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Polysilsesquioxane materials containing a dienic unit: unexpected reactivity of the organic unit

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The hydrolytic sol–gel polymerisation of molecular precursors $(RO)_3Si\text{-}(CH_2)_n\text{-}(CH{=}CH)_2\text{-}(CH_2)_n\text{-}Si(OR)_3$, **1** (R = Et, $n = 1$), **2** (R = Et, $n = 2$), and **3** (R = ^{i}Pr, $n = 2$) was investigated under various conditions. In the case of the xerogels obtained from **1**, a partial cleavage of the allylic Si–C bond occurred during the hydrolytic process, whereas starting from **2** and **3** no Si–C breaking was observed. The storage conditions of the solids appeared to be of great importance on the stability of the various xerogels. Under inert conditions (sealed tubes under vacuum) all the xerogels were very stable. In contrast, under atmospheric humidity after several months the solids undergo a total chemical oxidation of the C=C bonds leading to the cleavage of C=C bonds with formation of acid and allenic functionalities. This oxidation is followed by a drastic decrease of the specific surface area. It has been shown that H_2O vapour and oxygen are both necessary for oxidation. Each of these reagents alone does not lead to degradation. Gels obtained from **1** exhibited extensive cleavage of the allylic Si–C bond and an oxidative degradation of the organic fragment. The xerogels derived from **2** exhibited the same degradation of the organic unit, however only a few Si–C bonds were cleaved. It has been shown that this unexpected behaviour occurred only when the dienic moiety was included and bound to the silica network, suggesting a catalytic effect of the oxide matrix since the total oxidative cleavage of C=C bonds in organic chemistry needs either powerful reagents like O_3 or catalytic conditions.

Introduction

The sol–gel process permits access to materials through a very simple one pot procedure under smooth conditions.[1–6] Over the past years we have focused our interest on the study of organic–inorganic hybrid materials obtained by hydrolytic polycondensation of organically substituted alkoxysilanes.[6–8] This reaction leads to a hybrid material in which the silica matrix is covalently bound to the organic moiety (Scheme 1).

It has been pointed out that the formation of these materials is kinetically controlled.[9] All the parameters (catalyst, solvent, concentrations, temperature) susceptible to modification of the kinetics of the hydrolytic polycondensation are of importance for the textural properties of the elaborated solid. ^{13}C and ^{29}Si spectroscopies clearly established the conservation of the organic unit inside the solid without any cleavage of the Si–C bond and yielded information about the polycondensation around the silicon atom.[10] Furthermore the chemical reactivity of these solids depends strongly on the structure of the organic precursor[9d] and the functionality at the silicon atom.[9c]

Our interest in this area led us to investigate solids resulting from the hydrolysis–polycondensation of molecular precursors containing dienic systems. Such materials could exhibit specific properties due to the reactive functionalities of the organic moiety. We have studied two dienic systems in order to determine i) the chemical accessibility of the functional groups in the solid; ii) the possibilities of interaction between these groups leading to a possible internal cross-linking of C=C bonds in the solid. In fact the results showed a surprising very high chemical reactivity leading to the slow oxidation of dienic groups included in the matrix. The details are reported here.

Results and discussion

Synthesis of precursors 1 and 2

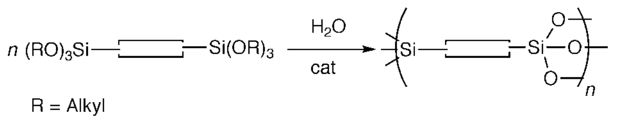
We investigated the formation of bis-silylated molecular precursors containing an unsaturated dienic chain (Scheme 2).

Compound **1** was prepared in two steps from 1,6-dibromohexa-2,4-diene.[11] The first step was the direct silylation of 1,6-dibromohexa-2,4-diene with trichlorosilane in the presence of triethylamine and CuCl[12] (Scheme 3). The crude 1,6-bis(trichlorosilyl)hexa-2,4-diene was converted into **1** by ethanolysis. The overall yield was 71%.

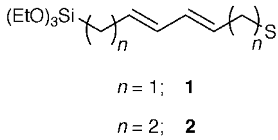
The precursor **2** was obtained in three steps (Scheme 4). Treatment of 1,6-dibromohexa-2,4-diene with 2.2 equivalents of the (triisopropyloxysilyl)methyl Grignard reagent[13] led to 1,8-bis(triisopropyloxysilyl)octa-3,5-diene **3** (63%) which was reduced to the corresponding trihydrosilyl compound **4**. Ethanolysis of **4** in the presence of CsF[14] allowed the isolation of compound **2** in 49% yield.

Sol–gel processing of 1

It has been shown that the formation of organic–inorganic hybrid materials is kinetically controlled. All the parameters involved in the hydrolytic process are of importance for the



Scheme 1



Scheme 2

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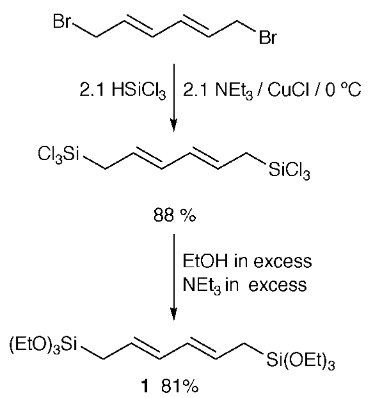
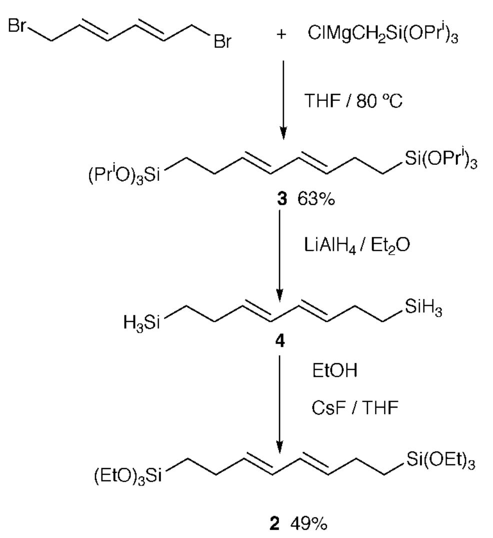
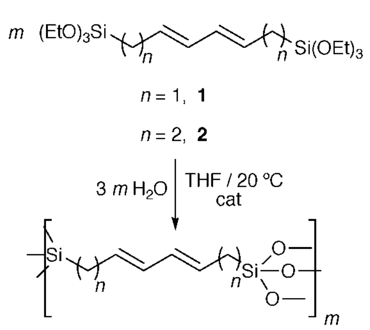


