers in the case of hybrid materials containing buta-1,3-diyne or thiophene bridging fragments.[10,11] Moreover, the inclusion of charge transfer complexes in gels[11a] illustrates the importance of weak interactions between the organic units on the texture of the solid. In a preliminary report, we have shown that the nature of the organic spacer appears as a very important parameter in the control of the properties of the solid[14a] such as the specific surface area, the hydrophilicity and the chemical reactivity.

In this context, we were interested in investigating to which extent can the structure of the precursor be a determining parameter for the solid state properties of the resulting materials. We therefore examined the gel formation from precursors with different structures, under the same experimental conditions.

We report here our studies concerning the relationships between the structure of the organic groups and the textural and chemical properties of different aryl bridged silsesquioxane xerogels.

Experimental

All the syntheses of precursors and reactions of complexation with $Cr(CO)_6$ were carried out under argon using a vacuum line and Schlenk tube techniques.[15] Solvents were dried and distilled before use. IR spectra were recorded using a Perkin Elmer 1600 FTIR spectrophotometer using KBr pellets or by the DRIFT method. Solid state NMR spectra were obtained with a Bruker FTAM 300 spectrometer: ^{13}C CP MAS NMR at 75.47 MHz, recycling delay 5 s, and contact time 5 ms; ^{29}Si CP MAS NMR at 59.62 MHz, recycling delay 10 s, and contact time 2 ms. Chemical shifts are given relative to tetramethylsilane. To obtain quantitatively reliable ^{29}Si data, single-pulse MAS NMR experiments (SPE-MAS) have been performed on a Bruker ASX 200 spectrometer at 39.74 MHz, using a pulse angle of 30°, a recycling delay of 60 s and high-power proton decoupling during the acquisition. These experiments have been done for two xerogels derived from precursors **1** and **4** by hydrolysis in MeOH. The spinning rate was 5000 Hz in all cases.

Specific surface areas, pore volumes and pore size distribution were determined using a Micromeritics Gemini III 2375 apparatus. Elemental analyses were carried out by the 'Service Central de Micro-Analyse du CNRS'. Oxygen percentages were deduced by difference. X-Ray powder diffraction measurements were performed using a Seifert MZ4 apparatus.

Compounds **1**, **2** and **3** were prepared according to literature procedures[4a,12b] while **4** was commercial and purified before use.

Gels starting from **1**,**2** and **3** have been already described under different experimental conditions.[4a,5a,13]

Preparation of silsesquioxane gels

The preparation of the gels was carried out according to the following general procedure. The preparation of **1M** is given as an example. To 2.52 g (7.92×10^{-3} mol) of **1** in 10 ml of

Table 1 Experimental conditions and gelation time of xerogels

Entry	Precursor	Solvent	Xerogel	Precursor conc./ mol L^{-1}	Gelation time/min
1	**1**	MeOH	**1M**	0.5	160
2	**1**	THF	**1T**	0.5	135
3	**2**	MeOH	**2M**	0.5	7
4	**2**	THF	**2T**	0.5	4
5	**3**	MeOH	**3M**	0.5	45
6	**3**	THF	**3T**	0.5	<1
7	**4**	MeOH	**4M**	0.5	720
8	**4**	THF	**4T**	0.5	<5

methanol was added a solution of 79×10^{-3} ml of TBAF (solution 1 mol l^{-1} in THF) and 428×10^{-3} ml of water (3 mol. equiv.) in 5.33 ml of methanol. After 160 min a monolithic opaque gel formed. After ageing during 5 days at room temperature the solid was collected, then ground and washed with ethanol, acetone and diethyl ether. The resulting solid was dried at 120 °C *in vacuo* during 3 h yielding 1.23 g of a white powder **1M**.

The experimental conditions and the gel times of the xerogels are reported in Table 1.

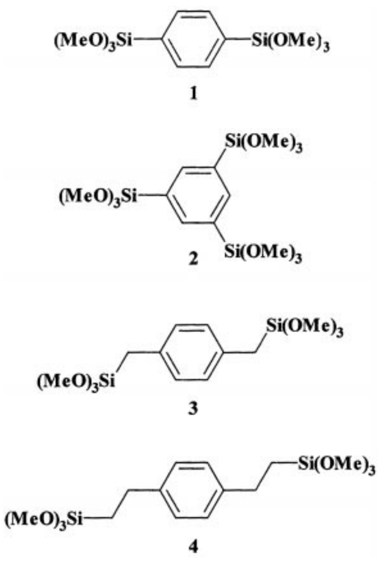
Reaction of complexation with $Cr(CO)_6$

The reaction of complexation of the xerogel was carried out according to the following general procedure.[14a]

The complexation of **1M** is given as an example. The xerogel **1M** (0.58 g, 3.22×10^{-3} mol) and an excess of $Cr(CO)_6$ (1 g, 4.8×10^{-3} mol) were introduced in a mixture of 10 ml of THF and 40 ml of $Bu^n{}_2O$. The mixture was refluxed during 65 h. After this, the yellow–green solid was filtered, washed with dichloromethane and diethyl ether, then dried *in vacuo* at room temperature during 3 h. A pale green solid (0.72 g) was obtained which was analysed by IR and NMR spectroscopy. The degree of complexation was determined by chemical and EDS elemental analysis. The experimental ratio $(Cr/Si)_{exp}$ was determined from the elemental analysis and compared to the theoritical value $(Cr/Si)_{th}$ assuming a degree of complexation of 100%. For xerogel **1M**, $(Cr/Si)_{exp} = 0.09$; degree of complexation = 18%. The results obtained were confirmed by elemental EDS analysis.

