Hybrid Xerogels from Dendrimers and Arborols

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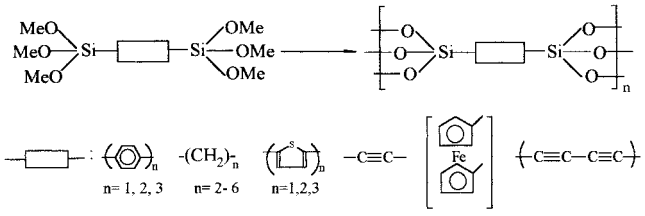
Dendrimers and arborols with a carbosilane core have been prepared by a divergent hydrosilylation/vinylation reaction sequence followed by methoxylation of the silicon chloride end groups. Dendrimers with respectively 12 [first generation (1G)] and 36 [second generation (2G)] methoxysilane groups and arborols with octadecyl and phenyl group of first and second generation have been prepared. They were characterized by elemental analyses and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. Polycondensation by a sol−gel process yields the hybrid materials. 2G dendrimers formed porous materials while nonporous materials were obtained from 2G arborols containing the octadecyl group. The precursor of the second generation containing the phenyl group formed different gels depending on the solvent used for the polycondensation process. Nevertheless, no gel was obtained for dendrimers and arborols of the first generation. The solid-state ^{29}Si NMR spectroscopy was used to evaluate the integrity of the material and to determine the degree of polycondensation in the network material. Oxidative thermal treatment was performed in order to remove the organic part of the hybrids. The texture of the solid was detremined by BET measurement for xerogel before and after oxidation. Porous silica were obtained with similar porosity and pore size diameter from all the precursors.

I. Introduction

Polyphasic[1−3] and monophasic[4−7] hybrid organic−inorganic materials can exhibit both properties associated with the organic moiety and with the inorganic framework. Their preparation can be achieved by sol−gel hydrolysis of molecular structures containing both nonhydrolyzable Si−C bonds and hydrolyzable $Si(OR)_3$ groups. The mild conditions used for the polycondensation step have pointed out the potential of this process, which allowed the formation of materials with various organic groups grafted with hydrolyzable alkoxysilane, as presented on Scheme 1.

For example, hybrid materials were prepared from rigid molecules such as the acetylenic moiety,[8] thiophene,[9,10] polyphenylene,[9−12] and flexible structures

Scheme 1. Hybrid Materials from $(RO)_3SiYSi(OR)_3$ Precursors



such as alkyl groups.[13] Rigid structures were found to form gels with high specific surface areas, whereas nonporous materials were formed when using long alkyl groups.[14]

Using dendrimers of the first generation end-grafted with SiOEt or $SiOCH_2CF_3$ groups, star gels with mechanical properties were prepared by Michalczyk et al.[15−21] Dendrimers have specific chemical and physical properties,[22−25] and among them, polycarbosilane den-

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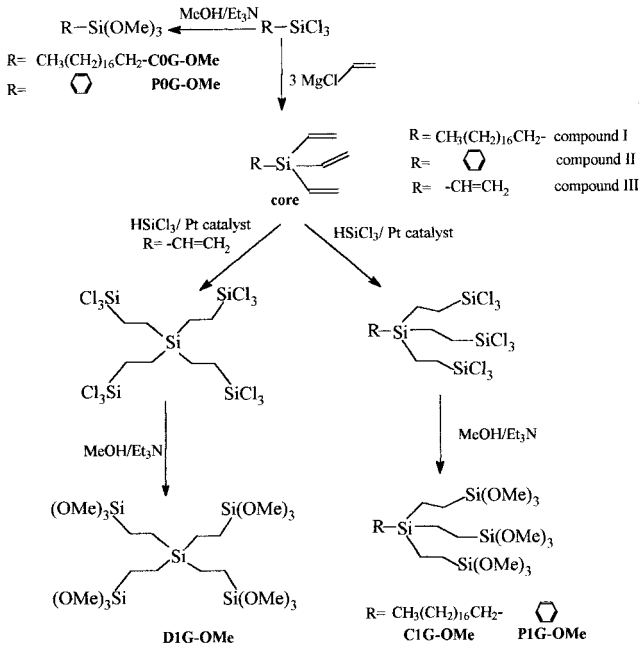
drimers with regular structure can be prepared and functionalized in high yield.[26,27] They were shown to be completely lipophilic due to the nonpolar nature of the Si−C bond and to have excellent thermal and chemical stability due to the thermodynamic stability of the Si−C bond (316 kJ/mol).

Arborols are another class of interesting compounds similar to dendrimers, and their study arouses the following questions: will arborol compounds react like dendrimers, will the use of arborols allow the introduction of a long hydrophobic alkyl chain in a gel; will it be possible to obtain a well-defined porosity by removing of the organic part; what will the differences be when using precursors of increasing generation? We investigate the preparation and the gel precursor properties of phenyl and octadecy arborols of first generation (G1) and second generation (G2) end-grafted with a Si-$(OMe)_3$ hydrolyzable group. Depending on the size of the group attached to the hydrolyzable head of the arborol, completely different behavior might be expected, and they can be seen as a sophisticated class of the alkylsilsesquioxanes that where reviewed recently by Baney et al.[28] In this paper, we report the preparation of new arborol compounds; dendrimers were also prepared and compared to arborols since their structure present some similarities. We were particularly attracted by the possibility of producing porous silica by removing of the organic part of the precursors and looking at their templating effect. Synthesis, characterization, and polycondensation by sol−gel process of G1 and G2 arborol and dendrimer precursors, as well as the starting compounds (G0), are reported along with the characterization of the texture of the solids (surface, porosity), before and after thermal oxidation.