Scheme 3



Scheme 4



Scheme 5

properties of the elaborated solids (catalyst, solvent, concentrations, temperature).[9] Therefore gel formation from **1** has been examined under various reaction conditions. The hydrolysis–polycondensation reactions were performed in THF solutions, at room temperature without catalyst or in the presence of a nucleophilic catalyst (F^-, 1 mol% using tetrabutylammonium fluoride, TBAF) or under acidic conditions (HCl, 1 mol%) (Scheme 5). Two different concentrations of precursor were employed: 0.5 M and 1 M (Table 1).

Transparent gels formed within various periods of time. When TBAF was used as catalyst, gels formed after 15–35 min, whereas with acidic catalyst gel times were longer: 3–8 days and 6 months without catalyst. The gels were allowed to age for 6 days and were then powdered and washed with ethanol, acetone, diethyl ether and dried *in vacuo* (10^{-2} mmHg) at 120 °C for two hours.

Spectroscopic and textural data for xerogels obtained from 1

The white solids were analysed by FTIR and solid state ^{13}C TOSS MAS (Total Side band Suppression Magic Angle Spinning) and ^{29}Si CP MAS NMR spectroscopies. In all cases, whatever the catalyst used the ^{29}Si CP MAS NMR spectra displayed strong resonances in the range -60 to -70 ppm and very weak ones in the range -90 to -100 ppm (Table 1). When a nucleophilic catalyst was used the xerogels **1XA** and **1XB** exhibited two main resonances at -61 ppm and -68 ppm, assigned respectively to substructures T^2 [C-Si(OR)(OSi)$_2$] and T^3 [C-Si(OSi)$_3$)] and two very weak signals at -90 and -100 ppm attributable to Q^2 and Q^3 [Si(OR)$_2$-(OSi)$_2$ and Si(OR)(OSi)$_3$ (R = H, CH$_3$)] substructures of SiO$_{4/2}$.[10] Under acidic conditions the spectra obtained for **1XC** and **1XD** were similar, however the intensity of signals corresponding to Q^2 and Q^3 units was stronger. The presence of Q^x units appeared indicative of some Si–C bond cleavage during the hydrolytic process: the cleavage of the allylic C–Si bond is known to occur under both acidic and nucleophilic reaction conditions.[15] The same results were obtained in the case of **1XE**. However it is interesting to note that the sol–gel polymerisation of monoethylenic monomer (MeO)$_3$Si-CH$_2$-CH=CH-CH$_2$-Si(OMe)$_3$ has been previously reported without cleavage of the allylic Si–C bond.[8a,16] This difference in the behaviour of these similar precursors might be attributed to the higher reactivity of a dienic unit for Si–C cleavage.

It has been shown that single pulse experiments did not reveal any significant variation in relative peak intensity from the CP MAS spectra in systems without hydrogen atoms directly bound to the studied nucleus.[9d,17] So the percentages of the different substructures determined by deconvolution of CP MAS spectra may be considered as an approximate estimate of the degree of polycondensation of the polysilsesquioxane network. The xerogels appeared highly polycondensed (90%) in the case of **1XA** and **1XB** and moderately polycondensed in the case of **1XC**, **1XD** and **1XE** (50–55%). The ^{13}C TOSS MAS NMR spectra displayed resonances at 125 and 132 ppm which were assigned to ethylenic carbons, another one at 58 ppm attributable to CH$_2$ from residual ethoxy groups and a broad one at 18 ppm due to CH$_2$-Si and CH$_3$ from ethoxy end groups. The ^{13}C and ^{29}Si NMR spectra of **1XB** are given in Fig. 1.

The elemental analyses of xerogels **1XA**–**1XE** deviated from the ideal stoichiometry and revealed an excess of carbon and oxygen confirming the presence of non-condensed residual hydroxy and ethoxy groups (see Experimental section).

Nitrogen BET measurements [18] gave specific surface areas

Table 1 Hydrolysis–polycondensation of precursor **1**

Xerogels	Precursor concn./mol l^{-1}	Catalyst (1 mol%)	Specific surface area/m^2 g^{-1}	$E_{0.6}$ (%)	^{29}Si CP MAS NMR δ/ppm
1XA	0.5	TBAF	930	13	**−68** (br); −90 (w); −100 (w)
1XB	1	TBAF	930	15	−61; **−68**; −90 (w); −100(w)
1XC	0.5	HCl	<10	8	**−61**; −68; −90; −100
1XD	1	HCl	<10	8	**−61**; −68; −91; −100
1XE	0.5	No	<10	8	**−49**; **−61**; **−67**; −93; −100

[a] w: weak; br: broad; major resonances for T^x are in bold.