Results and discussion

The molecular precursors **1**–**4** containing phenylene units with various geometries have been investigated[4a,12b] (Scheme 1). Compounds **1** and **2** have a 'rigid' spacer, whereas **3** and **4** contain more 'flexible' organic groups.



Scheme 1 Molecular precursors **1**–**4**.

Preparation and characterization of silsesquioxane gels

The sol–gel polymerization of monomeric precursors **1**–**4** was performed in MeOH and in THF, in the presence of (TBAF) tetrabutylammonium fluoride (1 mol%) as a catalyst,[16] for a concentration of 0.5 mol l^{-1} of the precursor at room temperature (reaction 1). The experimental procedure was strictly controlled, all the reactions were performed three times and were rigorously reproducible.

When the reaction was performed in MeOH, opaque gels formed within a short period of time for **1** and **2** whereas white precipitates were obtained for **3** and **4**. When the solvent was THF, transparent gels formed in all the cases. Gel times are reported in Table 1. The gels were allowed to stand at room temperature for 5 days. After washing with ethanol, acetone and ether, the powders were dried *in vacuo* at 120 °C during 3 h. Elemental analysis showed that in all cases the hybrid gels deviated from the ideal stoechiometry based on totally polycondensed silsesquioxane materials (Table 2). These analyses revealed an excess of carbon and hydrogen indicating the presence of residual hydroxy and methoxy groups. This excess of carbon and hydogen was larger when the reaction was carried out in MeOH (Table 2, entries 1, 3) than in THF (Table 2, entries 2, 4) as shown by the experimental formula. This can be attributed to a higher degree of hydrolysis in THF than in MeOH.

The X-ray powder diffraction pattern of the samples showed absence of crystallinity in all cases.

NMR characterization of the xerogels

The IR and NMR characteristics of the xerogels prepared from **1**–**4** have been determined and are in agreement with the conservation of the organic units bonded to the silica matrix: ^{29}Si CP MAS NMR (Table 2) clearly established that the Si-C bond was retained within the gel in all cases:[17] no ^{29}Si resonances attributable to $SiO_{4/2}$ units were detected [18] (only T^0, T^1, T^2, T^3 units were observed). Futhermore ^{13}C CP MAS NMR spectra showed that the organic fragments were not modified.

When the hydrolysis–polycondensation reaction was performed in methanol, in the case of gels prepared from **1** and **2**, ^{29}Si CP MAS NMR showed a major substructure T^2: $CSiO_2(OX)$ (X = Me or H). Starting from **3** and **4** a major substructure T^2 and signals corresponding to a substructure of type T^0: $CSi(OX)_3$ (X = Me or H) were observed (Fig. 1).

When the solvent was THF, the ^{29}Si CP MAS NMR characteristics were very similar to those obtained in methanol in the case of **1T** and **2T**. However the solid **3T** appeared more polycondensed (T^2 and T^3 major substructures). Solid **4T** showed a major substructure T^3: $CSiO_3$ indicative of a higher degree of polycondensation (Fig. 2).

Quantitatively reliable ^{29}Si SPE MAS NMR spectra have been collected for two typical silsesquioxane xerogels, **1M** and **4M**, and compared to the CP MAS NMR spectra of the same precursors (Fig. 3). The percentages of the different T^x units, obtained by deconvolution of the spectra are reported in Table 3. The SPE MAS and CP MAS percentages found for the different T^x units were comparable in both cases. Accordingly, the degrees of condensation derived from the ^{29}Si CP MAS spectra were close to those derived from the quantitative SPE MAS NMR spectra. It was not possible to perform quantitative SPE MAS experiments for all the samples; thus the degrees of condensation reported in Table 4 have been estimated from CP MAS spectra.

All the samples derived from the rigid precursors **1** and **2**

Table 2 Elemental analyses, experimental formulas, and ^{29}Si CP MAS NMR data of xerogels

Elemental analysis (found %)						^{29}Si CP MAS NMR (δ)^{e}			
Entry	Xerogel	C	H	Si	Experimental formula	T^0	T^1	T^2	T^3
1	**1M**	38.73	3.77	23.40	$C_{7.76}H_{9.01}Si_2O_{5.16}$^{a}	—	−61	**−70**	−78
2	**1T**	36.15	3.21	25.40	$C_{6.66}H_{7.06}Si_2O_{4.88}$^{a}	—	−61	**−70**	−78
3	**2M**	33.36	3.82	26.10	$C_{8.93}H_{12.22}Si_3O_{7.38}$^{b}	—	−62	**−70**	−78
4	**2T**	30.85	3.20	27.35	$C_{7.89}H_{9.78}Si_3O_{7.44}$^{b}	—	−61	**−70**	−78
5	**3M**	46.62	5.88	25.45	$C_{8.62}H_{12.94}Si_2O_{3.16}$^{c}	−46	−55	**−63**	−71
6	**3T**					−47	−55	**−63**	−70
7	**4M**					−42	−50	**−59**	−67
8	**4T**	50.31	5.42	22.75	$C_{10.32}H_{13.24}Si_2O_{3.30}$^{d}	—	—	−57	**−66**

Ideal formula: $^{a}C_6H_4Si_2O_3$; $^{b}C_6H_3Si_3O_{4.5}$; $^{c}C_8H_8Si_2O_3$; $^{d}C_{10}H_{12}Si_2O_3$; ^{e}major resonances in bold type.