II. Results and Discussion

II. 1. Synthesis of Precursors. The methodology described by Seyferth et al.[29] was used to prepare carbosilane arborols and dendrimers. The starting materials were octadecyltrichlorosilane, phenyltrichlorosilane, and vinyltrichlorosilane. An alternative vinylation of the Si−Cl bonds, followed by a Pt-catalyzed hydrosilylation of the vinyl groups with $HSiCl_3$, was used to obtain the arborolic structure. The final reaction is the methanolysis of Si−Cl bonds with MeOH/NEt_3 (Scheme 2). An alternative method for the preparation of these compounds was the hydrosilylation of the corresponding vinyl precursors directly with HSi-$(OMe)_3$ using Karstedt catalyst. However, this method

Scheme 2. Schematic Representation of the Preparation of Precursors of the First Generation



was not successful and led to a mixture of products, as shown by ^1H and ^{13}C NMR data. Similar results were found by Michalczyk et al. in the syntheses of cyclo-$(CH_3(CH_2CH_2Si(OCH_2CH_3)_3)_4SiO)_4$.[17] Octadecyltrivinylsilane (**I**) was prepared by vinylation of the corresponding chlorosilane, and the phenyltrivinylsilane[30] (**II**) and the tetravinylsilane[31] (**III**) were prepared according to literature procedures.

First Generation. Hydrosilylation reactions of **I**, **II**, and **III** were performed with an excess of $HSiCl_3$ using the usual Pt catalysts such as $H_2PtCl_6{\cdot}6H_2O$ in 2-propanol (Speier's catalyst),[32] Pt/C, or Karstedt platinum catalyst[33] (Scheme 2). All these catalysts allowed the complete hydrosilylation of vinyl groups, as was observed in the NMR spectrum; however, when $H_2PtCl_6{\cdot}6H_2O$ was used, a mixture of the α- and β-adduct was obtained according to ^{29}Si and ^1H NMR spectroscopies. Karstedt platinum catalyst or Pt/C were used to lead to **C1G-Cl** and **D1G-Cl**, the corresponding β-adduct. However, pure β-adduct was not obtained for **P1G-Cl** whatever the catalyst used, and the formation of a small amount of α-adduct (5−10%) was observed according to NMR data. Such branching due to Markovnikov addition during hydrosilylation was also observed by Michalczyk et al.[19] In this reaction, other impurities were formed and were assumed to be due to redistribution reactions occurring in the presence of transition metals.[34] Purification of the products was limited to a treatment with black carbon powder. Methanolysis of Si−Cl groups by methanol was performed in hexane at 0−5 °C with triethylamine as hydrochloric acid trap (see

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Scheme 3. Schematic Representation of the Preparation of Precursors of the Second Generation

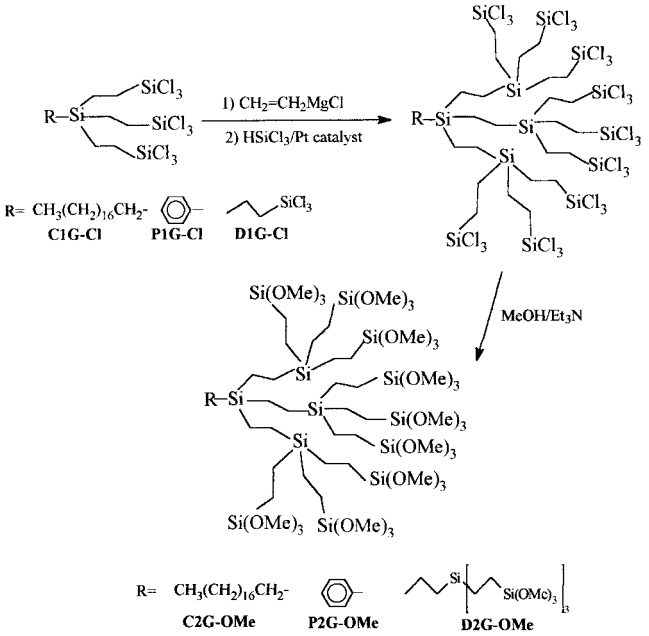


Table 1. ^{29}Si NMR Chemical Shifts for the Dendrimers and Arborols Alkoxysilane of the Second Generation

	^{29}Si NMR (ppm)		
precursor	Si_a	Si_b	Si_c
C2G-OMe	−41.92	9.79	7.35
P2G-OMe	−41.98	9.98	2.63
D2G-OMe	−42.04	9.77	8.76

Scheme 2). The corresponding methoxylated compounds, **C1G-OMe**, **P1G-OMe** and **D1G-OMe**, were obtained in quantitative yield as light and slightly yellow oils. For **C1G-OMe** and **D1G-OMe**, ^{29}Si NMR data showed two signals corresponding to the silicon atom at the periphery of the molecule ($Si(OCH_3)_3$) and to the silicon atom at the core of the molecule. For **P1G-OMe,** additional signals were observed due to the presence of α-adduct, as discussed previously. Elemental analyses are in good agreement with the spectroscopic data, and the presence of the Si−OMe groups was confirmed by ^{1}H and ^{13}C NMR.

Second Generation. The preparation of the arborols and the dendrimer of the second generation is presented in Scheme 3. Vinylation of **C1G-Cl**, **P1G-Cl**, and **D1G-Cl** was performed with a large excess (50%) of vinyl Grignard reagent in THF at reflux for 24 h (Scheme 3), giving vinylated compounds **C1G-Vi**, **P1G-Vi**, and **D1G-Vi**.