Table 2 Hydrolysis–polycondensation of **2** and **3**

Xerogel	Precursor concn./mol l^{-1}	Catalyst	Catalyst concn./mol%	Specific surface area/m^2 g^{-1}	$E_{0.6}$ (%)	^{29}Si CP MAS NMR δ/ppm
2XA	0.5	TBAF	1	175	11	−56; **−65**
2XB	1	TBAF	1	535	12	−57; **−65**
3XA	1	HCl	1	<10	7	−48; **−57**; **−65**
3XB	0.5	HCl	5	<10	7	**−57**; **−64**; −90 (w); −100(w)
3XC	1	HCl	5	<10	7	**−57**; **−65**; −90 (w); −100(w)

[a] w: weak; major resonances for T^x are in bold.

which were very different depending on the nature of the catalyst as illustrated by its drastic influence on the texture of the solids (Table 1). The xerogels **1XA** and **1XB** prepared under nucleophilic conditions exhibited very high specific surface areas (930 m^2 g^{-1}) while no significant specific surface areas were observed in the case of acidic catalysis (**1XC** and **1XD**) or without catalysis (**1XE**). The xerogels **1XA** and **1XB** showed type IV isotherms[19] characteristic of mesoporous solids. The pore size ranged from 20 to 90 Å.

Interestingly these xerogels were not hydrophobic in contrast with the results obtained in the case of semi rigid spacers.[9d] Their affinity for water appeared to be moderate: the weight increases in a 60% humidity atmosphere at 20 °C ($E_{0.6}$) lay in the range 8–15% (Table 1).

Sol–gel processing of 2 and 3

The hydrolysis–polycondensation of **2** was performed in THF solution at room temperature in the presence of 1 mol% of TBAF. The concentration of **2** was 0.5 M and 1 M. Transparent gels formed after 15–30 minutes (Table 2).

After usual processing, the xerogels **2XA** and **2XB** were isolated as white powders. They were studied by solid state NMR spectroscopies. In this case, only substructures T^2 at −56 ppm and T^3 at −65 ppm were observed in ^{29}Si CP MAS NMR. No C–Si bond cleavage had occurred since no ^{29}Si resonances attributable to $SiO_{4/2}$ were detected. The level of condensation for xerogels **2XA** and **2XB** was 90%. The ^{13}C TOSS MAS NMR spectra of **2XA** and **2XB** displayed resonances at 130 ppm (ethylenic carbons), 58 ppm (CH_2O), 26 ppm (CH_2-CH=), 18 ppm (CH_3CH_2O) and 13 ppm (CH_2CH_2-Si). The ^{13}C and ^{29}Si NMR spectra in solid state of **2XB** are given in Fig. 2.

The BET surface areas of xerogels obtained from **2** were dependent on the concentration of the precursor (174 m^2 g^{-1} for **2XA** and 536 m^2 g^{-1} for **2XB**). Theses solids were mesoporous with a microporous contribution.[19] The microporous volume represented 40% of the total porous volume.[20]

2XA and **2XB** exhibited a moderate hydrophilic character ($E_{0.6} \approx 11\%$).

The hydrolysis–polycondensation of **3** was performed in THF solution at room temperature in the presence of HCl. The gelation times observed in the case of the bulkier isopropyloxy group were longer: in the case of **3XA** it was 20 days and 2.5 days for **3XB** and **3XC** (Table 2). After usual processing the xerogels **3XA**–**3XC** were isolated as yellow powders. They were studied by solid state NMR spectroscopies. From these studies it appeared that some cleavage of the Si–C bond occurred. For **3XA**, the ^{29}Si CP MAS NMR spectrum exhibited the resonances assigned to T^0, T^2 and T^3 substructures normally expected for this xerogel and a very weak signal at −90 ppm attributable to Q^2 substructure of $SiO_{4/2}$. In the case of **3XB** and **3XC**, the spectra displayed T^2, T^3, Q^2 and Q^3 resonances respectively attributed to the hybrid silsesquioxane and some silica. Furthermore ^{13}C TOSS MAS NMR spectra showed in all cases the resonances normally expected for the organic group, and in addition two new broad signals appeared at ~77 and ~205 ppm. The resonance at ~205 ppm could be attributed to a carbonyl group since at the same time the

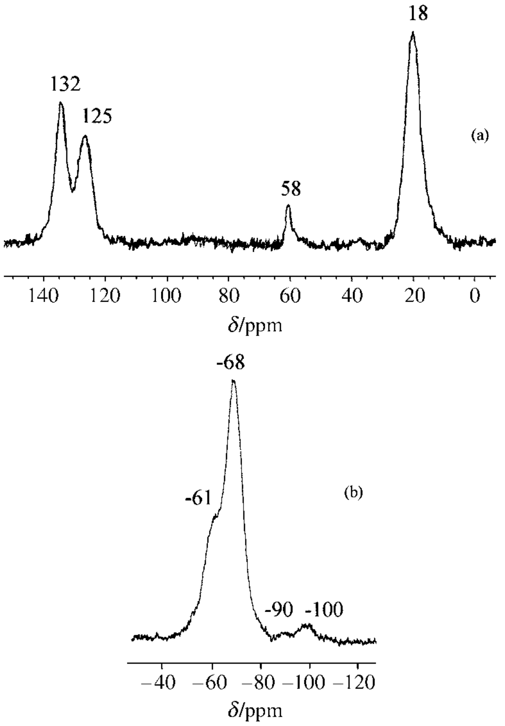


Fig. 1 ^{13}C TOSS NMR (a) and ^{29}Si CP MAS NMR (b) spectra of **1XB**.