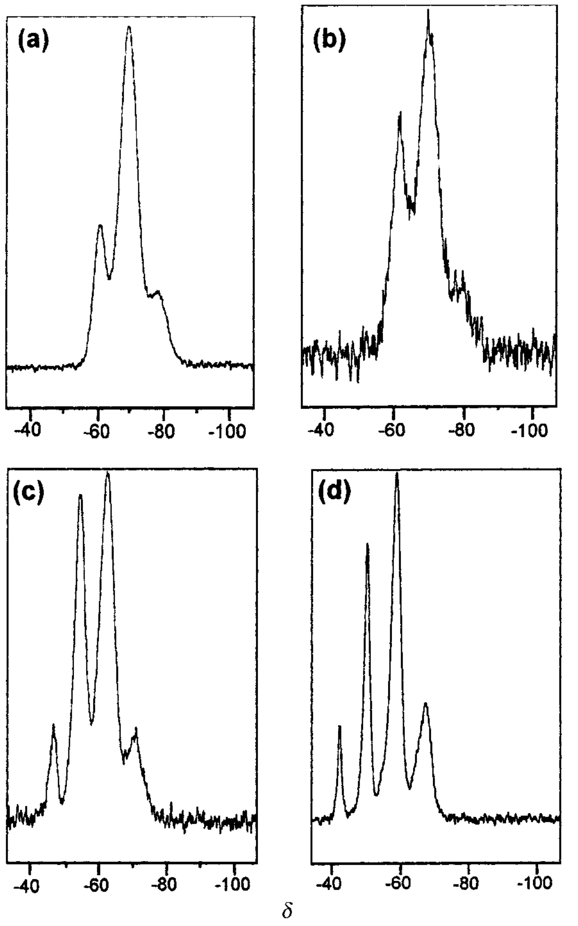


Fig. 1 ^{29}Si CP MAS NMR spectra of xerogels; (a) **1M**, (b) **2M**, (c) **3M**, (d) **4M**.

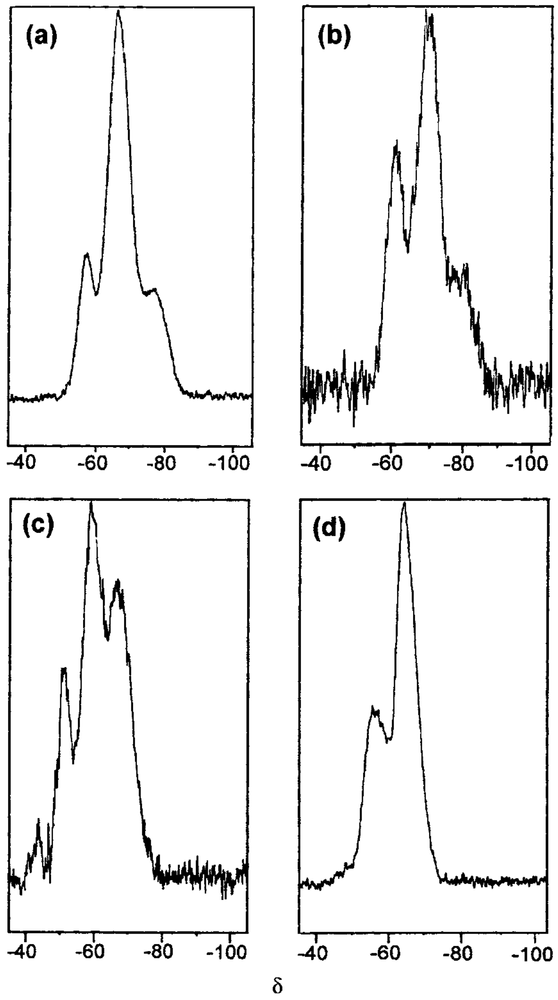


Fig. 2 ^{29}Si CP MAS NMR spectra of xerogels; (a) **1T**, (b) **2T**, (c) **3T**, (d) **4T**.

had similar degrees of condensation, lying in the range 61–67%, whatever the solvent and concentration. These values are comparable to those reported by Shea and coworkers[6] on other examples.

On the other hand, the degree of condensation of the samples derived from the more flexible precursors **3** and **4** depended on the nature of both the solvent and the precursor. Thus, the samples prepared in THF showed significantly higher degrees of condensation than those prepared in MeOH; for a given solvent, the samples prepared from precursor **4** showed significantly higher degrees of condensation than those prepared from precursor **3**.

^{13}C CP MAS NMR spectra (Fig. 4) showed very weak signals attributable to residual methoxy groups when the solvent was THF and more intense signals in the case of methanol indicative of a higher degree of hydrolysis in THF than in MeOH, in good agreement with the elemental analysis reported in Table 2.

Hydrophilic character of the xerogels

All the solids obtained from **1** and **2** exhibited significant hydrophilic character, whereas the gels derived from **3** and **4** always showed a low affinity for water independent of the gelation solvent. Weight increases in a 60% humidity atmosphere at 25 °C ($E_{0.6}$%) are reported in Table 4 and are in agreement with the IR data of the xerogels: the ν(OH) absorption band centered at 3370 cm^{-1} due to the presence of silanol groups was stronger for the xerogels obtained from **1** and **2** than from **3** and **4**.