Elemental analyses and NMR data indicate that the vinyl groups were quantitatively introduced, and their hydrosilylation with an excess of $HSiCl_3$ in hexane catalyzed by Karstedt's platinum catalyst or Pt/C leads to the preparation of **P2G-Cl, C2G-Cl**, and **D2G-Cl**, respectively. The ^{29}Si and ^{13}C NMR data showed that only β-adducts were formed in this step. After the methanolysis reaction, **C2G-OMe**, **P2G-OMe**, and **D2G-OMe** were obtained in quantitative yields. Only three signals were observed in the ^{29}Si NMR spectra (Table 1) of **C2G-OMe** and **D2G-OMe**, corresponding to the three types of silicon atoms of the molecule, as is presented in Scheme 4. For **P2G-OMe**, additional signals were attributed to the presence of the remaining α-adduct formed at the first hydrosilylation step, which represent less than 2%. The elemental analyses performed with the alkoxides of the second generation were in good agreement with the calculated values.

Scheme 4. Representation of the Different Types of Silicon Atom in the Precursors

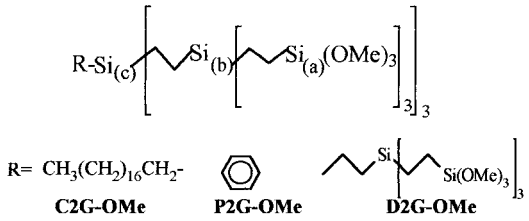


Table 2. Time of Formation of the Gels (Gellation Time) of Precursors C2G-OMe, P2G-OMe, and D2G-OMe

precursor	solvent	precursor concn, (mol/L)	catalyst concn (mol/L)	gellation time (h)
C2G-OMe	THF	0.1	0.027	36
C2G-OMe	EtOH	0.1	0.027	26
C2G-OMe	acetone	0.1	0.027	72
P2G-OMe	THF	0.1	0.027	48
P2G-OMe	EtOH	0.1	0.027	24
P2G-OMe	acetone	0.1	0.027	120
D2G-OMe	THF	0.07	0.92	2
D2G-OMe	EtOH	0.07	0.92	0.5
D2G-OMe	acetone	0.07	0.92	12

II. 2. Preparation of Hybrid Organic−Inorganic Gels and Xerogels. The sol−gel polycondensation of all the precursors was carried out at room temperature using a stoechiometric amount of water (1/2 $H_2O/SiOCH_3$) in different solvents, generally used for this type of studies: THF and acetone as apolar, aprotic solvents, ethanol as a polar, protic solvent. All the precursors presented a low solubility in these solvents, specially the precursors of the second generation (methanol was excluded due to the lack of solubility of G2 precursors). The highest concentration of Si−OMe functions allowed in ethanol was 2.9 M; therefore, it was used for all the precursors. Thus, concentrations of precursor as low as 0.1 and 0.07 M were respectively used for arborols and dendrimers of the second generation, due to their high molecular weight (see Table 2). The condensation reactions were catalyzed by NH_3, because, in the absence of any catalyst, the formation of gels does not occurs within 6 months for all the precursors. The concentration of NH_3 used was 1 mol % with respect to the concentration of SiOMe groups in the precursor (see Table 2). Under these conditions, the starting compounds **C0G-OMe** and **P0G-OMe** did not form gels. For **C0G-OMe**, a white solid was obtained; the ^{1}H, ^{13}C, and ^{29}Si NMR data showed the presence of the substructures T^0, T^1, T^2 and T^3, corresponding to an incomplete hydrolysis, yielding a mixture of incompletely condensed silsesquioxane and siloxane structures. This is similar to the well-known hydrolysis of $R'Si(OR)_3$ compounds which depends on the size of the R′ group, a bulky group leading to the formation of cage or low molecular weight products.[28,35] The precursors of the first generation **C1G-OMe**, **P1G-OMe**, and **D1G-OMe** did not form gels or solids under these conditions, but ^{1}H NMR analysis of the soluble material indicates