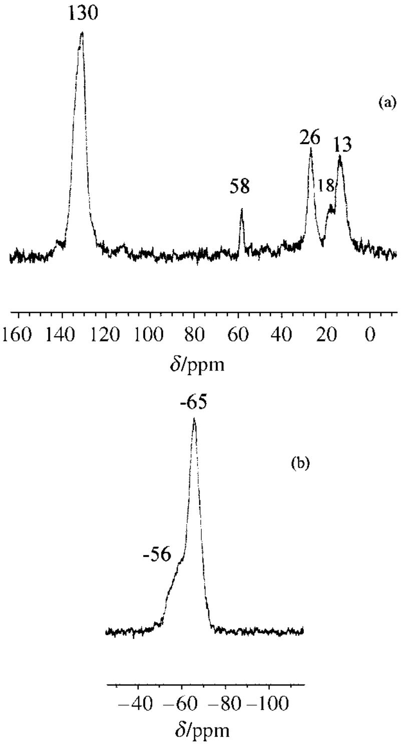


Fig. 2 ^{13}C TOSS NMR (a) and ^{29}Si CP MAS NMR (b) spectra of **2XA**.

Table 3 Specific surface areas of xerogels after different ageing times

	Specific surface area/m^2 g^{-1}		
Xerogel	Initial	After ageing (*t*/months)	After 15 months
1XA	930	160 (10)	<10
1XB	930	<10 (6.5)	<10
2XA	175	40 (3.5)	<10
2XB	535	20 (6.5)	<10

FTIR spectra exhibited a new absorption band at ~1704 cm^{-1}.

Ageing of the xerogels derived from 1 and 2

It has been clearly shown that the formation of hybrid organic–inorganic materials by the sol–gel route is controlled by all the kinetic parameters involved in the process.[9] The study of the ageing of the resulting solids under different conditions appeared to be of great interest since variations in the textural properties of some hybrid materials have been evidenced.[21]

The ageing of the solids has been studied only in the case of xerogels obtained by hydrolysis–polycondensation of bis(triethoxysilyl) precursors **1** and **2** under nucleophilic catalysis by TBAF because the resulting solids exhibited high specific surface areas.

Two sets of ageing conditions were investigated. On one hand the solids **1XA**, **1XB**, **2XA** and **2XB** were stored in sealed tubes under vacuum. After 18 months, the xerogels were analysed. No significant changes were noticed: the ^{29}Si CP MAS and ^{13}C TOSS MAS NMR spectra were unchanged and specific surface areas lay in the same range as before in all cases.

In contrast when the xerogels were stored under an air atmosphere, drastic changes were observed in the structural and textural properties of the solids. Furthermore, the white powders became yellow. Drastic decreases of the specific surface areas were observed in the case of **1XA**, **1XB**, **2XA** and **2XB** after ageing times varying from 6 to 15 months (Table 3). The corresponding xerogels had no more significant surface area.

The spectroscopic data of these yellow solids were investigated. FTIR spectra exhibited in all cases two strong new absorption bands: a broad absorption band between 2500 and 3500 cm^{-1} characteristic of the OH stretching vibration in carboxylic acids and a strong band at *ca.* 1710 cm^{-1} assigned to the vibration of a C=O bond were observed. At the same time the absorption bands corresponding to the ethylenic system had disappeared. The ^{13}C TOSS MAS and ^{29}Si CP MAS NMR spectra showed profound changes. The ^{29}Si CP MAS NMR spectrum of **1XB** after ageing time of 6.5 months is given as an example (Fig. 3). It displays the resonances at −61 and −68 ppm corresponding to T^2 and T^3 substructures of silsesquioxane materials and three new strong resonances at −91, −100 and −107 ppm which were assigned to Q^2, Q^3 and Q^4 substructures of $SiO_{4/2}$. The presence of very strong resonances in the range −90 to −110 ppm was indicative of the cleavage of many Si–C bonds. A comparison between the ^{13}C TOSS MAS NMR spectra of the xerogel **1XB** before and after ageing for 6.5 months clearly showed that the intensity of the signals corresponding to the organic moiety drastically decreased (18, 58, 125 and 132 ppm). At the same time new broad resonances were observed at ~80, ~180 and ~220 ppm (Fig. 2). These two later signals might be attributed to carbonyl groups belonging to an aldehyde or a carboxylic acid. The signal at around 80 ppm might be attributed to allenic carbons.

In the case of **2XA** and **2XB**, the same behaviour was observed. As shown on the spectrum (Fig. 4) only a few Si–C bond cleavages occurred (only weak Q^2 and Q^3 signals can be observed). However the intensity of the ^{13}C resonances attributable to the ethylenic carbons at around 130 ppm were weaker and three new ones at ~80, ~180 and ~220 ppm (Fig. 4) were observed similar to those exhibited by **1XA** and **1XB**. Another related xerogel[16] having only one double bond, $O_{1.5}Si\text{-}CH_2\text{-}CH_2\text{-}HC{=}CH\text{-}CH_2\text{-}CH_2\text{-}SiO_{1.5}$, did not exhibit any degradation after 2 years under the same conditions. Spectroscopic data did not change and specific surface area decreased from 630 to 530 m^2 g^{-1} after 8 months and 250 m^2 g^{-1} after 2 years under an air atmosphere.

The results presented here show the drastic influence of the

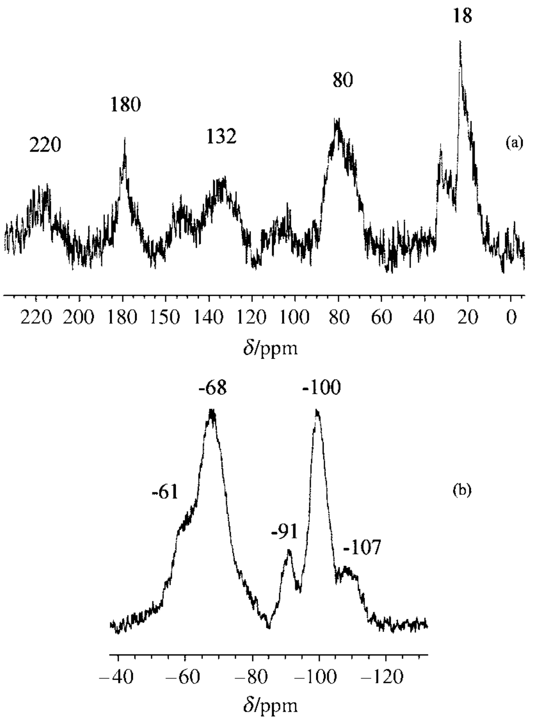


Fig. 3 ^{13}C TOSS NMR (a) and ^{29}Si CP MAS NMR (b) spectra of **1XB** after ageing (6.5 months).