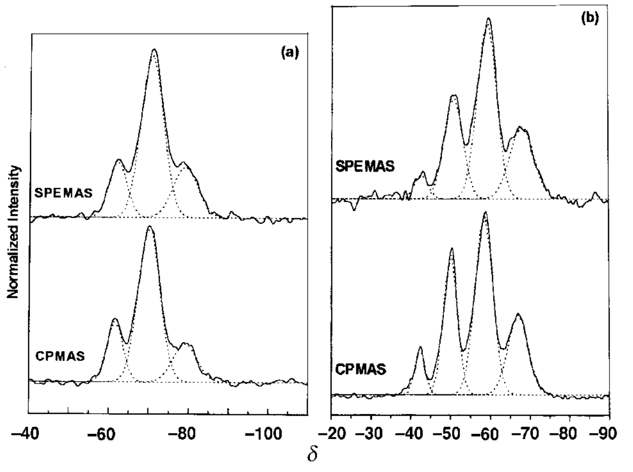


Fig. 3 ^{29}Si SPE MAS NMR and ^{29}Si CP MAS NMR spectra of xerogels; (a) **1M**, (b) **4M**.

Table 3 Comparison between SPE MAS and CP MAS ^{29}Si NMR data for samples **1M** and **4M**

Xerogel	%T^0 SPE/CP	%T^1 SPE/CP	%T^2 SPE/CP	%T^3 SPE/CP	%condensation SPE/CP
1M	0/0	17.0/18.7	61.5/63.5	21.5/17.8	68.2/66.4
4M	4.5/6.4	26.0/27.1	46.2/44.3	23.4/22.3	62.9/60.9

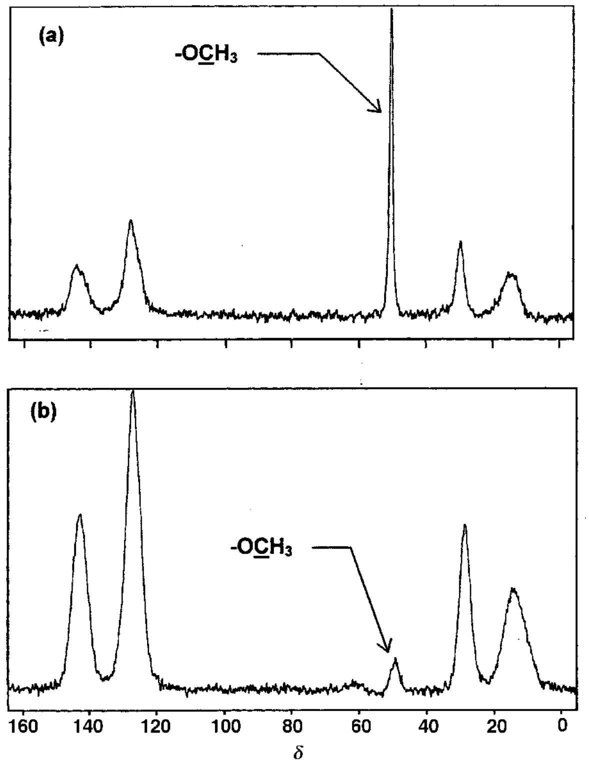


Fig. 4 ^{13}C CP MAS NMR spectra of xerogels; (a) **4M**, (b) **4T**.

Texture of the solids

Nitrogen BET measurements[19] gave specific surface areas which were very different depending on the structure of the precursor and the nature of the solvent. The solids obtained from **1** and **2** exhibited very high specific surface areas whatever the solvent used: 549–1018 m^2 g^{-1} in MeOH and 370–766 m^2 g^{-1} in THF (Table 4, entries 1–4).

By contrast, the solvent employed for the hydrolysis–polycondensation reaction had a drastic influence on the texture of the solids in the case of **3** and **4**. The xerogels **3M** and **4M** prepared in MeOH exhibited no significant surface areas (Table 4, entries 5, 7) while high specific surface areas were observed for samples **3T** and **4T** prepared in THF (Table 4, entries 6, 8).

Adsorption–desorption isotherms of **1M**, **1T**, **2M**, **2T**, **4T** are shown in Fig. 5 and 6. The determination of the porous volume by the BJH method [20] and the evaluation of the microporous volume by the analysis of the t-plot diagram have been performed in each case. The BET specific surface areas and porous volumes of the xerogels are reported in Table 5.

The xerogels **1M** and **1T** (Table 5, entries 1 and 2) showed type I isotherms,[21] characteristic of microporous solids. Indeed, the microporous volume represented respectively 60 and 79% of the total porous volume. The BET constant *c* was very high for both samples, which is also indicative of microporosity.

All the xerogels prepared from **2** exhibited isotherms intermediate between type I and IV (characteristics of mesoporous solids) and high specific surface areas (Table 5, entries 3 and 4). No narrow pore size distribution was observed in all cases.

Sample **3T** (Table 5, entry 5) was mesoporous and showed a substantial specific surface area (277 m^2 g^{-1}), whereas **3M** presented no significant specific surface area.