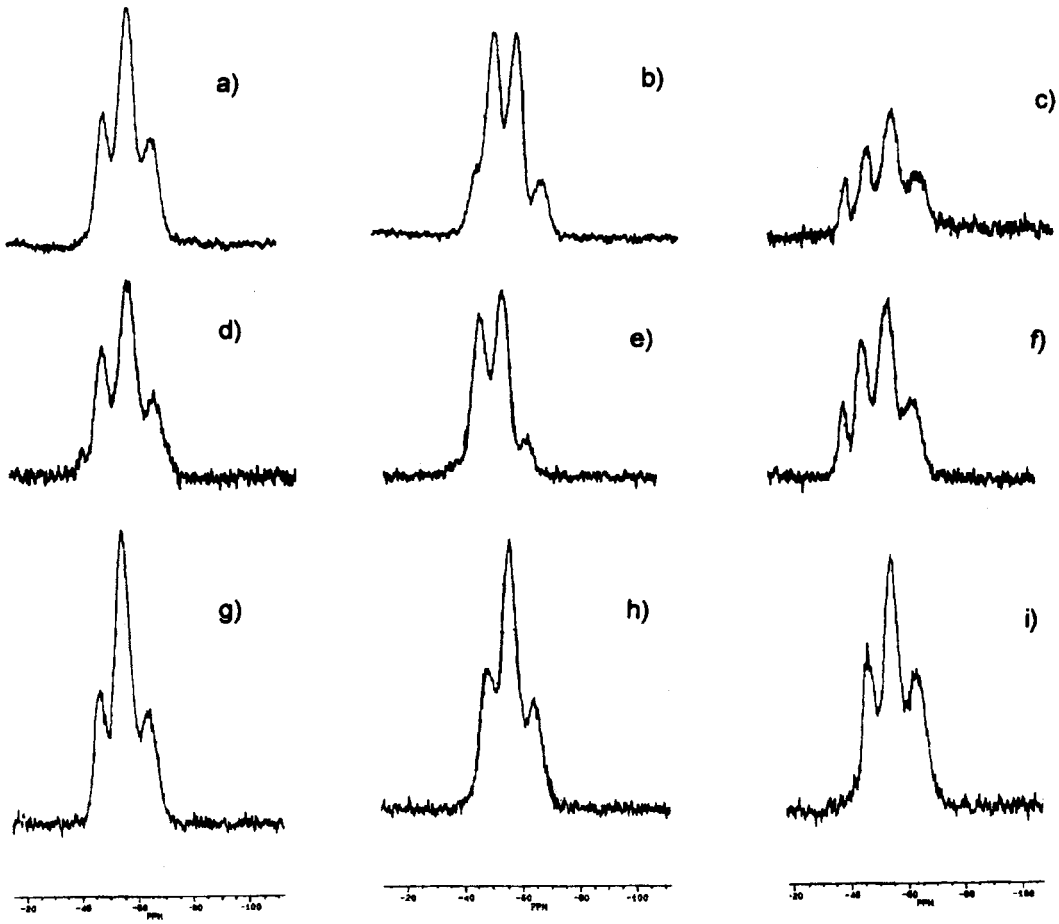
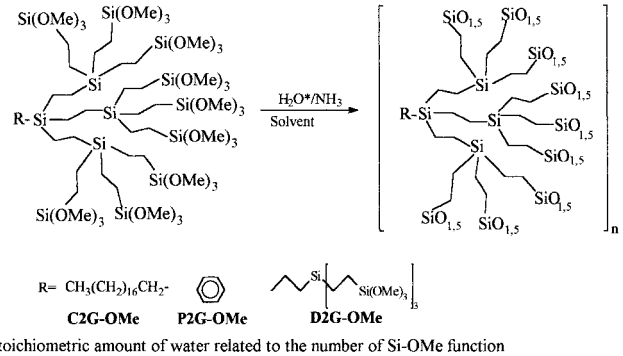


Figure 1. ^{29}Si CP MAS-NMR spectra of xerogels of precursors of second generation (δ, ppm): (a) **C2G-OMe** in THF, (b) **C2G-OMe** in EtOH, (c) **C2G-OMe** in acetone, (d) **P2G-OMe** in THF, (e) **P2G-OMe** in EtOH, (f) **P2G-OMe** in acetone, (g) **D2G-OMe** in THF, (h) **D2G-OMe** in EtOH, (i) **D2G-OMe** in acetone.

that 30% of the SiOMe groups have disappeared. Thus, partial hydrolysis occurs but does not result in the formation of a gel. One possible interpretation of the present result is the occurrence of intramolecular hydrolysis, as will be discuss below for the precursors of the second generation. It must be mentioned that Michalczyk et al. have reported that **D1G-OEt** gels in 8 h in an uncatalyzed H_2O/EtOH mixture at pH 7, albeit with residual T^0 units corresponding to a low degree of condensation.[20] This is rather surprising and one might expect that without catalyst SiOMe would hydrolyze faster than SiOEt.[36,37]

For the precursors of the second generation **C2G-OMe**, **P2G-OMe**, **D2G-OMe**, different times for gel formation were measured depending on the experimental conditions used, such as solvent and catalyst concentration. The ideal equation corresponding to the polycondensation of the precursors is represented in Scheme 5. The formation of the gels was faster in ethanol than in THF or acetone (Table 2) for all precursors. The precursors **C2G-OMe** and **P2G-OMe** formed gels within a period of time of 30 min to 5 days. **D2G-OMe** required a much higher catalyst concentration in order to obtain a gel in 10 days (a SiOMe/NH_3 ratio equal to 3 was used).

Scheme 5. Hydrolysis and Polycondensation of Precursors of the Second Generation



*stoichiometric amount of water related to the number of Si-OMe function

All gels were allowed to age at room temperature for 7 days. After washing with the corresponding solvent, the xerogels were dried for 24 h at 100 °C under 0.1 mmHg. The resulting materials were insoluble, brittle, and were ground to powders.

The IR analyses of the hybrids revealed the absorption bands of the different structures: ν(O−H), 3444 cm^{-1}; ν(Si−O), 905 cm^{-1}; ν(Si−CH_2), 1261 cm^{-1}; ν(C−H), 2922, 2856, and 1466 cm^{-1}; ν(Si−O−Si) and ν(Si−CH_2−CH_2−Si), broad, from 1065 to 1150 cm^{-1}.[38] A qualitative evaluation of the degree of condensation of the network polysiloxanes (Figure 1) was obtained with

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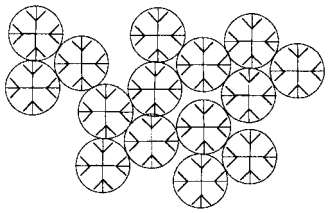
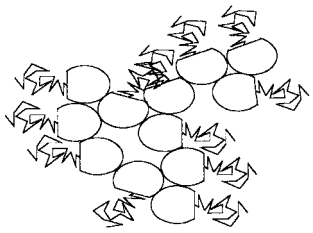
Scheme 6. Representation of the Association of Dendrimers and Arborols in the Xerogels



Dendrimer Xerogel



Arborol Xerogel

^{29}Si CP MAS NMR spectroscopic analyses of the materials.[39] Broad signals centered at 2 and 9 ppm were attributed to the silicon atom of the core of the molecules. These chemical shifts were similar to those measured for the corresponding precursors. No signals in the range of −100 to −110 ppm, indicating the presence of Q^n substructures, were observed, and this fact confirmed that Si−C bonds were not cleaved during the polycondensation process.

