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New Mixed Organic–Inorganic Polymers: Hydrolysis and Polycondensation of Bis(trimethoxysilyl)organometallic Precursors

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A variety of bis(trimethoxysilyl)organometallic precursors, with different structural features, have been obtained in 30–64% yield upon reaction of organic bromides with $ClSi(OR)_3$ (R = Me, Et) in the presence of Mg/THF. The hydrolysis and polycondensation of $(MeO)_3Si$–X–$Si(OMe)_3$ (X = 1,4-C_6H_4, 2,5-C_4H_2S), $(MeO)_3Si$–C_6H_4–$Si(OMe)_2$–C_6H_4–$Si(OMe)_3$, 1,3,5-$[Si(OMe)_3]_3$ C_6H_3, $(MeO)_3Si$–$(C{\equiv}C)_n$$Si(OMe)_3$ (*n* = 1, 2), and $(MeO)_3Si$–CH_2–CH=CH–CH_2–$Si(OMe)_3$, under nucleophilic catalysis by fluoride ion, led quantitatively to new hybrid organic–inorganic silica gels. The derived xerogels were characterized by IR and solid-state ^{13}C and ^{29}Si NMR spectroscopy. The silicon–carbon bond was retained within the gel. The major environment of the Si atoms corresponded to a T_2:X*Si*(OR)$(OSi)_2$ substructure. A higher degree of condensation with a major T_3:X*Si*$(OSi)_3$ was obtained when an excess of fluoride ion was used. In most cases, the gels were amorphous microporous materials with high surface areas (up to 1260 m^2 g^{-1}). The latter was shown to be dependent rather on the reaction conditions during gel formation, than on the flexible or rigid-rod-like structure of the organic moiety. The cleavage of the Si–C bond, with elimination of the organic moiety, was achieved upon treatment of the bis(silyl)acetylene-derived gel with MeOH/H_2O in the presence of fluoride ion catalyst. Amorphous microporous $(SiO_2)_n$ gel with a surface area of 1055 m^2 g^{-1} was produced.

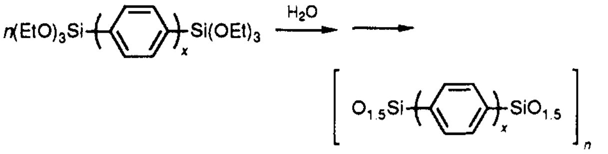
Introduction

The sol–gel methodology was originally directed toward the synthesis of purely inorganic polymers and provides a very promising route to glasses and ceramics.[1] It allows a smooth preparation of metal oxides in two steps: hydrolysis of a metal alkoxide and polycondensation of hydroxyl groups. It has been proven to offer unique possibilities to improve material or processing properties. One of the main features of the method is that it represents a low-temperature process. It therefore also opens the possibility of incorporating organic components and synthesizing mixed organic-inorganic polymers. Such organolithic macromolecular materials[2] constitute an interesting new class of materials. Inorganic–organic hybrid gels have been produced by polycondensation reactions of metal alkoxide and hydroxyl terminated molecules or macromolecules[3-6] and also by hydrolysis–polycondensation of organometallic precursors.[7] The use of organically substituted alkoxides such as $RSi(OR')_3$ allows the introduction of organic groups into a silicate framework (eq 1).

$$nRSi(OR')_3 \xrightarrow[(-R'OH)]{H_2O} \rightarrow [R\text{–}SiO_{1.5}]_n \qquad (1)$$

The resulting silsesquioxanes $(RSiO_{1.5})_n$ have been explored as models for silica surface[8] and particles,[9] as ceramic precursors,[10-12] or to anchor metal complexes moieties to a silicate matrix.[13]

Besides the intrinsic properties that the organic component can bring to such materials, some attention has been recently devoted to the structure of the sol–gel-derived silica on the molecular size scale. Ceramic microporous materials have been produced by use of molecular silicate building blocks.[14-16] Very high surface area xerogels were obtained by sol–gel polymerization of a cubic octamethyl octasilicate precursor. This property was concluded to result from the structure of the gel at the molecular level,[17] the rigidity of the precursor inhibiting extensive crosslinking. Recent work also showed that new silsesquioxane materials resulted from the hydrolysis and polycondensation of bis(triethoxysilyl)phenylene derivatives[18-21] (eq 2). Upon subsequent processing, the resulting



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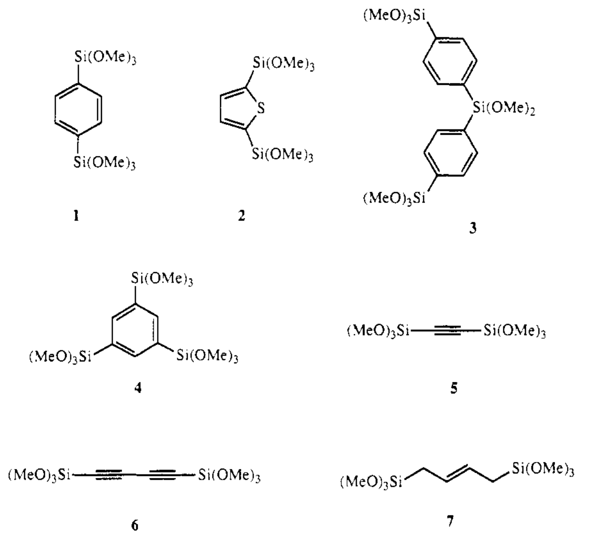


Figure 1. Trimethoxysilylated organometallic gel precursors 1–7.

xerogels were microporous materials with high surface areas, and it was suggested that this property of the solid was related to the presence of rigid-rod organic spacers interspaced at regular intervals in the silicate framework.[18]

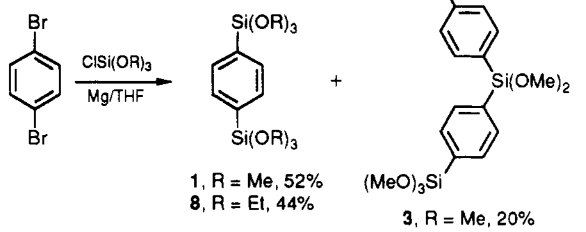
The control of the gel formation and solid morphology by using not only the chemical process but also the molecular structure of the precursor is a very interesting challenge. However, it is well-known in sol–gel process studies that the solid properties and morphology are strongly dependent on the sol–gel polymerization conditions[22,23] (solvent, concentration, temperature, nature of the catalyst, etc.).

In this context, we were interested in investigating whether the reactions conditions are more important than the structure of the precursor in determining the solid-state properties of the resulting materials. We therefore set out to examine gel formation from precursors of various structures and under various reaction conditions. Polysilylated organic molecules constitute interesting precursors since the structure of the organic moiety can be varied and allow facile modification of the shape of the molecular gel precursor. We wish to report here the synthesis and characterization of a variety of gels formed upon hydrolysis of trimethoxysilyl organometallic precursors with different structural features (Figure 1). Beside the known[18–20] linear rigid rod *p*-phenylene precursor 1, we considered precursors with different geometries: bent structures such as 2,5-bis(silyl)thiophene 2 and diphenylene derivative 3, as well as molecules presenting multiple condensation directions such as 3 and 4 respectively with eight and nine functional methoxy groups. We also studied acyclic precursors with rigid (5, 6) or flexible (7) structures. Moreover the hydrolysis and polycondensation reactions were carried out under different reaction conditions. We studied particularly the use of a nucleophilic catalyst. The well-documented nucleophilic activation at silicon[24,26,27] by fluoride ion proved to be very efficient for sol–gel polymerization.[25]

Results and Discussion

Preparation of Trimethoxysilyl-Group-Containing Organic Derivatives. The preparation of linear α,ω-bissilylated molecules with rigid or flexible structures was first considered. Whereas a variety of methods can be used for the trimethylsilylation of organic molecules,[28] only the hydrosilylation reaction[29] constitutes a general method for the preparation of trialkoxysilylderivatives. Moreover, the attachment of several trifunctional silicon atoms to an organic molecule often resulted in low yields of silylated products. To prepare polysilylated molecules with various structures, we examined several methods.