For xerogels derived fom precursor **4**, the nature of the solvent used during the hydrolysis–polycondensation had a drastic influence on the texture of the resulting solids since sample **4T** exhibited a high specific surface area (565 m^2 g^{-1}) whereas sample **4M** had no significant specific surface area. This difference may be correlated to the increase of the rigidity of the network of the sample prepared in THF owing to the higher degree of condensation (61% for **4M** and 87% for **4T**). For **4T** the solid was mainly mesoporous, with a low microporous contribution (estimated to be *ca.* 20% of the total porous volume). No narrow pore size distribution was observed. Despite its high specific surface area, gel **4T** had a low affinity for water (5–6%) in accord with the low amount of hydroxy groups as shown by IR spectroscopy.

Table 4 Degree of condensation, hydrophilicity, specific surface area and degree of complexation of xerogels

Entry	Xerogel	Degree of condensation (%)[a]	$E_{0.6}$ (%)	Surface area/ m^2 g^{-1}	Degree of complexation (%)
1	**1M**	66	22	549	18
2	**1T**	67	18–22	370	11
3	**2M**	61	22–24	1018	27
4	**2T**	64	30–31	766	33
4	**3M**	55	2	<10	25
6	**3T**	72	3	277	42
7	**4M**	61	2	<10	84
8	**4T**	87	5–6	565	64

[a] Estimated from the ^{29}Si CP MAS NMR spectra.

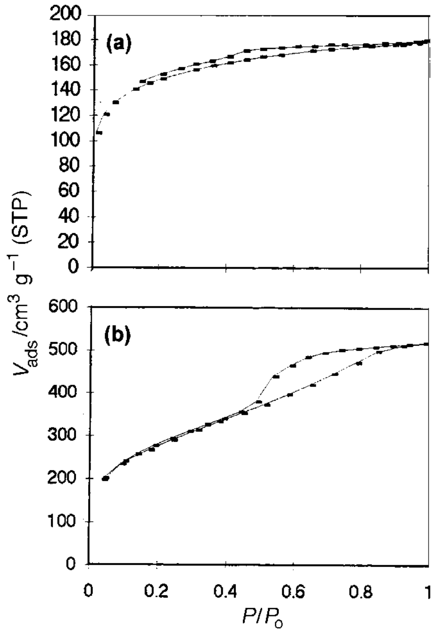


Fig. 5 N_2 adsorption–desorption isotherms of xerogels; (a) **1M**, (b) **2M**.

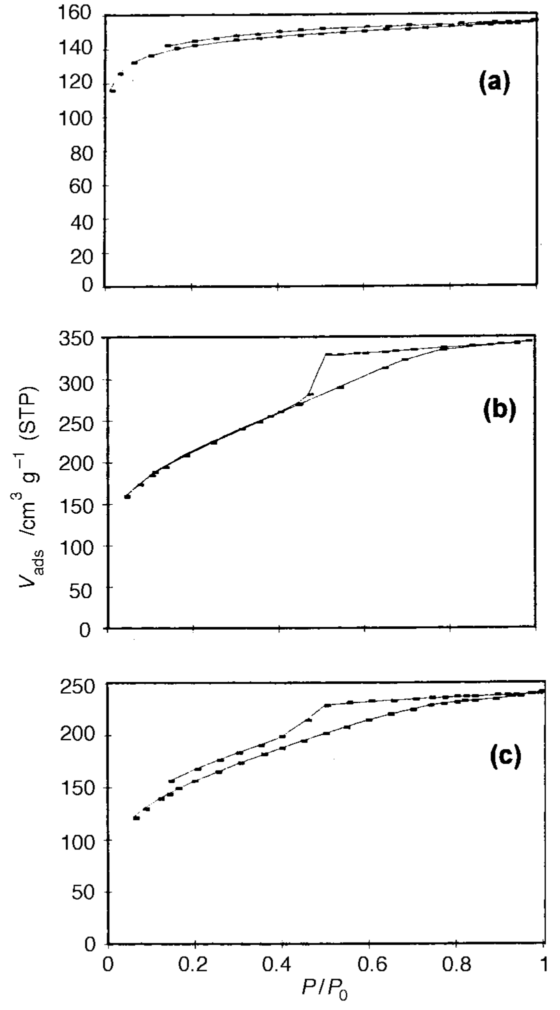


Fig. 6 N_2 adsorption–desorption isotherms of xerogels; (a) **1T**, (b) **2T**, (c) **4T**.

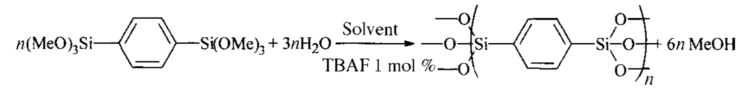
The most important feature for the silsesquioxanes reported here is the difference of the texture of the solids connected with the geometry of the organic unit: the materials with a 'rigid' bridge obtained from **1** and **2** exhibit in all cases a high hydrophilicity (18–31%) and a high surface area (370–1018 m^2 g^{-1}). The hydrophilic character ($E_{0.6}$) is larger in THF than in MeOH for **2** (Table 4, entries 3, 4) although the surface area is lower, which suggests a larger amount of hydroxy groups. This observation is consistent with the IR and ^{13}C NMR data. By contrast, with more 'flexible' spacers **3** and **4**, the texture is dependent on the nature of the solvent used in the hydrolysis–polycondensation reaction. No significant surface areas were observed using MeOH while high surface areas were obtained using THF.