For the xerogels prepared using arborols **C2G-OMe** and **P2G-OMe**, T^0, T^1, T^2, and T^3 substructures were observed between −40 and −80 ppm, by ^{29}Si NMR spectroscopy. For xerogels formed in ethanol or acetone, the presence of T^0 units and an intense signal for T^1 units indicated a rather low degree of polycondensation. On the contrary, the xerogels prepared in THF exhibited a major signal corresponding to the substructure T^2, and no T^0 unit was observed (Figure 1). However, for the xerogels prepared from dendrimers, **D2G-OMe**, the degree of polycondensation is similar whatever the solvent used: the ratios between the T^1, T^2 and T^3 substructures remain almost identical, with a majority of T^2 and no T^0 units observed. Therefore, arborols and dendrimers present different behaviors toward base-catalyzed hydrolysis. It can be assumed that the variation of the degree of polycondensation for arborols depends at least on two kinds of interactions: those between the solvent and the lipophilic parts of the precursors (tail and $SiCH_2CH_2Si$ arms), and those between the solvent and the species evolved during the hydrolysis, silanol and silanolate (as previously reported).[36] Such interactions might emphasized or diminish the sterical hindrance effect of these precursor. Indeed, they can be seen as a sphere with a tail; the head-to-head junction of some of them can lead to $-Si(OMe)_3$ groups that are not accessible to reagent because they are surrounded by bulky molecules such as those depicted in Scheme 6.

It must be pointed out that the formation of the Si−O−Si network can occur by either intermolecular or intermolecular process, due to the structure of the compounds (Scheme 7). Such phenomenon was clearly established using K^+IDS mass spectroscopy.[17,40] These two possibilities are not equivalent, as the intramolecular polycondensation cannot provide cross-linking between the molecules necessary for the formation of the gel. The preponderance of the intramolecular process for the G1 precursor is a possible explanation for the lack of formation of gels despite the level of polycondensation.

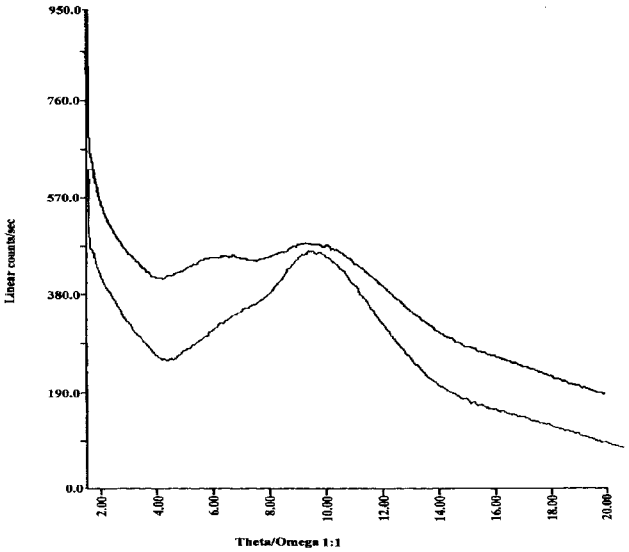


Figure 2. X-ray powder diffractogram of xerogel of **C2G-OMe** and **P2G-OMe** in EtOH.

The results of X-ray powder diffraction analyses of xerogels are presented in Figure 2. All the diffractogram patterns correspond to an amorphous material and present a broad band corresponding to a *d* spacing near 4.8 Å. For xerogels of tetramethyl orthosilicate, a signal with a *d* spacing near 3.6 Å is generally observed, which could be due to the contribution of Si−O−Si and Si−O distances of the Si−O−Si network. Such units are present in the gels, but the corresponding signal is not observed or is masked by the more intense signal at 4.8 Å, which might result from the $Si-CH_2-CH_2-Si$ unit with an average Si···Si distance of 4.5 Å measured for all these precursors using the Cerius2 simulation. For gels of **C2G-OMe** and **P2G-OMe** prepared in ethanol, an additional broad band with a *d* spacing near 6.9 Å is observed but is not yet interpreted. Such unexpected maximum were reported for similar hybrids material like $(RO)_{1.5}SiYSi(OR)_{1.5}$ and is currently under investigation.[41,42]

The pore structure and the specific surface area of the materials was determined by nitrogen adsorption porosimetry, using 5 measurements, or by determination of the adsorption/desorption isotherm (Table 3).[43,44]

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Scheme 7. Representation of the Ideal Inter- and Intramolecular Si−O−Si Network