We first investigated a possible extension of the Calas–Dunogues silylation reaction[30] for the trimethoxysilylation of organic molecules. We found that the direct silylation of aromatic bromides with chlorotrimethoxysilane in the presence of magnesium led to the expected silylated arenes. The reaction of 1,4-dibromobenzene (eq 3) afforded a mixture of silylated compounds 1 and 3 respectively in 52 and 20% yields. It is noteworthy that the use of tetramethoxysilane $Si(OMe)_4$ as silylating agent only afforded a 10% yield of 1 under the same reaction conditions. By using $ClSi(OEt)_3$, a 44% yield of the known[18] triethoxysilyl analog 8 was isolated (eq 3). The silylation of 2,5-dibromothiophene proceeded similarly (eq 4) and allowed isolation of compounds 2 (64% yield) and 9 (21% yield). The direct silylation reaction with $ClSi(OMe)_3$ is of particular interest in the case of aromatic polyhalides. The silylation of 1,3,5-tribromobenzene (eq 5) proceeded smoothly to give a 31% yield of the trisilylbenzene derivative 4. Compound 4 was only formed in trace amounts



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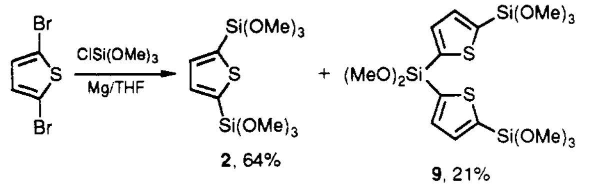

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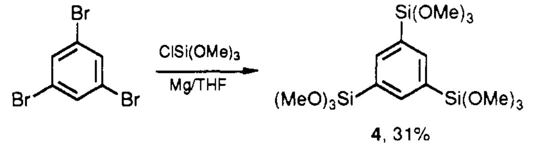

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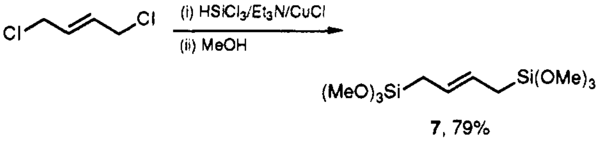
when $Si(OMe)_4$ was used as silylating agent. The trimethoxysilylation reaction with $ClSi(OMe)_3$ therefore offers a short route to polysilylated arenes.

Other rigid-rod type disilylated molecules (Figure 1) were obtained upon silylation of dilithiated derivatives. Bis(trimethoxysilyl)acetylene **5**[31] and bis(trimethoxysilyl)butadiyne **6**[32] were prepared according to literature procedures. The preparation of bis(trimethoxysilyl) precursors in which the two silicon atoms are separated by a flexible carbon chain was also achieved using the silylation of allyl chloride with trichlorosilane/Et_3N.[33] 1,4-Bis(trimethoxysilyl)but-2-ene (**7**) was obtained in two steps. The silylation of 1,4-dichlorobut-2-ene[34] was followed by a quantitative methanolysis (eq 6).



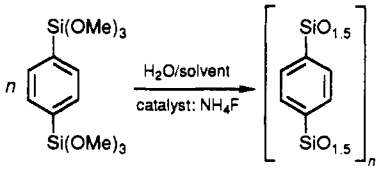
(6)

7, 79%

Synthesis and Characterization of Organic-Inorganic Hybrid Gels. The gels were synthesized by hydrolysis and polycondensation of the trimethoxysilyl precursors **1**–**7**.

1. Hydrolysis of Bis(silyl)-p-phenylene Precursors **1**. The formation of phenylene-bridged[18-20] polysilsesquioxane gels was already reported by Shea et al. upon acid- and base-catalyzed hydrolysis of triethoxysilyl precursors. We first examined the influence of a nucleophilic catalyst in the hydrolysis of the 1,4-phenylene precursor **1**. The use of nucleophilic catalysis by fluoride ion is of interest, since it was recently proved to be very efficient for the sol–gel process[25] and because the hydrolysis step under fluoride ion catalysis proceeds by a mechanism different from those of acid- and base-catalyzed reaction.[24,26,27]

The sol–gel polymerization of **1** (eq 7) was performed in the presence of NH_4F (0.1 mol %) in MeOH or THF.



(7)

1 10

Transparent gels generally formed within a short period of time (several seconds to a few hours) and were allowed to stand at 20 °C for 48 h. After air drying, the solid was collected, washed with ether, and dried in vacuo at 150 °C. The results are summarized in Table I. Two experiments respectively in the presence of NH_4OH and HCl as catalyst, according to the reaction condition reported by Shea et al.,[18] have been carried out and are included for comparison. The gels that were obtained in all cases deviated from the ideal stoichiometry $[O_{1.5}SiC_6H_4SiO_{1.5}]_n$ and contained numerous un-cross-linked units and residual hydroxy and methoxy groups. The carbon to silicon ratio as calculated from elemental analysis measurements varies from 3 to 3.5 indicating that 0–0.5 residual methoxy group per silicon can be present in the material. FT-IR spectra of the dried gels effectively showed bands at 3455 and 2845 cm^{-1} attributable to the presence of Si–OH and Si–OMe groups, respectively. The conservation of the molecular structure of the precursor in the gel and the absence of cleavage of the Si–C bond during the gelation process was established by NMR studies. ^{13}C solid-state MAS NMR clearly revealed the expected aromatic resonances at δ = 133 ppm and minor resonances at δ = 50 ppm arising from residual methoxy carbon. No ^{29}Si resonances attributable to SiO_4 units were detected. ^{29}Si NMR also provides structural information about the silicate framework within the gel. The local environment about silicon centers in silicates has been found to give rise to characteristic ^{29}Si chemical shifts,[35] and these correlations have been used to establish the kinds of environments present in silica gel by ^{29}Si CP MAS spectroscopy.[36-39] Sil-paraphenylene gels have been reported[18] to show three resonances corresponding to branched silicates with the substructures T_1, T_2, and T_3 according to the degree of condensation about the central silicon atom. The fluoride ion catalyst derived gels exhibited similar features (Table II).