Chemical reactivity of xerogels

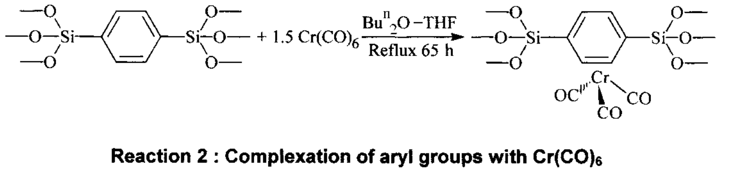
We have previously shown that the chemical reactivity of hybrid solids can be used as a tool for studying the solid arrangement as a function of molecular structure.[10,14] The accessibility of the aromatic groups of the hybrid network has been studied, using the reaction of complexation of aryl fragments with $Cr(CO)_6$ according to reaction 2.

Complexation reactions occur under heterogeneous conditions. The silsesquioxanes obtained from **1**–**4** were treated with $Cr(CO)_6$. After 65 h of reflux in a 80/20 mixture of $Bu^n{}_2O$–THF a yellow–green powder was isolated. The complexation of arene groups was evidenced by FTIR and ^{13}C CP MAS NMR spectroscopies as described in the case of 'authentic' materials.[12b] FTIR spectra showed new absorption bands at *ca.* 1970 and 1880 cm^{-1} due to carbonyl groups, the intensity of which depended on the degree of complexation with $Cr(CO)_3$. ^{13}C CP MAS NMR spectra clearly revealed the presence of both uncomplexed aryl and aryl–$Cr(CO)_3$ units: for example, for **4M,** the spectrum showed signals corresponding to carbonyl groups at δ 234, complexed aromatic carbons aryl–$Cr(CO)_3$ at δ 93 and 117 and uncomplexed aromatic groups at δ 128 and 145 (Fig. 7). These ^{13}C CP MAS NMR data are reported in Table 6. ^{29}Si CP MAS NMR spectra before and after complexation with $Cr(CO)_6$ were unchanged. The degree of complexation was determined by EDS and chemical elemental analysis. The results deduced from elemental analysis (see Experimental section) showed a greater reproducibility and are reported in Table 4.

The xerogels obtained from 'rigid' precursors **1** and **2** led to



Reaction 1 : Hydrolysis–condensation of molecular precursor



Reaction 2 : Complexation of aryl groups with Cr(CO)$_6$

Table 5 N_2 adsorption desorption data of xerogels

Entry	Xerogel	BET surface/$m^2\ g^{-1}$	$V_{pore\ tot}{}^a/cm^3\ g^{-1}$	$V_{pore\ ads}{}^b/cm^3\ g^{-1}$	$V_{pore\ des}{}^b/cm^3\ g^{-1}$	$V_{micropore}{}^c/cm^3\ g^{-1}$	c
1	**1M**	549	0.27	0.11	0.11	0.16	470
2	**1T**	370	0.19	0.04	0.03	0.15	814
3	**2M**	1018	0.80	0.74	0.74	0.10	106
4	**2T**	766	0.53	0.55	0.49	—	146
5	**3T**	277	0.20	0.17	—	—	83
6	**4T**	565	0.37	0.29	0.27	0.08	122

[a] $P/P_0 = 0.99$. [b] Cumulative pore volume of pores between 17 and 3000 Å diameter. [c] Estimated by the t-plot method, using Harkins and Jura standard isotherm and thickness range between 4 and 6 Å.

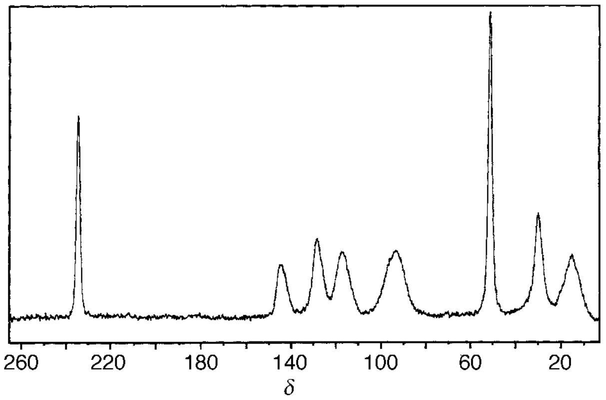


Fig. 7 ^{13}C CP MAS NMR spectrum of the solid obtained by reaction of xerogel **4M** with $Cr(CO)_6$.

Table 6 ^{13}C CP MAS NMR data (δ) of xerogels after reaction with $Cr(CO)_6$

Xerogel	CH_2Si	CH_2Ar	Residual CH_3O	Unchanged Ar	Complexed Ar	Complexed CO
1M	—	—	50	134	—[a]	—[a]
1T	—	—	50	134	—[a]	—[a]
2M	—	—	50	131, 143	88, 105	232
2T	—	—	51	130, 143	—[a]	—[a]
3M	—	21	50	129, 133	96, 109	235
3T	—	21	50	133, 129	106, 94	234
4M	14	29	51	145, 128	93, 117	234
4T	15	29	50	143, 128	114, 92	233

[a] Not detected.

poor levels of complexation (11–33%), despite their high specific surface areas (370–1020 $m^2\ g^{-1}$). However, the surface area and the degree of complexation of the xerogels derived from precursor **2** were about twice as high as those of the xerogels derived from precursor **1**. These results suggest an organization of the solids in which only a few aromatic groups are accessible at the surface. Futhermore the precursors **1** and **2** have different geometries: **1** is linear with six hydrolysable groups, while **2** has a planar geometry with nine hydrolysable groups.