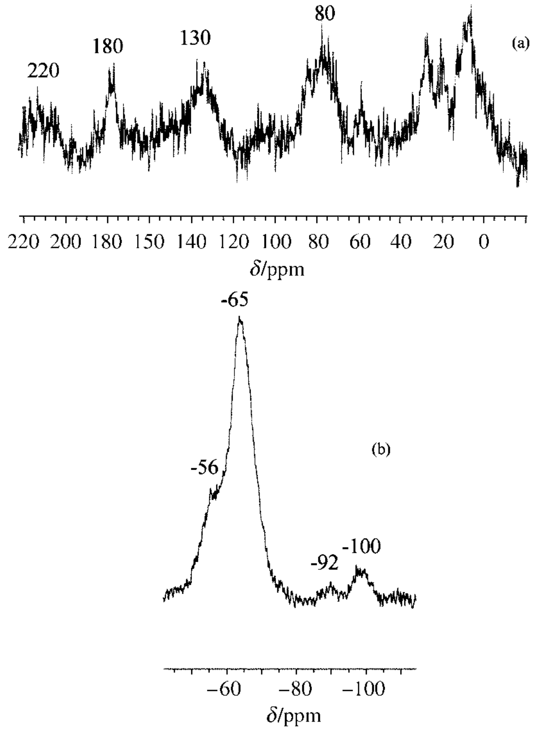


Fig. 4 ^{13}C TOSS NMR (a) and ^{29}Si CP MAS NMR (b) spectra of **2XA** after ageing (15 months).

storage conditions of the xerogels derived from **1** and **2**. Such behaviour has never been previously reported. In the case of the xerogels derived from **1** (**1XA**–**1XE**), the cleavage of the Si–C bond could be explained by the high reactivity of the allylic Si–C bond.[15] However the chemical oxidative degradation of the solids obtained from **1** and **2** could not be explained without further experimentation.

The purity of the starting precursors **1** and **2** was carefully checked since Zn–Cu amalgam[22] was used in the synthesis of 1,6-dibromohexa-2,4-diene. The titration of copper and zinc was achieved by atomic absorption: no copper was detected and only 21 ppm of zinc were measured.

Furthermore, the molecular precursor **2** was kept in an air atmosphere for several days and no changes were observed. When this compound **2** was kept during several weeks under an air atmosphere (atmospheric humidity) no degradation was observed; the only reaction which occurred was a slow partial gelification of the starting precursor. *Thus the chemical degradation of the xerogels seemed to be the result of an oxidative process of the dienic moiety occurring only in the polysilsesquioxane solid network*. This phenomenon seemed to be due to the presence of the dienic system within the matrix. These results led us to investigate in more detail the factors which might be involved in this oxidative degradation. For the first time the influence of oxygen on the hydrolysis reaction has been studied.

In this context, the hydrolysis–polycondensation of **2** has been achieved at room temperature at 1 M in THF in the presence of 1 mol% of TBAF, under argon (**2XB**), oxygen (**2Y**) and air (**2Z**). In the three cases, gels formed after 35 minutes. After the usual work up, white solids were isolated. The spectroscopic data (FTIR, ^{13}C and ^{29}Si solid state NMR) and the physical data (specific surface area and hydrophilicity) were identical to those reported for **2XB** (Table 2) for the three xerogels. These experiments showed that no oxidation and no degradation occurred during the hydrolytic process even under an oxygen atmosphere. Furthermore when **2XB**, **2Y** and **2Z** were stored in sealed tubes under vacuum, no degradation of the organic unit occurred after 18 months.

In contrast the storage conditions seemed to be of great importance. In this context the chemical degradation of the hybrid solids was studied under different conditions and it was monitored by FTIR spectroscopy:

a) when the xerogels were kept in the open air, the oxidative degradation occurred slowly. It increased when the solids were heated at 120 °C under vacuum during 2 hours after standing in the air atmosphere.

b) when the xerogels were kept under a dry oxygen atmosphere, nothing occurred, even after further heating at 120 °C under vacuum.

c) no chemical degradation was also observed when the solids were stored in a CO_2 atmosphere, even after further heating.

d) the xerogels were kept in an oxygen free 60% humidity atmosphere during various periods of time. A weak degradation of the organic fragment occurred only after 7 days. This degradation was increased if the solid was then heated at 120 °C under vacuum for 2 hours.

e) In a wet oxygen atmosphere, a fast degradation of the solids was observed after 4 days.

It was possible to conclude that the oxidative degradation of these solids could be mainly initiated by *water vapour*. It was increased either by heating or by the presence of oxygen which seemed to drive water vapour into the solids. It is interesting to point out that when liquid water was used no oxidative degradation occurred. These experiments clearly showed that the storage in the atmospheric humidity gave rise to the degradation of the solids.