Table I. Hydrolysis and Polycondensation of 1,4-Bis(trimethoxysilyl)benzene (Eq 7)

entry	solvt	precursor conc (M)	temp (°C)	catalyst	catalyst conc (mol equiv)	gel time (min)	surface area[a] (m^2 g^{-1})
1	MeOH	3	20	NH_4F	10^{-3}	10^{-1}	1030
2	MeOH	3	65	NH_4F	10^{-3}	*b*	*c*
3	MeOH	1	20	NH_4F	10^{-3}	10	516
4	THF	1	20	NH_4F	10^{-3}	5	548
5	MeOH	1	20	NH_4F	2.6	5	715
6	MeOH	0.3	20	NH_4F	10^{-3}	180	552
7	MeOH	0.1	20	NH_4F	10^{-3}	*b*	*c*
8	MeOH	1	20	NH_4OH	10^{-2}	5	*c*
9	THF	0.4	20	NH_4OH	2.6	45	1262
10	THF	0.4	20	HCl	5×10^{-3}	600	129

[a] BET surface from multipoint analysis of N_2 adsorption isotherm. [b] Slow precipitation of solid. [c] Not determined.

Some representative spectra of the gels are presented in Figure 2. Whatever the catalyst (NH_4F, HCl, or NH_4OH) used in the hydrolysis–condensation steps, the solid obtained showed very similar NMR spectra (Figure 2a–e). In all cases the major resonance is the central peak corresponding to the substructure T_2:$CSi(OR)(OSi)_2$. The major environment about the silicon atom is that represented in Figure 3 in which the silicon atom is linked to three oxygen atoms with an average of two condensation directions and one residual functional group. It is worth noting that the precursor condensation, the reaction temperature, the solvent (MeOH or THF), and the nature of the catalyst have led to oxide polymers with similar ^{29}Si NMR characteristics indicative of a similar degree of condensation for the gels described in Table I (entries 1–4, 6, 7, 10). Although quantitative conclusions are not valid for CP MAS NMR spectra, deconvolution of the ^{29}Si resonances and integration of the areas allowed an approximate estimation of the degree of condensation between 60 and 70% analogous to previous observation of Shea et al.[18] Higher degrees of condensation have been obtained only on increasing the catalyst concentration. As shown in Figure 2c and f, the use of an excess of catalyst led to an enhanced intensity of the ^{29}Si NMR signal cor-

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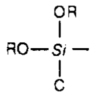
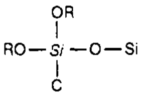
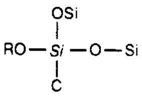
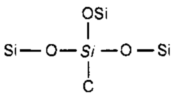
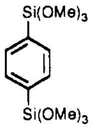
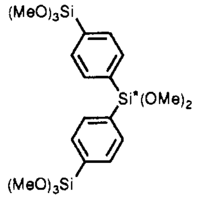
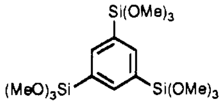
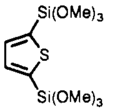
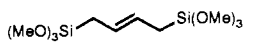
Table II. ^{29}Si CP MAS NMR Chemical Shifts (δ, ppm) of Poly(Organosilsesquioxanes) 10–16

	silicate substructure[a]			
precursor	 $\mathrm{RO{-}}\underset{\mathrm{C}}{\overset{\mathrm{OR}}{\mathit{Si}}}\mathrm{{-}OR}$	 $\mathrm{RO{-}}\underset{\mathrm{C}}{\overset{\mathrm{OR}}{\mathit{Si}}}\mathrm{{-}O{-}Si}$	 $\mathrm{RO{-}}\underset{\mathrm{C}}{\overset{\mathrm{OSi}}{\mathit{Si}}}\mathrm{{-}O{-}Si}$	 $\mathrm{Si{-}O{-}}\underset{\mathrm{C}}{\overset{\mathrm{OSi}}{\mathit{Si}}}\mathrm{{-}O{-}Si}$
	-55	-59	-68	-76
	-55	-62	-70	-78
	* -29 (D$_0$)[b]	* -37 (D$_1$)[b]	* -46 (D$_2$)[b]	
	-54	-61	-69	-77
	-58	-64	-72	-81
(MeO)$_3$Si—≡—Si(OMe)$_3$	-72	-81	-91	-100
(MeO)$_3$Si—≡—≡—Si(OMe)$_3$	-72	-80	-90	-100
	-46	-53	-61	-70

[a] R = H, Me. [b] D$_0$ = C$_2$*Si*(OR)$_2$, D$_1$ = C$_2$*Si*(OR)(OSi), D$_2$ = C$_2$*Si*(OSi)$_2$.

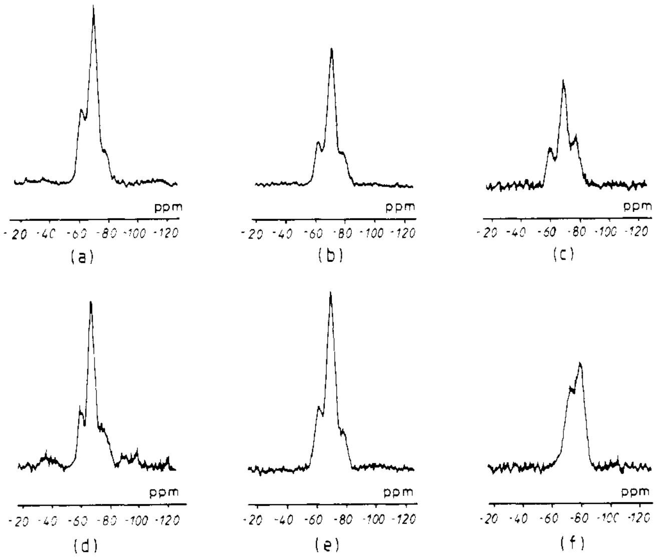


Figure 2. ^{29}Si CP MAS NMR spectra of *p*-phenylene gels **10**. Reaction conditions for gel formation in MeOH (concentration of **1**, nature of catalyst, catalyst/**1** molar ratio): (a) 0.4 mol L^{-1}, HCl, 0.5 mol %; (b) 1 mol L^{-1}, NH$_4$OH, 1 mol %; (c) 0.4 mol L^{-1}, NH$_4$OH, 2.6 mol equiv; (d) 3 mol L^{-1}, NH$_4$F, 0.1 mol %; (e) 1 mol L^{-1}, NH$_4$F, 0.1 mol %; (f) 1 mol L^{-1}, NH$_4$F, 2.6 mol equiv.

responding to the fully condensed T$_3$ substructure. A moderate enhancement was observed when an excess of NH$_4$OH was used. But, under nucleophilic activation with an excess of NH$_4$F (Table I, entry 5) and T$_3$ resonance became the major peak (Figure 2f). Compared to NH$_4$OH catalysis, fluoride ion catalyst produced a gel with a much higher degree of condensation. An estimated value near 90% was determined from the integrated relative intensities of the NMR signals.

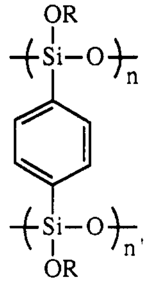


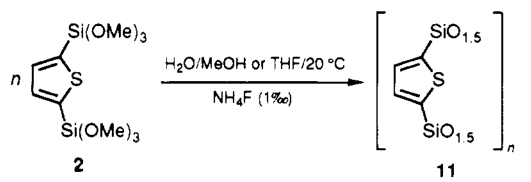
Figure 3. Mean structure of *p*-phenylene gels **10** (R = Me, H).