For xerogels obtained from 'flexible' precursors **3** and **4** the degrees of complexation were highly dependent on the nature of the organic spacer and the solvent and poor reactivity was observed when **3** was hydrolysed in MeOH (Table 4, entry 5). A moderate degree of complexation was observed for **3T** which may be attributed to the higher specific surface area observed in this case (277 $m^2\ g^{-1}$).

For **4**, a high degree of complexation (84%) was obtained in the case of **4M** (Table 4, entry 7), showing a high accessibility of the organic groups, although the specific surface area was very low ($< 10\ m^2\ g^{-1}$). This behaviour can be explained by the facile diffusion of $Cr(CO)_6$ in the network due to swelling of the solid in the presence of solvent. This may be attributed to flexibility due to the methylene groups present in the organic moiety.

When the gelation solvent was THF a decrease of the degree of complexation (64%) was observed for **4T** (Table 4, entry 8). This decrease can be explained by the higher degree of polycondensation of the hybrid material which induces a lower swelling of the solid corresponding to a lower diffusion of $Cr(CO)_6$.

However the poor reactivity observed with the gels obtained from **3** appears unexpected, since the solids obtained from **3** and **4** in MeOH exhibited the same specific surface areas ($< 10\ m^2\ g^{-1}$) and the same affinity for water (2%). This can be explained by a less 'flexible' organic spacer for **3** and consequently more difficult diffusion of $Cr(CO)_6$ in the hybrid network. The precursor **3** appears to be intermediate between **1** and **4**.

Analysis of the surface of solids **1M** and **4M** by time of flight secondary ion mass spectrometry (TOF SIMS) was in agreement with the results presented above. For **1M**, the main ion detected is at $m/z = 45$ ($SiOH^+$), in accord with the high hydrophilicity (OH groups at the surface) and poor chemical reactivity.[22] By contrast, for **4M**, ions at $m/z = 77$ (phenyl) and $m/z = 91$ (tropylium) are observed[23] in accord with an hydrophobic solid and a high chemical reactivity. For **1M**, the OH groups are located at the surface in agreement with the high hydrophilicity, while for **4M** the presence of ions at $m/z = 77$ and 91 is in accord with the hydrophobicity observed. This means that the arrangement of the organic groups in the two solids is completely different.

Conclusion

The results presented here show that the kinetic parameters involved in the hydrolysis–polycondensation reactions have an influence on both the physical and chemical properties of the resulting silsesquioxane materials.

The structure of the organic precursor appears to be a determining parameter for the solid state properties of the xerogels containing aromatic groups. Molecular precursors containing a 'rigid' organic group always led to hydrophilic solids with similar degrees of condensation. In all cases, these solids had high specific surface areas and no narrow pore size distribution whatever the solvent and the concentrations used during the hydrolysis–polycondensation process and poor chemical reactivity towards $Cr(CO)_6$ was observed (11–33%).

By contrast when the precursor contained a 'flexible' organic spacer, the texture, the degree of condensation and the reactivity towards $Cr(CO)_6$ of the resulting solids strongly depended on the solvent. The solids prepared in methanol had very low significant specific surface area, whereas in THF high specific surface area products were observed. The degree of complexation with $Cr(CO)_6$ depended on the flexibility of the organic group: when four methylene groups were present (high flexibility) a high reactivity was observed. By contrast, a low reactivity was observed when the flexibility was decreased (two methylene groups). In both cases, however, the solids were hydrophobic.

The results are rigorously reproducible if the experimental conditions are strictly controlled.

Work is now in progress in order to determine the influence of other kinetic parameters on the properties of the solids obtained by this sol–gel process.

References

1 (*a*) H.K. Schmidt, *Mater. Res. Soc. Symp. Proc.*, 1984, **32**, 327; (*b*) H.K. Schmidt, *Inorganic and Organometallic Polymers, ACS Symp. Ser.* 360, American Chemical Society, Washington DC, 1988, p. 133; (*c*) H.K. Schmidt, *Mater. Res. Soc. Symp. Proc.*, 1990, **180,** 961 and references therein; (*d*) *Hybrid Organic–Inorganic Composites, ACS Symp. Ser.* 585, American Chemical Society, San Diego DC, 1994; (*e*) *New J. Chem.*,1994, **18**, 989; (*f*) J.D. Mackenzie, *J. Sol–Gel Sci. Technol.*, 1994, **2**, 81 and references therein; (*g*) U. Schubert, N. Hüsing and A. Lorenz, *Chem. Mater.*, 1995, **7**, 2010; (*h*) D. A. Loy and K.J. Shea, *Chem. Rev.*, 1995, **95**, 1431; (*i*) P. Judenstein and C. Sanchez, *J. Mater. Chem.*, 1996, **6**, 511.

2 (*a*) R. J. P. Corriu and D. Leclercq, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 1420 and references therein; (*b*) R. J. P. Corriu, *C.R. Acad. Sci. Paris, Sér. II*, 1998, 83 and references therein; (*c*) R. J. P. Corriu, *Polyhedron*, 1998, **17**, 925 and references therein.