Furthermore, the results of both elemental analysis and spectroscopic data show a drastic change in the organic part of the hybrid solid. The observations can be analysed as follows:

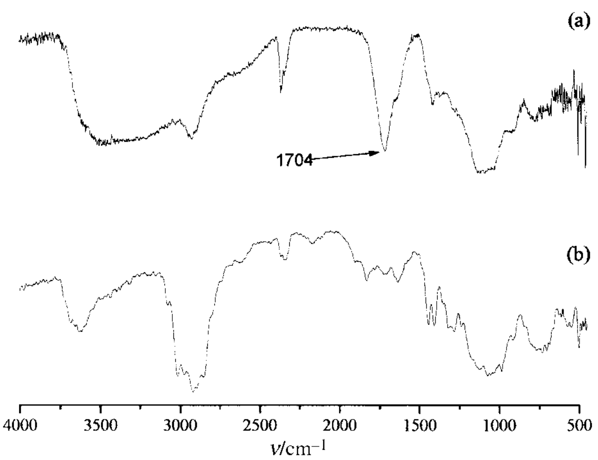


Fig. 5 FTIR spectra of **2XA** before (b) and after ageing (15 months) (a).

1) obviously the oxidation of the organic part occurs with cleavage of carbon–carbon bonds since aldehydes and acids are evidenced by ^{13}C NMR (Fig. 4) and by FTIR (Fig. 5).

2) the chemical analysis is in agreement with a general formula of $SiC_4H_7O_2$ (Table 4) taking into account that only a small part of the organic unit is lost by the Si–C bond breaking, evidenced by the presence of Q^2 and Q^3 signals (Fig. 4). Moreover the ratio C : Si did not change with time: 4.51 before ageing and 4.41 after 16 months.

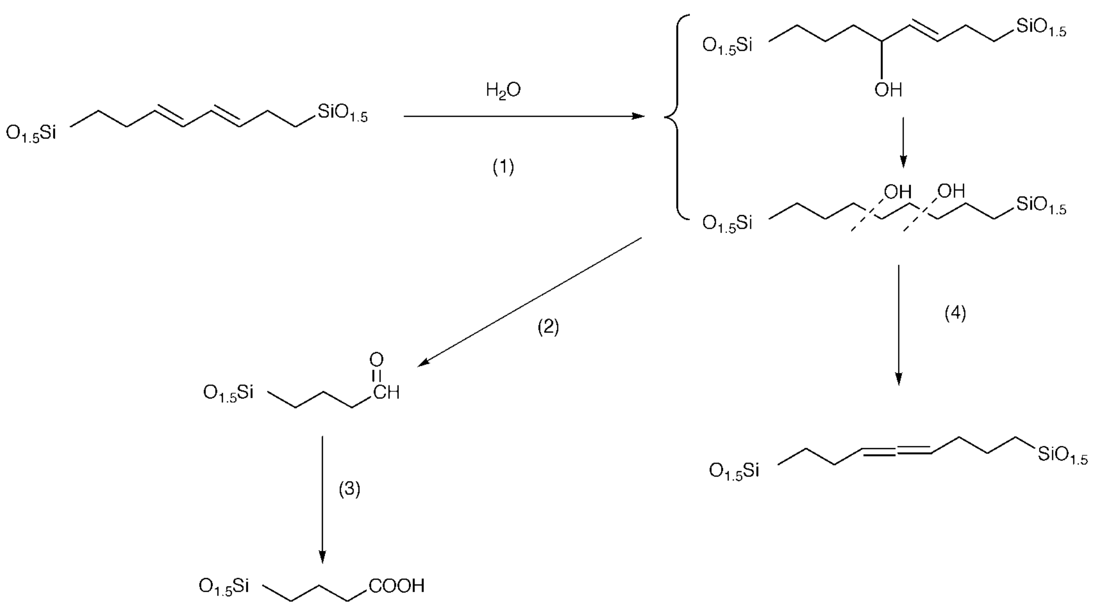
A detailed mechanism cannot be proposed for explaining the general trend of the degradation process. However some reasonable propositions can be made. We have observed that oxygen alone and H_2O vapour alone are not sufficient for inducing degradation. Moreover H_2O vapour is able to induce some modifications without degradation, but not to explain the acid and aldehyde formation. In these conditions we can propose that the first step might be the hydration of the dienic system leading to alcohols or polyols. This reaction could be followed by oxidation of the OH groups with cleavage of the C–C bonds (Scheme 6). The step (1) can be catalysed by the acidic properties of silica. The oxidation reactions are more surprising. However as a mater of fact this degradation process occurs only when the organic units are attached to a silica matrix. For instance this observation has been made in another case: the solid **4X** obtained by polycondensation of **4** exhibits[23] exactly the same degradation under the same experimental conditions (Scheme 7). Moreover we have shown that the precursor **2** does not undergo any oxidative degradation before being converted into hybrid material. The possible presence of the allenic carbons might be explained by dehydration of either allylic alcohols or diols (step (4)) which can also be catalysed by the acidity of silica.

Conclusion

In this paper we have described organic–inorganic hybrid materials containing dienic units as organic spacers. The chemical stability of the solids depends strongly on the storage

Table 4 Elemental analysis of **2XB** after ageing time

2XB after ageing	C (%)	H (%)	Si (%)
Found	36.41	5.42	19.30
Calculated for $O_{1.5}SiCH_2CH_2CH_2COOH$	34.53	5.03	20.14
Calculated for $O_{1.5}SiCH_2CH{=}CHCOOH$	35.04	3.65	20.50



Scheme 6

conditions of the samples. Under inert conditions they appeared very stable during a long period. In contrast under an air atmosphere an oxidative degradation of the dienic fragment in the organic moiety has been evidenced. In the case of olefinic or aromatic spacers such behaviour had never been previously observed. We have shown that the oxidation occurred only when the organic unit is bonded to silica. The oxidative processes were only observed in the presence of H_2O vapour plus oxygen. In these conditions (usual storage under an air atmosphere) the oxidation of dienic units occurred leading to formation of carboxylic acid, aldehyde and functional groups without loss of carbon. This oxidation of dienic units included in silica suggests a catalytic effect for hydration of C=C bond followed by silica catalysed oxidation. This behaviour is totally unexpected since it is well known in organic chemistry that the total oxidation of C=C bonds in solution needs either powerful reagents like O_3, $KMnO_4$ or catalytic conditions. The total oxidation with humid air without any catalyst has never been observed. For example, in solution the mixture O_2–H_2O leads to the dihydroxylation of alkenes in the presence of a catalyst.[24] Silica appeared here capable of promoting oxidation reactions from air. Work is in progress in order to develop the oxidative capacity of silica.