The solid-state properties of the various poly(silsesquioxanes) have been partially investigated. The X-ray powder diffraction pattern showed no crystallinity. Two broad bands with *d* spacings of 3.7–3.9 and 7.2–8.0 Å were observed whatever the reaction conditions used for gel formation. The materials are amorphous, and no long-distance order was detected. The materials are microporous with a mean pore diameter below 40 Å. N$_2$ BET measurements gave surface areas which vary widely. Surface areas as high as 1260 m^2 g^{-1} have been determined and were found to be quite dependent on the reaction conditions of the gel formation. The variations do not seem to be associated with the degree of condensation of the material. As can be seen in Table I for gels showing in their ^{29}Si NMR spectra a similar T$_1$/T$_2$/T$_3$ ratio, changing acid catalysis (entry 10) to base catalysis (entry 9) resulted in an increase of the surface area of the obtained material by 1 order of magnitude. Using fluoride ion catalysis, the surface areas varied in the range 500–1000 m^2 g^{-1}. This contrasts with recent results reported for [[Si$_8$O$_{12}$](OMe)$_8$]-derived xerogels[17] for which the high surface areas were associated to a low degree of crosslinking between the polymer chains in the structure. In the case of the *p*-$C_6H_4(SiOMe_3)_2$-derived gels **10**, the surface area does not seem to be associated with the extent of cross-linking in the material. A larger value was found for the material exhibiting a higher degree of condensation (Table I entries 3, 5; Figure 2d,f).

The gels **10**, obtained from precursor **1**, exhibited an affinity for water comparable to the one found for silica gels prepared by hydrolysis of $Si(OR)_4$. A weight increase of 18% (in a 60% humidity atmosphere at 25 °C) was found for the *p*-phenylene gel **10** (entry 5 in Table I; versus 30% for a SiO_2 gel with a comparable surface area). It contrasts with the hydrophobic character of $HSi(OEt)_3$-derived xerogels[40] and is consistent with the presence of few organic and many hydroxyl groups at the surface.

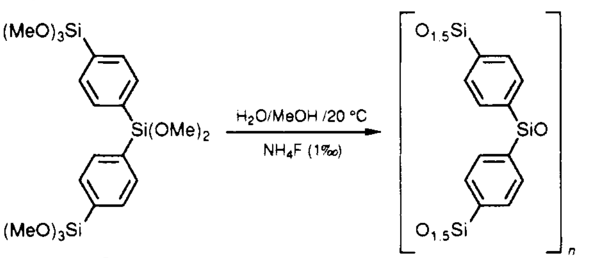
2. *Hydrolysis of Other Silylarylene Precursors.* The structural and morphological properties of the *p*-phenylene gels do not seem to be associated with the linear rigid-rod structure of the organic moiety. Thus, we found that polymers with similar properties were produced from other aromatic precursors with quite different structural features. The hydrolysis and polycondensation of alkoxysilane precursors **2**–**4** were performed under similar reaction conditions using fluoride ion catalysis.

The gel formation occured easily upon hydrolysis of 2,5-bis(trimethoxysilyl)thiophene (eq 8). The solid which formed quantitatively was collected, washed, and dried in vacuo. Spectroscopic analysis of the amorphous polymeric material revealed characteristics very similar to those obtained in the case of *p*-phenylene precursors. For example, ^{29}Si NMR analysis (Table II) also showed a major substructure of type T_2 with two directions of condensation. Interestingly the surface area of the solid was found to be extremely dependent on the solvent used in the condensation step. Whereas no spectroscopic differences were noted between the gels obtained in MeOH or THF, the surface areas varied from 685 $m^2\ g^{-1}$ (MeOH solvent) to only 19 $m^2\ g^{-1}$ (THF solvent). Such a difference was not observed in the case of *p*-phenylene (Table I, entries 3 and 4).



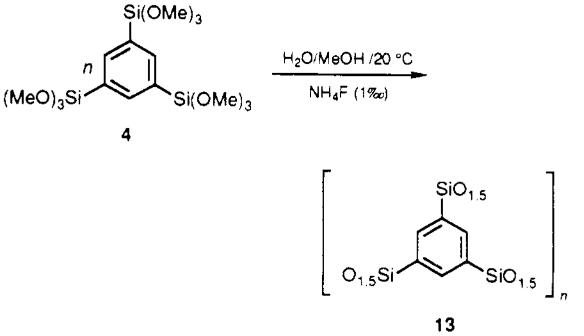
(8)

The hydrolysis reaction was also carried out on the phenylene derivatives **3** with two different silicon atoms (eq 9). The structure of the organometallic molecule is clearly retained in the gel. The ^{29}Si CP MAS NMR spectra of the polymer **12** showed two sets of three signals (cf. Table II). One corresponds to a silicon atom surrounded by three oxygen atoms (T-type substructure: 62, −70, −78 ppm). The other one is due to the central silicon atom with two C–Si bonds and two Si–O bonds (D-type substructure: −29, −37, −46 ppm). The major environment was $T_2{:}C\mathit{Si}(OR)(OSi)_2$ for the terminal silicon atom and $D_1{:}C_2\mathit{Si}(OR)(OSi)$ for the central silicon. The X-ray powder diffraction diagram is similar to the *p*-phenylene one, showing two broad bands with *d* spacings of 3.8 and 7.0 Å.



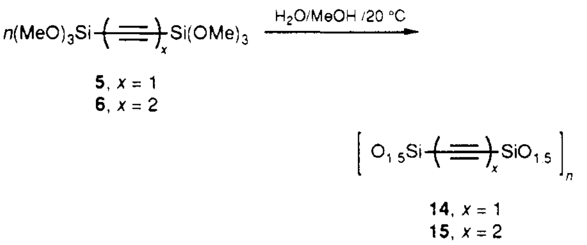
(9)

Finally the polycondensation reaction was also achieved with 1,3,5-tris(trimethoxysilyl)benzene (**4**, eq 10). The gel which formed within a few minutes was allowed to stand for 48 hours and was then powdered, washed, and dried in vacuo. The solid which was collected quantitatively showed spectroscopic characteristics similar to those of the gels obtained from *p*-phenylene precursors. As in all the previous cases, the molecular structure and the carbon–silicon bonds in the precursor are retained during the gelation. This leads here, since the alkoxysilane precursor has nine possible condensation directions, to an oxide polymer with a structure at the molecular level quite different from that of gels **10**–**12**. The major environment about the silicon atom is also $T_2{:}CSi(OR)(OSi)_2$. Examination of the amorphous material by X-ray diffraction only showed a broad band with *d* spacing of 4.5 Å. The solid was also a microporous material with a mean pore diameter of 23 Å and a surface area of 293 $m^2\ g^{-1}$. The morphology of the solid obtained is probably dependent on several experimental parameters. The structure of the precursor does not seem to be the predominant factor in these cases. Disilylated precursors with linear structure **1** or bent **2**, **3** as well as a trisilylated derivative **4** give rise to microporous materials with similar characteristics.

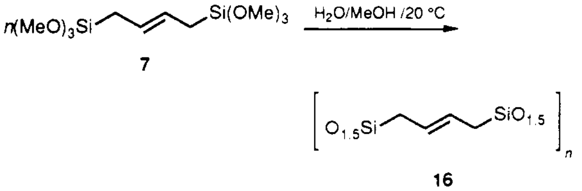


(10)

3. *Hydrolysis of Acyclic Precursors.* We finally examined the preparation of gels from acyclic precursors. We also chose rigid structures such as the acetylenic derivatives **5** and **6** as well as a flexible structure such as the ethylenic compound **7**. The hydrolysis and polycondensation reactions were performed, as in the previous cases, in MeOH solvent (eqs 11 and 12). In all three cases, the gel formation occured rapidly and after curing for 48 hours, the



(11)



(12)

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(40) Pauthe, M.; Phalippou, J.; Corriu, R. J. P.; Leclercq, D.; Vioux, A. *J. Non-Cryst. Solids* **1989**, *113*, 21.