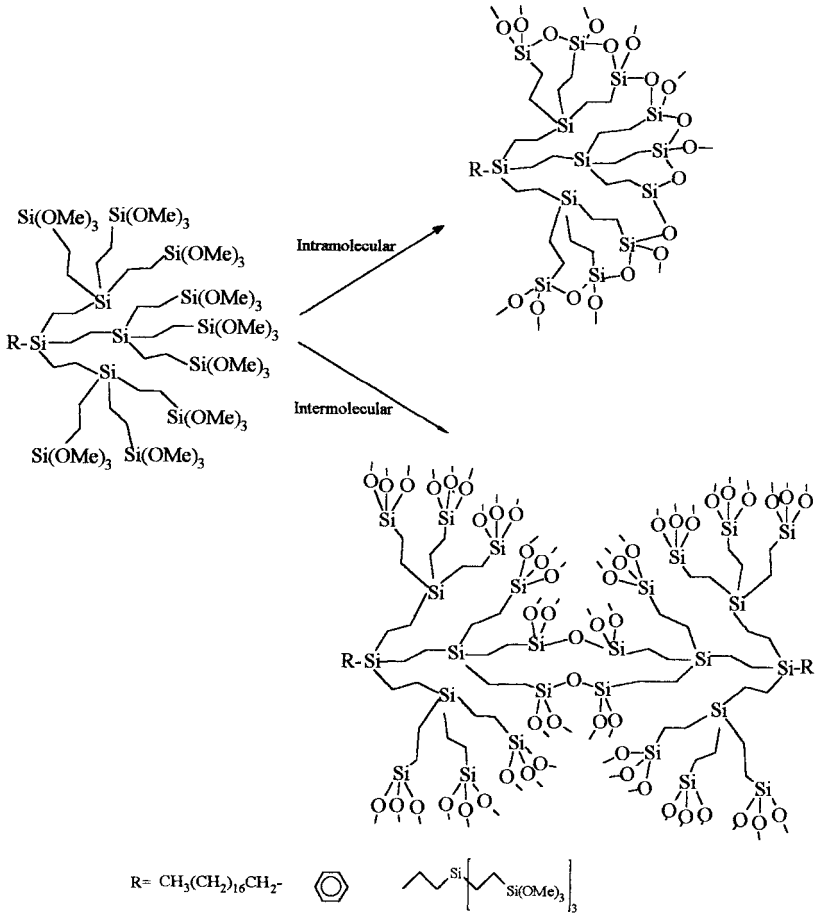

Table 3. Specific Surface Areas for Xerogels of C2G-OMe, D2G-OMe, and P2G-OMe and for Silica Obtained after Thermal Treatment

		specific surface area	
precursors	solvent	hybrids materials	silica
C2G-OMe	THF	<10	219
C2G-OMe	EtOH	<10	199 (191)
C2G-OMe	acetone	<10	298
P2G-OMe	THF	431	154
P2G-OMe	EtOH	<10	141 (138)
P2G-OMe	acetone	107	206
D2G-OMe	THF	585 (392)	179
D2G-OMe	EtOH	644 (256)	242 (228)
D2G-OMe	acetone	684 (575)	57

All the xerogels of **C2G-OMe** presented a low surface (0−10 $m^2\ g^{-1}$), which is consistent with previous observations related to the presence of a long alkyl group in this type of material.[10,13] Xerogels prepared from **D2G-OMe** have a high specific surface area (>500 $m^2\ g^{-1}$) with a broad distribution of micropores (2−20 Å) and mesopores (<150 Å), as shown in BET measurements. For xerogels prepared from **P2G-OMe**, the specific surface area depends on the solvent used for the gel formation (Table 3). However, these result cannot be related to the level of condensation or the time of gelation that also vary with the nature of the solvent.

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To obtain more information on the characteristics of the surface of the xerogels, the amount of water adsorbed at 25 °C in a 60% humidity atmosphere was determined. The xerogels obtained from the dendrimer **D2G-OMe** presented a good affinity with water. A respective increase in weight from 20 to 30% was found (Table 4) due to the high specific surface area of the material and the simultaneous presence of SiOH or residual $SiOCH_3$ groups at the periphery of the dendrimer. On the contrary, hydrophobic xerogels were obtained with **C2G-OMe** arising from the low specific surface area of the material and the presence of long hydrophobic alkyl groups associated with the surface of the material (cf. Scheme 6). For the xerogels prepared from **P2G-OMe**, the amount of adsorbed water depends on the solvent used in the polycondensation step. Therefore, the percentage of water adsorption cannot be directly related to the specific surface area of the material.

II. 3. Thermal Treatment of the Xerogels. Xerogels were thermolyzed in a flowing dry air atmosphere to remove the organic part of the hybrids by oxidation. This transformation was monitored by thermal gravimetric analysis (TGA). All the precursors presented the same general pattern (Figure 3): they started loosing weight near 200 °C, due to the oxidation of the material, elimination of CO_2, and formation of SiO_2. According to Shea et al., the onset temperature of oxidation is related to the nature of the organic part of the hybrid material, hexylene bridged [$(-CH_2-)_6$] polysiloxanes starting to oxidize at lower temperature (250 °C) than

Table 4. Hydrophilic Character of Xerogels of C2G-OMe, D2G-OMe, and P2G-OMe Determined by Water Adsorption Experiments

	C2G-OMe			P2G-OMe			D2G-OMe		
	THF	EtOH	acetone	THF	EtOH	acetone	THF	EtOH	acetone
water adsorption (wt %)	2.2	0.8	1.9	10.6	4.4	12.8	38.8	19.5	26.6

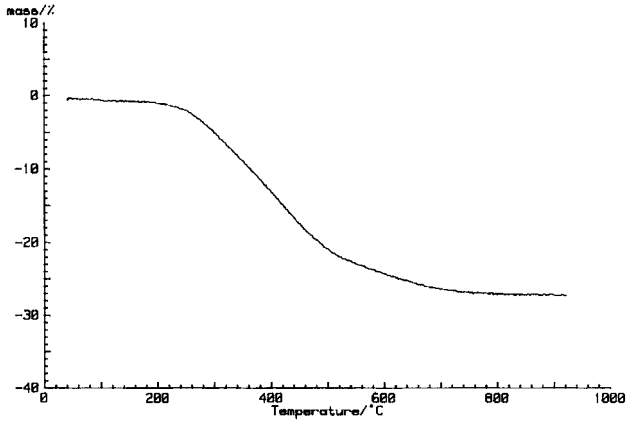

Figure 3. TGA curve of xerogel of **D2G-OMe** in acetone.

phenylene-bridged compounds (475 °C).[14] Thus, it is not surprising to find a weight loss onset at 200 °C, as all xerogels are present as $SiCH_2CH_2Si$ moieties.

The weight losses for xerogels of **C2G-OMe**, **P2G-OMe**, and **D2G-OMe** were respectively around 45%, 25%, and 25%. They were independent of the initial experimental conditions used in the polycondensation step and higher than expected for the total conversion of the hybrid material into silica. This is probably due to the presence of the remaining SiOMe functions before pyrolysis. All the residual materials have been characterized by infrared spectroscopy as pure silica.