Experimental

Syntheses of precursors and preparation of the gels were carried out under argon using a vacuum line and Schlenk tube techniques.[25] Solvents were dried and distilled before use. IR data (using KCl pellets or by the drift method) were obtained on a Perkin-Elmer 1600 FTIR spectrophotometer. The solution ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 200 spectrometer, ^{29}Si NMR spectra in solution on a Bruker AC 250. Solid state NMR spectra were obtained with a Bruker FTAM 300 spectrometer: ^{13}C TOSS (Total Side band Suppression) MAS NMR at 75.47 MHz, recycling delay 5 s and contact time 5 ms; ^{29}Si CP MAS NMR at 59.6 MHz, recycling delay 10 s and contact time 2 ms. The spinning rate was 5000 Hz in all cases. Chemical shifts are given relative to Me_4Si. Specific surface areas, pore volumes and pore size distribution were determined using a Micromeritics Gemini III 2375 apparatus. Affinity of xerogels for water ($E_{0.6}$) was determined by measurement of the weight increase of the solid in a 60% humidity atmosphere at 25 °C. This atmosphere is obtained with a saturated NaBr solution under vacuum. Elemental analyses were carried out by the "Service Centrale de Micro-Analyse du CNRS". Oxygen percentages were deduced by difference.

4 **4X**

Scheme 7

1,6-Dibromohexa-2,4-diene was prepared according to the literature procedure.[11]

1,6-Bis(triethoxysilyl)hexa-2,4-diene 1

In a first step, an ethereal solution (150 ml) containing 1,6-dibromohexa-2,4-diene[11] (10 g, 41 mmol) and 2.1 equiv. of $HSiCl_3$ (11.78 g, 87 mmol) was added dropwise to 150 ml ether solution of 2.2 equiv. of dry triethylamine (8.85 g; 87 mmol) and CuCl (0.2 g, 2 mmol) at −5 °C. After the addition, the white suspension was stirred at 35 °C for 15 hours. The mixture was then filtered and the solvent evaporated under vacuum to afford a crude yellow oil of 1,6-bis(trichlorosilyl)hexa-2,4-diene (12.60 g, 0.036 mol) in 88 % yield.

In a second step, a solution of 1,6-bis(trichlorosilyl)hexa-2,4-diene in dry ether was added dropwise to 150 ml ether solution containing an excess of dry triethylamine (6.5 equiv.) (21.04 g, 208 mmol) and dry ethanol in excess (11.80 g, 256 mmol) at 0 °C. After the addition, the mixture was stirred at 40 °C for 12 hours. The final white suspension was filtered and the filtrate concentrated under vacuum to give a crude yellow oil. Distillation of the residue (121–123 °C; 5×10^{-1} mbar) afforded 11.85 g (30 mmol) of 1,6-bis(triethoxysilyl)hexa-2,4-diene **1** in 81% yield.

^{1}H NMR ($CDCl_3$, δ/ppm): 5.76 (4H, m, C_2H_4), 3.83 (12H, q, OCH_2), 1.66 (18H, t, CH_3), 1.23 (4H, m, CH_2Si). ^{13}C NMR ($CDCl_3$, δ/ppm): 131.5 (Csp^2), 124.9 (Csp^2), 58.9 (OCH_2), 18.8 (CH_3), 17.2 (CH_2Si). ^{29}Si NMR ($CDCl_3$, δ/ppm): –49.9. Elemental analysis: Calc. for $C_{18}H_{38}O_6Si_2$: C, 53.11; H, 9.41; Si, 13.81%. Found: C, 52.94; H, 9.33; Si, 11.80%.

1,8-Bis(triethoxysilyl)octa-3,5-diene 2

The precursor **2** was elaborated in three steps.

1,8-Bis(triisopropyloxysilyl)octa-3,5-diene **3** was first prepared.

The Grignard reagent derived from chloromethyl(triisopropyloxy)silane[13] (23.36 g, 91.7 mmol; 1 M in dry THF) was added dropwise at 20 °C to 1,6-dibromohexa-2,4-diene[11] (10 g, 41.6 mmol) dissolved in dry THF. The mixture was heated at 80–85 °C for 20 hours. After evaporation of THF, the residue was extracted with 300 ml of dry pentane to give a grey suspension. After filtration, pentane was then pumped off to afford a crude yellow oil. Distillation under vacuum (142–146 °C; 5×10^{-1} mbar) afforded 13.55 g (26.1 mmol) of 1,8-bis(triisopropyloxysilyl)octa-3,5-diene **3** in 63% yield as a colourless oil.

^{1}H NMR ($CDCl_3$, δ/ppm): 5.80 (4H, m, C_2H_4), 4.23 (6H, septet, CH), 2.17 (4H, m, CH_2CH_2Si), 1.21 (36H, d, CH_3), 0.70 (4H, m, CH_2CH_2Si). ^{13}C NMR ($CDCl_3$, δ/ppm): 135.1 (Csp^2), 129.4 (Csp^2), 65.2 (CH), 26.4 (CH_2CH_2Si), 25.9 (CH_3), 12.2 (CH_2CH_2Si). ^{29}Si NMR ($CDCl_3$/δ, ppm): −49.2. Elemental analysis: calc. for $C_{26}H_{54}O_6Si_2$: C, 60.20; H, 10.41; Si, 10.82%. Found: C, 59.49; H, 10.53; Si, 10.80%.