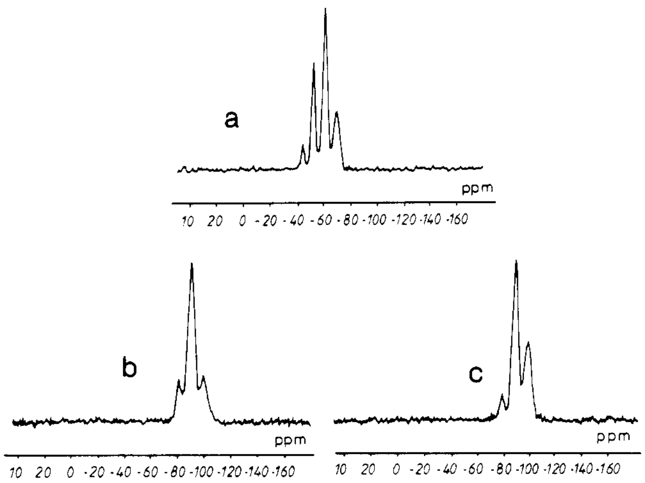

Figure 4. ^{29}Si CP MAS NMR spectra of oxide polymers 14–16. Reaction conditions for gel formation: solvent (MeOH), concentration of precursor (1 mol L^{-1}), catalyst (NH_4F), catalyst/precursor molar ratio (0.1 mol %): (a) $O_{1.5}Si—CH_2CH{=}CHCH_2—SiO_{1.5}$, (b) $O_{1.5}Si—C{\equiv}C—SiO_{1.5}$, (c) $O_{1.5}Si—C{\equiv}C—C{\equiv}C—SiO_{1.5}$.

gels were powdered and dried. The IR analysis showed the presence of residual hydroxy and methoxy groups and therefore that the stoichiometry deviated from the ideal silsesquioxane structure 14–16 presented in eqs 11 and 12. The ^{13}C CP MAS NMR examination of the gels is of particular interest here since it clearly established that the organic moiety is not affected during the polymerization and that no C–Si bond cleavage had occurred. This is the case even for the 1,4-butenediyl structure 16 in which a cleavage of the allylic C–Si bond might have occurred under nucleophilic reaction conditions.[41] The ^{13}C NMR spectra of polymer 16 presents two peaks at 124 and 18 ppm, in agreement with the conservation of the organic structure. The examination of the ^{13}C solid state NMR spectra is particularly useful in the case of the mono- and diyne structures 14 and 15. The C–Si bond of acetylenic derivatives is known to be cleaved readily under fluoride ion catalysis in methanol.[42] The ^{13}C NMR spectra of polymer 15 showed two signals at 80 and 90 ppm, consistent with two kinds of acetylenic carbon atoms. The absence of C–Si cleavage is further confirmed in the ^{29}Si NMR spectra by the absence of signals at −110 ppm attributable to a silicon atom surrounded by four oxygen atoms. Some cleavage of the C–Si bond was observed (particularly with compound 6) when the hydrolysis and polycondensation of 5 and 6 was carried out above room temperature in the presence of fluoride ion catalyst. As in the case of arylene gels, the ^{29}Si CP MAS NMR spectra of the oxide polymers 14–16 (Figure 4) presents peaks attributable to T_1, T_2, and T_3 substructures. The central peak corresponding to a T_2:C–*Si*(OR)(OSi)$_2$ substructure, with two directions of condensation, largely dominates. However, a higher degree of condensation was found for a gel arising from the hydrolysis of precursor 7 when performed in the presence of a large excess of NH_4OH. The ^{29}Si CP MAS NMR spectrum exhibited only two signals, assigned to T_2 and T_3 substructures with the same intensity. The X-ray analysis of the powdered xerogels 14–16 also showed that similar amorphous materials have been produced. Thus the gels which are produced upon hydrolysis of nonaromatic acyclic precursors with rigid or flexible structures seemed to have characteristics close to those previously obtained for arylene gels. BET (N_2) surface area was measured for polymer 16. Values as high as 977 m^2 g^{-1} was found in the case of gel 16 resulting from the NH_4OH catalyzed hydrolysis of 7, whereas surface areas between 0 and 300 m^2 g^{-1} were measured from the fluoride ion catalyzed hydrolysis.

Interestingly the silicon–carbon bond was successfully cleaved in the solid material 14. The gel was found to react with $MeOH/H_2O$ in the presence of a fluoride ion catalyst. After refluxing for several hours a suspension of the powdered gel, a complete Si–C bond cleavage was observed leading to silica gel 17 (eq 13). The elimination of acetylene was established by ^{13}C solid-state MAS NMR analysis of the new solid material 17. No signal attributable to an acetylenic carbon was detected; only a resonance due to residual methoxy groups was present. It was further confirmed in the ^{29}Si CP MAS NMR spectra. The gel 17 showed three resonances at −92, −101, and −109 ppm attributable to SiO_4 units with the substructures Q_2, Q_3, and Q_4, respectively, according to the degree of condensation about the silicon atom. The major resonance was the central peak corresponding to the substructure Q_3:*Si*(OR)(OSi)$_3$. BET (N_2) surface area were measured for both acetylenic silsesquioxane 14 and silica gel 17. The material 14 with 797 m^2 g^{-1} surface area led to 17 with 1055 m^2 g^{-1} after elimination of the organic moiety.

$$\underset{14}{\left[O_{1.5}Si{-}C{\equiv}C{-}SiO_{1.5}\right]_n} \xrightarrow[\text{catalyst: }NH_4F]{H_2O/MeOH\ /60\ °C} \underset{17}{(SiO_2)_n} \qquad (13)$$

Conclusions

The use of polysilylated organic molecules allows a general and easy preparation of mixed organic–inorganic gels. The sol–gel process is of general applicability even with precursors having labile carbon–silicon bonds. It leads to a wide variety of hybrid gels where the molecular structure of the organometallic molecule is always retained. The resulting solids are amorphous microporous materials generally presenting high surface areas. The solid morphology is probably the result of several directing factors. The nature and the structure of the precursor as well as the experimental conditions (solvent, concentration, etc.), which may influence the kinetics of the hydrolysis and the polycondensation steps, are probably important parameters. Whereas it is clear that the secondary structure or the arrangement of the chains in the polymeric material can differ according to the molecular structure of the precursor, the simple flexible or rigid-rod type structures studies do not seem to introduce large differences depending on the molecular structure. The experimental conditions used to form the gel, produced larger differences in the morphology of the resulting solid. The cleavage of the Si–C bond in the solid opens the possibility of removing the organic moiety after gel formation and to control in a different way the solid morphology. The control of the porosity of amorphous materials by the temporary introduction of a template molecule is an interesting approach. We are currently investigating gel formation from molecular precursors of various sizes which could lead to solids with defined porosity.

Experimental Section

All reactions were carried out under nitrogen by use of a vacuum line and Schlenck tube techniques. Solvents were dried and distilled before use. The reported yields refer to pure isolated materials. Melting points were determined with a Gallenkamp

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[41] Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200.