The thermal treatment of the xerogels prepared from arborols **C2G-OMe** and **P2G-OMe** generally leads to the formation of silica with specific surface areas (100−300 $m^2\ g^{-1}$), higher than those of the starting hybrid materials. A more accurate analysis was performed by gas sorption analysis of material initally prepared in ethanol. The isotherms of adsorption and desorption for **P2G-OMe** and **C2G-OMe** were found to be of H1 type according to the de Boer classification.[43] The high volume adsorbed for low P/P_o and the high microporous surface of these materials were also a clear indication that their were mainly microporous silica (see Table 3). Using the B. J. H. calculation,[45] the cumulative pore volume plot give information regarding the pore size distribution. A broad pore size distribution is observed for this type of the material, all the pore being of diameter lower than 35 to 40 Å.

For these xerogels of the dendrimer **D2G-OMe**, the same type of hysteresis loop was observed, corresponding to micro- and mesoporous silica. In that case, a lower specific surface area than the initial xerogel was obtained. We observed a narrow distribution of pores size-centered at 35 Å, but the material is mainly microporous, with an average pore diameter below 10 Å. The size of the dendrimers as determined by Cerius2 simulation is ≈15 Å.

In both cases, no control of the porosity could be achieved using the templating effect of the oxidative organic part of the arborols and dendrimer precursors. Removal of the organic part corresponds to an important mass loss and probably results in a collapse of the three-dimensional silica network formed upon oxidation, because it is too thin to withstand the stress and the heat generated by thermal oxidation. This is in agreement with the criteria proposed by Brinker et al. for the role of covalently bonded template ligands in pore size direction for this type of hybrid material.[46] The cogelation of these dendrimers and arborols with TMOS or TEOS will be undertaken in order to embed them in a dense silica matrix and to improve the pore templating of this material. It is also important to consider that the silicon atoms of the core structure, not initally bonded to the silica network, are not removed upon oxidation, as it is evidenced by the TG yield of the hybrid materials. The silica that is formed can precipitate and modify the pore structure.

In conclusion, it has been found that arborols can be used for the formation of hybrid materials by a sol−gel process. These types of precursors allow the introduction of bulky groups like octadecyl in a xerogels, which is impossible with $R'Si(OR)_3$ precursors. Arborols were found to be different from dendrimers; for example, unlike the dendrimers, the degree of polycondensation of arborols was found to be related to the gelation conditions; simultaneously dendrimers gives porous material while arborols formed porous or nonporous material, depending on their structure and the gelation conditions. To remove the organic part by thermal oxidation is a critical step, and the silica network organization and formation of well-defined porosity could not be controlled by varying the size of these arborols or dendrimers.

III. Experimental Section

Materials. All reactions were carried out under an atmosphere of purified nitrogen using standard Schlenck techniques. Solvents were purified, dried, and distilled by standard procedures. The Karstedt platinum catalyst was purchased from ABCR as a 5% solution in xylene, chloroplatinic acid (CPA) solution was prepared as a 0.1 M solution in *i*-PrOH, and platinum on activated carbon (5% Pt) was used as received from ACROS. Octadecyltrichlorosilane, phenyltrichlorosilane, and phenyltrimethoxisilane are commercial products and were used as purchased from Aldrich, Fluka, and ACROS. Vinylmagnesium chloride was purchased from ACROS as a 15wt % solution in THF. Phenyltrivinylsilane (**II**),[30] tetravinylsilane,[31] **D1G-Cl**, and **D2G-Cl**[29] were prepared according to literature procedures.

Instrumentation. Infrared spectra were measured in NaCl and KBr pellets on a Perkin-Elmer 1600 FTIR spectrophotometer. NMR spectra were measured using samples in $CDCl_3$ solution at room temperature; chemical shifts (δ relative to Me_4Si) are indicated. ^1H and ^{13}C NMR spectra were recorded on Bruker DPX200, ^1H NMR at 200 MHz and ^{13}C

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NMR spectra at 50.323 MHz. ^{29}Si NMR spectra in solution were recorded on a WP200SY at 39.763 MHz, and solid-state CP MAS ^{29}Si NMR spectra were obtained on a AM300 at 59.620 MHz. Elemental analyses were performed by the "Service de Micro-Analyse du CNRS". Thermogravimetric analysis (TGA) of the network materials were performed on a Netzsch STA 409 thermobalance under a 50 mL/min air flow. Samples were heated from 20 to 1000 °C at 10 °C/min. Pyrolysis was carried out using Eurotherm furnaces by pouring weighed samples of solids in an aluminum oxide boat placed in a aluminum oxide tube. The gas flow was maintained around 50 mL min^{-1} during pyrolysis. X-ray powder diffraction measurements were performed using a Seyferth MZ4 apparatus from 1.5 to 20° θ. The specific 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. FAB$^+$ mass spectrometry experiments were performed with a JMS SX 102A instrument using a (50:50) glycerol:thioglycerol matrix mixed with IK salt at 25 °C in a xenon atmospere.