In a second step, a solution of 13.55 g (26.1 g, 687 mmol) of 1,8-bis(triisopropyloxysilyl)octa-3,5-diene **3** in 100 ml of dry ether was slowly added dropwise to a suspension of 5 g (133 mmol) of lithium aluminium hydride in 100 ml of dry ether at 0 °C. The final grey suspension was stirred at 20 °C for 24 hours. The solvent was then evaporated under vacuum and the resulting solid was extracted with 400 ml of dry pentane. After filtration, the solvent was removed under vacuum to give 3.7 g (21.7 mmol) of crude 1,8-bis(trihydrosilyl)octa-3,5-diene **4** in 83% yield.

In a last step, **4** was then transformed into 1,8-bis(triethoxysilyl)octa-3,5-diene **2** by ethanolysis. To a mixture consisting of 3.56 g (21 mmol) of 1,8-bis(trihydrosilyl)octa-3,5-diene **4**, a catalytic amount (0.5 mol%) of dry caesium fluoride (16 mg, 10^{-2} mmol) and 100 ml of dry THF at −30 °C, was added slowly dry ethanol in excess (11.74 g, 255 mmol). After stirring for *ca.* 6 hours at room temperature, the solvents were pumped off and the crude yellow oil was distilled under vacuum (129–135 °C, 5×10^{-1} mbar) to afford 4.45 g (10.2 mmol) of 1,8-bis(triethoxysilyl)octa-3,5-diene **2** in 49% yield as a colorless oil.

^{1}H NMR ($CDCl_3$, δ/ppm): 0.71 (4H, m, CH_2Si), 1.22 (18H, t, CH_3), 2.16 (4H, m, CH_2CH_2Si), 3.80 (12H, q, CH_2), 5.80 (4H, m, CH_2CH_2Si).^{13}C NMR ($CDCl_3$, δ/ppm): 134.8 (Csp^2), 129.6 (Csp^2), 58.7 (OCH_2), 26.1 (CH_2CH_2Si), 18.7 (CH_3), 10.6 (CH_2CH_2Si). ^{29}Si NMR ($CDCl_3$, δ/ppm): –45.2. Elemental analysis: calc. for $C_{20}H_{42}O_6Si_2$: C, 55.26; H, 9.74; Si, 12.23%. Found: C, 55.06; H, 9.66; Si, 12.00%.

Sol–gel processing

The preparation of xerogel **1XA** is given as an example.

To a solution of **1** (3 g, 74 mmol) in THF (7.4 ml) placed in a 12.5 ml flask were added successively at 20 °C 400 µl (222 mmol) of water and a solution of 74 µl of TBAF (solution 1 M in THF). After 15 min, a monolithic transparent gel formed. After ageing for 6 days at 20 °C the solid was collected, then ground and washed with ethanol, acetone and diethyl ether. The resulting solid was dried at 120 °C under vacuum during two hours yielding 1.5 g of a white powder **1XA**. Specific surface areas, ^{29}Si CP MAS NMR spectroscopic data and hydrophilic measurements are indicated for **1XA**–**1XE**, **2XA**–**2XB**, **3XA**–**3XC** in Tables 1 and 2.

Xerogels from 1. Elemental analysis: calc. for $C_6H_8O_3Si_2$: C, 39.13; H, 4.34; Si, 30.43%. Found for **1XA**: C, 30.62; H, 4.14; Si, 23.60% which corresponds to $C_{6.06}H_{9.77}Si_2O_{6.19}$. Found for **1XB**: C, 33.69; H, 4.55; Si, 23.25% which corresponds to $C_{6.76}H_{11.04}Si_2O_{5.82}$.

Xerogels from 2 and 3. Elemental analysis: calc. for $C_8H_{12}O_3Si_2$: C, 45.28; H, 5.66; Si, 26.42%. Found for **2XA**: C, 45.51; H, 6.22; Si, 23.60% which corresponds to $C_{9.02}H_{14.78}Si_2O_{3.72}$. Found for **2XB**: C, 48.26; H, 6.51; Si, 23.95% which corresponds to $C_{9.42}H_{15.14}Si_2O_{3.12}$. Found for **3XA**: C, 40.51; H, 6.05; Si, 21.55% which corresponds to $C_{8.77}H_{15.67}Si_2O_{5.19}$. Found for **3XB**: C, 40.32; H, 5.95; Si, 21.70% which corresponds to $C_{8.68}H_{15.28}Si_2O_{5.18}$. Found for **3XC**: C, 41.53; H, 5.98; Si, 20.30% which corresponds to $C_{9.56}H_{16.41}Si_2O_{5.38}$.

In the case of xerogels **2Y** (under an oxygen atmosphere) and **2Z** (under an air atmosphere), the same experimental procedure as for **2XB** was used.

Xerogel 2Y. $S_{BET} = 565$ m^2 g^{-1}, $E_{0.6} = 2.5\%$, elemental analysis: calc. for $C_8H_{12}O_3Si_2$: C, 45.28; H, 5.66; Si, 26.42%. Found for **2Y**: C, 45.87; H, 5.98; Si, 24.60% which corresponds to $C_{8.72}H_{13.55}Si_2O_{3.36}$.

Xerogel 2Z. $S_{BET} = 580$ m^2 g^{-1}, $E_{0.6} = 2\%$, elemental analysis: calc. for $C_8H_{12}O_3Si_2$: C, 45.28; H, 5.66; Si, 26.42%. Found for **2Z**: C, 46.86; H, 5.38; Si, 24.86% which corresponds to $C_{10.14}H_{13.87}Si_2O_{3.72}$.

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