[42] Kuwajima, I.; Nakamura, E.; Hashimoto, K. *Tetrahedron* **1983**, *39*, 975.

apparatus and are uncorrected. IR spectra were recorded by using a Perkin-Elmer 1600 FTIR spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AW 80 spectrometer, ^{13}C and ^{29}Si NMR spectra both in solution and in the solid state, on BRUKER WP 250 SY and FT AM 300 apparatus. Solvents and chemical shifts (δ relative to Me_4Si) are indicated. Mass spectra were measured on a JEOL JMS-D 100 or JMS-DX 300 mass spectrometer (ionization energy 70 ev). The surface areas, porous volume, and the pore size distribution were determined by analyzing the N_2 adsorption/desorption isotherms according to the BET method using a Micromeritic apparatus. X-ray powder diffraction measurements were performed using a Seifert MZ4 apparatus. Elemental analysis were carried out by the "Service Central de Micro-Analyse du CNRS".

Chorotrimethoxysilane. This compound was prepared by mixing 18.2 mL (0.159 mol) of tetrachlorosilane, 71.16 mL (0.478 mol) of tetramethoxysilane, and 1 g of $AlCl_3$. After stirring at room temperature for one week, chlorotrimethoxysilane was distilled off the reaction mixture in vacuo and trapped in a Schlenck tube immersed in liquid nitrogen. The residue was then distilled (112 °C, 760 mmHg) to give 77.6 g (78%) of pure compound having physical characteristics identical to those previously reported.[43]

1,4-Bis(trimethoxysilyl)benzene (1). To a solution of 2.19 g (1.4×10^{-2} mol) of chlorotrimethoxysilane and 0.77 g (3.18×10^{-2} mol) of magnesium chips in 20 mL of THF, placed under nitrogen in a three-neck flask equipped with a magnetic stirrer, a condenser and an addition funnel, was added dropwise 1.5 g (6.36×10^{-3} mole) of *p*-dibromobenzene dissolved in 20 mL of THF. When 1 mL of the dibromide solution has been added, the addition was stopped and stirring was continued until a mild exothermic reaction began (usually within 20–30 min). The mixture was then cooled to 0 °C, the remaining solution was added in 20 min. After stirring at room temperature for 15 h, the resulting solution was filtered, and the THF was pumped off. The mixture was then extracted with dry pentane. The solvent was evaporated under vacuum and the residue distilled at 120 °C (0.08 mmHg) to give 1.05 g (52% yield) of a liquid which solidified when cooling at room temperature: mp 52–54 °C. ^{1}H NMR (CCl_4, δ) 3.56 (18 H, s), 7.58 (4 H, s); ^{13}C NMR ($CDCl_3$, δ), 51.19, 132.45, 134.45; ^{29}Si NMR ($CDCl_3$, δ) –54.92; mass spectrum (rel intensity, assignment) *m/e* 318 (3, M^+), 287 (7, M^+ – MeO), 257 (2, M^+ – 2MeO + H), 227 (11, M^+ – 3MeO + 2H), 197 (15, M^+ – 4MeO), 167 (23, M^+ – 5MeO + 4H), 136 (16, M^+ – 6MeO + 4H), 121 (97, Si $(OMe)_3$), 91 (100, $HSi(OMe)_2$). Anal. Calcd for $C_{12}H_{22}O_6Si_2$: C, 45.26; H, 6.96; Si, 17.64. Found: C, 44.88; H, 6.91; Si, 17.41.

Bis(4-(trimethoxysilyl)phenyl)dimethoxysilane (3). This compound was obtained as a byproduct of the reaction described above and distilled at 190–200 °C, 0.3 mmHg, to give 0.31 g (20% yield) of pure compound. ^{1}H NMR (CCl_4, δ) 3.54 (24 H, s), 7.58 (8 H, s); ^{13}C NMR ($CDCl_3$, δ) 51.22, 51.35, 131.06, 134.41, 134.54, 135.12; ^{29}Si NMR ($CDCl_3$, δ) –30.00, –55.10. Anal. Calcd for $C_{20}H_{32}O_8Si_3$: C, 49.56; H, 6.65. Found: C, 49.88; H, 6.71.

1,4-Bis(triethoxysilyl)benzene (8). This compound was prepared as described for 1 from 29.6 g (0.149 mol) of chlorotriethoxysilane, 16 g (6.78×10^{-2} mol) of *p*-dibromobenzene and 8.24 g (0.34 mol) of magnesium chips. Distillation of the residue (165 °C, 1.5 mmHg) afforded 12.04 g (44% yield) of compound 8. ^{1}H NMR (CCl_4, δ) 1.15 (18 H, t), 3.75 (12 H, q), 7.5 (4 H, s); ^{13}C NMR ($CDCl_3$, δ) 18.56, 59.11, 133.55, 134.39; ^{29}Si NMR ($CDCl_3$, δ) –57.93. Anal. Calcd for $C_{18}H_{34}O_6Si_2$: C, 53.65; H, 8.45. Found: C, 54.58; H, 8.57.

2,5-Bis(trimethoxysilyl)thiophene (2). This compound was prepared according to the procedure described for 1, from 13.77 g (8.8×10^{-2} mol) of chlorotrimethoxysilane, 9.7 g (4×10^{-2} mol) of 2,5-dibromothiophene, and 3.9 g (0.16 mol) of magnesium chips. After usual workup, 8.3 g (64%) yield of 2 were obtained by distillation under vacuum (123 °C, 0.1 mmHg). ^{1}H NMR (CCl_4, δ) 3.55 (18 H, s), 7.42 (2 H, s); ^{13}C NMR ($CDCl_3$, δ) 51.29, 135.40, 138.13; ^{29}Si NMR ($CDCl_3$, δ) –58.11. Anal. Calcd for $C_{10}H_{20}O_6Si_2S$: C, 35.41; H, 6.21; Si, 17.31. Found: C, 35.01; H, 6.08; Si, 17.42.

Bis[2-(5-(trimethoxysilyl)thienyl)]dimethoxysilane (9). As for compound 2, compound 9 was obtained as a byproduct of the reaction described above and was isolated by distillation (192 °C, 0.2 mmHg) to give 2.08 g (21% yield) of pure **9**. ^{1}H NMR (CCl_4, δ) 3.53 (18 H, s), 3.58 (6 H, s), 7.44 (4 H, s); ^{13}C NMR ($CDCl_3$, δ) 51.39, 51.66, 135.78, 138.19, 138.41, 138.59; ^{29}Si NMR ($CDCl_3$, δ) –37.00, –58.18.

1,3,5-Tris(trimethoxysilyl)benzene (4). As previously, 4 was obtained using 33.6 g (0.215 mol) of chlorotrimethoxysilane, 20.46 g (6.5×10^{-2} mol) of 1,3,5-tribromobenzene, and 9.5 g (0.39 mol) of magnesium chips. Distillation of the residue (160 °C, 0.1 mmHg) afforded 8.83 g (31% yield) of compound 4. ^{1}H NMR (CCl_4, δ) 3.59 (27 H, s), 7.82 (3 H, s); ^{13}C NMR ($CDCl_3$, δ) 51.18, 128.8, 143.6; ^{29}Si NMR ($CDCl_3$, δ) –53.92. Anal. Calcd for $C_{15}H_330O_9Si_3$: C, 41.07; H, 6.89. Found: C, 39.52; H, 6.74.