3 K. J. Shea, D. A. Loy and O. W. Webster, *Polym. Mater. Eng. Sci.*, 1990, **63**, 281.

4 (*a*) R. J. P. Corriu, J. J. E. Moreau, P. Thépot and M. Wong Chi Man, *Chem. Mater.*, 1992, **4**, 1217; (*b*) R. J. P. Corriu, J. J. E. Moreau and M. Wong Chi Man, *J. Sol-Gel, Sci. Technol.*, 1994, **2**, 87.

5 (*a*) K. J. Shea, D. A. Loy and O. Webster, *J. Am. Chem. Soc.*, 1992, **114**, 6700 and references therein; (*b*) K. M. Choi and K. J. Shea, *J. Am. Chem. Soc.*, 1994, **116**, 9052; (*c*) D. A. Loy, G. M. Jamison, B. M. Baugher, S. A. Myers, R. A. Assink and K. J. Shea, *Chem. Mater.*, 1996, **8**, 656.

6 H. W. Oviatt Jr, K. J. Shea and J. H. Small, *Chem. Mater.*, 1993, **5**, 943.

7 A. Antony, R. J. P. Corriu, J. J. E. Moreau and M. Wong Chi Man, unpublished results.

8 S. T. Hobson and K. J. Shea, *Chem. Mater.*, 1997, **9**, 616.

9 (*a*) K. M. Choi and K. J. Shea, *Chem. Mater.*, 1993, **5**, 1067; (*b*) K. M. Choi and K. J. Shea, *J. Phys. Chem.*, 1994, **98**, 3207; (*c*) K. M. Choi, J. C. Hemminger and K. J. Shea, *J. Phys. Chem.*, 1995, **99**, 4720 and references therein.

10 R. J. P. Corriu, J. J. E. Moreau, P. Thépot and M. Wong Chi Man, *Chem. Mater.*, 1996, **8**, 100.

11 (*a*) R. J. P. Corriu, J. J. E. Moreau, P. Thépot, M. Wong Chi Man, C. Chorro, J. P. Lère-Porte and J. L. Sauvajol, *Chem. Mater.*, 1994, **6**, 640; (*b*) J. L. Sauvajol, C. Chorro, J. P. Lère-Porte, R. J. P. Corriu, J. J. E. Moreau, P. Thépot and M. Wong Chi Man, *Synth. Met.*, 1994, **62**, 233.

12 (*a*) G. Cerveau, R. J. P. Corriu and N. Costa, *J. Non-Cryst. Solids*, 1993, **163**, 226; (*b*) G. Cerveau, R. J. P. Corriu and C. Lepeytre, *Chem. Mater.*, 1997, **9,** 2561; (*c*) R. J. P. Corriu, P. Hesemann and G. Lanneau, *J. Chem. Soc. Chem. Commun.*, 1996, p. 1845.

13 (*a*) P. J. Barrie, S. W. Carr, D. Li Ou and A. C. Sullivan, *Chem. Mater.*, 1995, **7**, 265; (*b*) S. W. Carr, M. Motevalli, D. Li Ou and A. C. Sullivan, *J. Mater. Chem.*, 1997, **7**, 865.

14 (*a*) G. Cerveau, R. J. P. Corriu and C. Lepeytre, *J. Mater. Chem.*, 1995, **75**, 793; (*b*) G. Cerveau, C. Chorro, R. J. P. Corriu, C. Lepeytre, J. P. Lère-Porte, J. Moreau, P.Thépot and M. Wong Chi Man, *Hybrid Organic–Inorganic Silica Materials*, *ACS Symp. Ser.* 585, American Chemical Society, Washington DC, 1995, p. 210 and references therein; (*c*) G.Cerveau, P. Chevalier, R. J. P. Corriu, C. Lepeytre, J. P. Lère-Porte, J. Moreau, P. Thépot and M. Wong Chi Man, *Tailor-maide Silicon Oxygen Compounds. From Molecules to Materials*, ed. R. Corriu and P. Jutzi, Vieweg Publ., 1996, p. 273 and references therein.

15 D. F. Schriver, *The manipulation of air-sensitive compounds*, MacGraw-Hill, New York, 1969.

16 R. J. P. Corriu, D. Leclercq, A. Vioux, M. Pauthe and J. Phalippou, *Ultrastructure Processing of Advanced Ceramics*, ed. J. D. Mackenzie and D. R. Ulrich, Wiley, New York, 1988, p. 113.

17 E. A. Williams, *NMR Spectroscopy of Organosilicon Compounds*, ed. S. Pataï and Z. Rappoport, Wiley, New York, 1989, p. 511.

18 (*a*) M. Mägi, E. Lippmaa, A. Samoson, G. Engelhardt and A. R. Grimmer, *J. Phys. Chem.*, 1984, **88**, 1518; (*b*) H. Marsmann, *^{29}Si NMR Spectroscopic Results*, ed. P. Diehl, E. Fluck and R. Kosfeld, Springer Verlag, Berlin.

19 S. Brunauer, P. H. Emmet and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309.

20 E. Barett, L. Joyner and P. Halenda, *J. Am. Chem. Soc.*, 1951, **73**, 373.

21 S. Brunauer, L. S. Deming, W. S. Deming and E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.

22 G. Cerveau, R. J. P. Corriu, J. Dabosi, J. L. Aubagnac, R. Combarieu and Y. de Puydt, *J. Mater. Chem.*, 1998, **8**,1761.

23 G. Cerveau, R. J. P. Corriu, C. Lepeytre and R. Combarieu, to be published.

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