Bis(trimethoxysilyl)acetylene (5). This compound was prepared by reaction of dilithioacetylene[31] with chlorotrimethoxysilane. To a solution of 120 mL of *n*-BuLi (2.5 M in hexane) in 50 mL of THF and 25 mL of ether was added dropwise at –78 °C a solution of 13.15 g (0.1 mol) of trichloroethylene in 25 mL of ether. A white precipitate formed, and the mixture was stirred at room temperature for 2 h. It was cooled to 0 °C, and 40 g (0.26 mol) of chlorotrimethoxysilane was rapidly added. The reaction mixture was then allowed to warm to room temperature and then stirred for 5 h. The resulting solution was filtered, and the salts extracted with pentane. The solvents and unreacted chlorotrimethoxysilane was removed by distillation up to 110 °C, 760 mmHg. Then distillation under reduced pressure of the residue (80 °C, 0.1 mmHg) afforded 6.7 g (25% yield) of compound **5**. ^{1}H NMR (CCl_4, δ) 3.53 (s); ^{13}C NMR ($CDCl_3$, δ) 51.12, 103.22; ^{29}Si NMR ($CDCl_3$, δ) –79.34. Anal. Calcd for $C_8H_{18}O_6Si_2$: C, 36.07; H, 6.81. Found: C, 37.26; H, 6.79.

1,4-Bis(trimethoxysilyl)-1,3-butadiyne (6). Compound **6** was prepared according to a literature procedure.[32]

1,4-Bis(trichlorosilyl)but-2-ene. This compound was prepared according to a procedure described by Miehling.[34] An ethereal solution (200 mL) containing 42.26 mL (0.4 mol) of 1,4-dichlorobut-2-ene and 84.8 mL (0.84 mol) of trichlorosilane was added dropwise to a mixture of triethylamine (0.85 mol) and cuprous chloride (0.02 mol) in 500 mL of ether cooled to 0 °C. After the addition was complete, the solution was stirred at 35 °C for 2 h. The mixture was then filtered, the solvent evaporated in vacuo, and 101.4 g (79% yield) of 1,4-bis(trichlorosilyl)but-2-ene isolated by distillation (87 °C, 4 mmHg). ^{1}H NMR (CCl_4, δ) 2.30 (4 H, d), 5.52 (2 H, t). Mass spectrum (rel intensity, assignment) *m/e* 320(4, M^+), 188 (61, M^+ – $SiCl_3$), 54(68, M^+ – $2SiCl_3$), 153 (15, M^+ – $SiCl_4$), 223 (4, M^+ – $SiCl_2$).

1,4-Bis(trimethoxysilyl)but-2-ene (7). To a solution of 177 mL (1.27 mol) of Et_3N and 63 mL (1.56 mol) of methanol in 1.5 L of ether was added dropwise an etheral solution of 63.4 g (0.195 mol) of 1,4-bis(trichlorosilyl)but-2-ene. After the addition was complete, the mixture was stirred at 35 °C for 7 h and then filtered. The solvent was evaporated in vacuo and distillation of the residue (108 °C/0.5 mmHg) afforded 44.7 g (77% yield) of compound 7. ^{1}H NMR (CCl_4, δ) 1.54 (4 H, d), 3.51 (18 H, s); 5.33 (2 H, t); ^{13}C NMR ($CDCl_3$, δ) 15.43, 50.67, 123.82; ^{29}Si NMR ($CDCl_3$, δ) –46.20. Anal. Calcd for $C_{10}H_{24}O_6Si_2$: C, 40.51; H, 8.16; Si, 18.95. Found: C, 41.00; H, 8.27; Si, 18.10

Hydrolysis and Polycondensation of 1,4-Bis(trimethoxysilyl)benzene (1). The preparation of the gels were carried out according to the following general procedure. The solvents, concentrations of the reagents, and catalysts are indicated in Table I. To 1.76 g (5.55 10^{-3} mol) of 1,4-bis(trimethoxysilyl)benzene in methanol or THF were added 3 mol equiv of water and the catalyst. The homogeneous solution was allowed to stand at 20 °C. Transparent gels formed in most cases within several hours (cf. Table I). After curing at 20 °C for 48 h, the gel was powdered. After air drying, the solid was collected, washed with ether and then dried in vacuo at 150 °C yielding 1.1 g of a white powder (quantitative yield based on $C_6H_4SiO_3$). Elemental analysis of the various gels gave $30.63 \le C \le 36.01$; $3.75 \le H \le 4.10$; $22.80 \le Si \le 24.60$; carbon to silicon ratio calcd for $C_6H_4SiO_3$ C/Si = 3, found $3 \le C/Si \le 3.5$. Spectroscopic analysis of the various samples obtained showed similar characteristics as follows: FT IR (KBr): 2845, 3455 cm^{-1}. ^{13}C CP MAS NMR: 50, 133 ppm. ^{29}Si CP MAS NMR: –59, –68, –76 ppm. Some representative spectra are given in Figure 2. In most cases similar intensities of the signals were observed; an estimated degree of condensation

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(43) Peppard, D. F.; Brown, W. G.; Johnson, W. C. *J. Am. Chem. Soc.* **1946**, *68*, 70.

is given in Table I. The gels also showed similar X-ray powder diffraction pattern with no crystallinity. Two broad bands with *d* spacings of 3.7–3.9 and 7.2–8.0 Å were observed whatever the reaction conditions used for gel formation. Surface areas as measured using the N_2 BET technique are listed in Table I.

Hydrolysis and Polycondensation of Bis(4-(trimethoxysilyl)phenyl)dimethoxysilane (3). The gels were obtained as above using 3, 1, and 0.3 M MeOH solutions of 3 (1.61 g, 3.33×10^{-3} mol) by addition of 3.33×10^{-6} mol (1‰) of NH_4F and 10^{-2} mol (3 equiv) of water. Gelation occurred respectively after 1, 12, and 180 mm and the gels were treated as described above; 1.2 g of a colorless solid was collected. All samples showed identical spectroscopic characteristics: FT IR (KBr): 2845, 3455 cm^{-1}; ^{13}C CP MAS NMR 49.8, 133.6 ppm; ^{29}Si CP MAS NMR −29.3, −37.7, −46.1, −62.5, −70.8 ppm. X-ray powder diffraction: two broad bands, *d* spacing 3.8 and 7.0 Å.

Hydrolysis and Polycondensation of 2,5-Bis(trimethoxysilyl)thiophene (2). As above using 3, 1, and 0.3 M MeOH solutions of 2,5-bis(trimethoxysilyl)thiophene (2, 1.74 g, 5.38×10^{-3} mol) and addition of 5.38×10^{-6} mol (1‰) of NH_4F and 1.61×10^{-2} mole (3 equiv) of water, transparent gels formed in respectively 0.1 min, 15 min, and 2 days. The gels obtained were allowed to stand at room temperature for 48 h. After washing with ether and drying under vacuum at 150 °C, about 1 g of a colorless solid was collected. All samples showed identical spectroscopic characteristics: FT IR (KBr) 2845, 3455 cm^{-1}; ^{13}C CP MAS NMR 51.4, 138.2 ppm; ^{29}Si CP MAS NMR −64.2, −72.6, −84.7 ppm. Analysis: C, 26.87; H, 2.99; Si, 25.16; carbon to silicon ratio calcd for $C_4H_2O_3Si_2$ C/Si = 2, found C/Si = 2.5. X-ray powder diffraction showed two very broad bands, with *d* spacings of 4.0 and 7.6 Å. The N_2 BET surface area was 685 m^2 g^{-1}.

The same hydrolysis and polycondensation reaction conducted using a 1 M THF solution of 2 led to a transparent gel after 15 min. The above workup gave 1 g of xerogel 11 with spectroscopic characteristics identical to those obtained in the case of MeOH solvent. X-ray powder diffraction showed two very broad bands, with *d* spacings of 4.0 and 8.8 Å. The N_2 BET surface area was 19 m^2 g^{-1}.

Hydrolysis and Polycondensation of 1,3,5-Tris(trimethoxysilyl)benzene (4). As above using 3, 1, and 0.3 M MeOH solutions of 1,3,5-tris(trimethoxysilyl)benzene (4, 1.90 g, 4.33×10^{-3} mol) and addition of 4.33×10^{-6} mol (1‰) of NH_4F and 1.9×10^{-2} mol (4.5 equiv) of water, transparent gels formed in respectively 0.1 min, 5 min and 1 day. The gels obtained were allowed to stand at room temperature for 48 h. After washing with ether and drying under vacuum at 150 °C, about 1 g of a colorless solid was collected. All samples showed identical spectroscopic characteristics: FT IR (KBfr) 2845, 3455 cm^{-1}; ^{13}C CP MAS NMR 50.2, 130.5, 142.6 ppm; ^{29}Si CP MAS NMR −54.7, −62.6; −71.0 ppm. Anal. Calcd: C, 26.10; H, 3.72; Si, 26.58; carbon to silicon ratio calcd for $C_6H_3O_{4.5}Si_3$:C/Si = 2, found C/Si = 2.3. X-ray powder diffraction: one broad band, *d* spacing 4.3–5.0 Å. N_2 BET surface area of the xerogel obtained by gelation in a 1 M MeOH solution: 293 m^2 g^{-1}.

Hydrolysis and Polycondensation of Bis(trimethoxysilyl)acetylene (5). Following the above procedure, 9×10^{-6} mol (1‰) of NH_4F and 2.7×10^{-2} mol (3 equiv) of water were added to a solution of 2.4 g (9×10^{-3} mol) of 5 in 9 mL of MeOH. Gelation occured within 10 h, and the gel was allowed to stand for 48 h. The solid was then powdered and dried in vacuo at room temperature; 1.2 g of colorless powder was collected. FT IR (KBr) 2845, 3455 cm^{-1}; ^{13}C CP MAS NMR 52.5, 105.0 ppm; ^{29}Si CP MAS NMR −80.7, −90.8, −99.8 ppm. Anal. Calcd: C, 27.86; Si, 30.87; carbon to silicon ratio calcd for $C_2O_3Si_2$ C/Si = 1, found C/Si = 2.1. X-ray powder diffraction: one broad band, *d* spacing 4.8 Å. The N_2 BET surface area of the xerogel obtained by gelation in a 1 molar MeOH solution: 797 m^2 g^{-1}. A gel with similar characteristics was produced in the absence of catalyst for the hydrolysis/polycondensation step.

Cleavage of the Si–C Bond in Gel 14. In a flask equipped with a magnetic stirrer and a condenser were placed 2.5 g of the powdered gel 14 prepared above, 7.8 mL (3.9×10^{-4} mol) of a 0.025 M solution of NH_4F, 20 mL (1.1 mol) of water, and 7.5 mL of MeOH. After stirring for 36 h at 64 °C, the mixture was filtered, and the solid obtained was washed with ether and then dried under vacuum at room temperature for 24 h to afford 1.7 g of a colorless powder. ^{13}C CP MAS NMR 50.7 ppm; ^{29}Si CP MAS NMR −92.0, −101.0, −109.3 ppm. Anal. Found: C, 2.93; Si, 40.03; O, 49.28%. The N_2 BET surface area of the xerogel 17 obtained was 1055 m^2 g^{-1}.

Hydrolysis of Polycondensation of 1,4-Bis(trimethoxysilyl)-1,3-butadiyne (6). As described above for compound 5, the reaction was carried out using 2.87 g (9.87×10^{-3} mole) of 6, 9.9 mL of MeOH, 9.87×10^{-6} mol (1‰) of NH_4F, and 2.96×10^{-2} mol (3 equiv) of water. The gel, which formed after 10 min at 20 °C was allowed to stand for 48 h. It was then powdered, washed, and dried in vacuo, yielding 1.5 g of white powder. FT IR (KBr): 2845, 3455, 2092 cm^{-1}. A weak band at 2202 cm^{-1} $[\nu(C\equiv C{-}H)]$ indicative of some Si–C bond cleavage was also present in this case. ^{13}C CP MAS NMR 52.4, 79.4, 87.8 ppm; ^{29}Si CP MAS NMR 80.7, −89.9, −99.5 ppm. Anal. Found: C, 26.80; H, 1.48; Si, 28.31. Carbon to silicon ratio calcd for $C_4O_3Si_2$ C/Si = 2, found C/Si = 2.2. X-ray powder diffraction: two broad bands, *d* spacing 3.9 and 8.0 Å. Using a 0.3 M solution of 6 and in the absence of catalyst for the hydrolysis/polycondensation step, a gel with spectroscopic characteristics identical to the ones listed above was produced. No Si–C bond cleavage was noted from the IR and NMR spectra in this case.

Hydrolysis and Polycondensation of 1,4-Bis(trimethoxysilyl)but-2-ene (7). As above using 3 and 1 M MeOH solutions of 1,4-bis(trimethoxysilyl)but-2-ene (7) (1.88 g, 6.33×10^{-3} mol) and addition of 6.33×10^{-6} mol (0.1%) of NH_4F and 1.9×10^{-2} mol (3 equiv) of water, transparent gels formed in respectively 1 h and 10 days. The gels obtained were allowed to stand at room temperature for 48 h. After washing with ether and drying under vacuum at 150 °C, about 1 g of a colorless solid was collected. Both samples showed identical spectroscopic characteristics: FT IR (KBr) 2845, 3455 cm^{-1}; ^{13}C CP MAS NMR 18.3, 49.8, 124.2 ppm; ^{29}Si CP MAS NMR −44.8, −53.0, −61.6, −70.8 ppm. Anal. Calcd: C, 25.22; H, 4.62; Si, 28.42. Found: C, 24.90; H, 4.17; Si, 26.40; carbon to silicon ratio calcd for $C_4H_6O_3Si_2$ C/Si = 2, found C/Si = 2.1–2.2. X-ray powder diffraction: two broad bands, *d* spacing 4.0 and 7.5 Å. N_2 BET measurements revealed no surface area for the xerogel obtained by gelation in a 1 M MeOH solution, and 300 m^2 g^{-1} when a 3 M MeOH solution was used. Using 0.3 M MeOH solution of 7, in the presence of 2.6 mol equiv of NH_4OH, the above procedure led to 1 g of xerogel. FT IR (KBr) 2845, 3455 cm^{-1}; ^{13}C CP MAS NMR 18.5, 48.9, 123.9 ppm; ^{29}Si CP MAS NMR −61.4, −70.7 ppm. Anal. Found: C, 29.90; H, 4.22; Si, 30.60; Carbon to silicon ratio calcd for $C_4H_6O_3Si_2$ C/Si = 2, found C/Si = 2.3. X-ray powder diffraction: two broad bands, *d* spacing 4.0 and 9.7 Å. N_2 BET surface area 977 m^2 g^{-1}.

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