Preparation of Octadecyltrivinylsilane (I). A 500 mL, three-necked, round-bottomed flask equipped with a pressure-equalizing addition funnel, a reflux condenser, and a rubber septum was charged with 40 g (0.103 mol) of octadecyltrichlorosilane in 100 mL of THF. A solution of 300 mL (0.618 mol) of vinylmagnesium chloride as a 15 wt % solution in THF was added dropwise while the reaction stirred. A slight exotherm was observed. After the addition was completed, the mixture was stirred overnight at room temperature and then heated at 50 °C for 24 h. Finally, 1% KF was added and the mixture was refluxed for 3 h more. Subsequently, it was cooled to room temperature and poured into a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted twice with diethyl ether, and the combined organic layers were washed twice with water and once with saturated aqueous NaCl and dried over anhydrous $MgSO_4$. The volatile components were removed at low-pressure, leaving a yellow oil. The residual liquid was distilled at reduced pressure to give 28.47 g (77%) of **I** as a clear, colorless liquid: 100−110 °C/10^{-2} mbar; IR (NaCl, cm^{-1}) 3050, 3007, 2912, 2854, 1909, 1592, 1403, 1269, 1007, 954, 732; ^{1}H NMR (200 MHz, δ, ppm) 0.78 (m, 2H), 0.95 (t, 3H), 1.33 (s, 32H), 5.76−6.00 (dd, 3H), 6.10−6.30 (m, 6H); ^{13}C NMR (50.32 MHz, δ, ppm) 13.10, 14.54, 23.15, 24.08, 29.77, 29.85, 30.06 30.18, 32.40, 34.02; ^{29}Si NMR (39.76 MHz, δ, ppm) −19.55. Anal. Calcd for $C_{24}H_{46}Si$: C, 79.54; H, 12.70. Found: C, 79.61; H, 12.50.

Preparation of C0G-OMe. A 500 mL, three-necked, round-bottomed flask equipped with a reflux condenser, a thermometer, and a rubber septum was charged with a solution of 242 g (0.608 mol) of octadecyltrichlorosilane in 250 mL of pentane. The solution was stirred and 254 mL (1.824 mol) of triethylamine was added dropwise. After the addition was completed, the solution was cooled at a temperature between 0 and 5 °C and a solution of 74 mL (1.824 mol) of MeOH in 100 mL of pentane was added at a rate sufficient to maintain the temperature. After completion of the addition, the reaction mixture was stirred 2 h at room temperature and heated at reflux for 4 h. The mixture was cooled at room temperature and filtered through Celite. The filtrate was washed with 150 mL of pentane and the solvent evaporated at reduced pressure to leave **C0G-OMe** as a transparent liquid: IR (NaCl, cm^{-1}) 2926, 2853, 1466, 1411, 1256, 1192, 1090, 816, 721; ^{1}H NMR (200 MHz, δ, ppm) 0.67 (m, 2H), 0.91 (t, 3H), 1.23 (s, 32H), 3.59 (s, 9H,OMe); ^{13}C NMR (50.32 MHz, δ, ppm) 11.44, 15.89, 24.59, 31.21, 31.32, 31.48, 31.65, 33.69, 35.05, 52.04; ^{29}Si NMR (39.76 MHz, δ, ppm) −41.54 (s, $Si(OMe)_3$). Anal. Calcd for $C_{21}H_{46}O_3Si$: C, 67.38; H, 12.29. Found: C, 67.60; H, 12.42.

Preparation of C1G-Cl. A 250 mL, round-bottomed flask equipped with a reflux condenser, a stir bar, and a septum was charged with 25 g (0.069 mol) of **I**, 56 g (0.414 mol) of $HSiCl_3$, 50 mL of hexane, and 20 drops of Karstedt catalyst. The resulting mixture was stirred for 15 h at room temperature. Volatiles were removed at reduced pressure to leave 51.27 (98%) of **C1G-Cl** as a slight yellow liquid: ^{1}H NMR (200 MHz, δ, ppm) 0.70 (m, 2H), 0.80−0.95 (m, 9H), 1.31 (m, 38H); ^{13}C NMR (50.32 MHz, δ, ppm) 2.87, 10.99, 14.60, 17.71, 23.15, 23.88, 29.60, 29.82, 29.96, 30.16, 32.38, 34.02; ^{29}Si (39.76 MHz, $CDCl_3$) δ 9.48 (s, core Si), 12.75 (s, $SiCl_3$).

Preparation of C1G-OMe. A 250 mL, three-necked, round-bottomed flask equipped with a reflux condenser, a thermometer, and a rubber septum was charged with a solution of 3 g (0.004 mol) of **C1G-Cl** in 125 mL of hexane. The solution was stirred and 7 mL (0.047 mol) of triethylamine was added dropwise. After the addition was completed, the solution was at a temperature between 0 and 5 °C, and a solution of 2.5 mL (0.047 mol) of MeOH in 15 mL of hexane was added at a rate sufficient to maintain the temperature. After completion of the addition, the reaction mixture was stirred 2 h at room temperature and heated at reflux for 4 h. The mixture was cooled at room temperature and filtered through Celite. The filtrate was washed with 50 mL of hexane and the solvent evaporated at reduced pressure to leave 2.6 g (92%) of **C1G-OMe** as a slight orange liquid: IR (NaCl, cm^{-1}) 2920, 2854, 1466, 1411, 1256, 1189, 1145, 1083, 951, 823, 778; ^{1}H NMR (200 MHz, δ, ppm) 0.56 (br s, 12H), 0.89 (t, 3H), 1.22 (br s, 34H), 3.58 (s, 27H, OMe); ^{13}C NMR (50.32 MHz, δ, ppm) 1.24, 2.05, 10.77, 14.04, 22.64, 23.78, 29.31, 29.61, 29.66, 31.88, 33.92, 50.53; ^{29}Si NMR (39.76 MHz, δ, ppm) −41.79 (s, $Si(OMe)_3$), 8.41 (s, core Si). Anal. Calcd for $C_{33}H_{76}O_9Si_4$: C, 54.39; H, 10.44. Found: C, 54.66; H, 10.59.

Preparation of C1G-Vi. The procedure used was identical to that used in the preparation of **I**, reacting 25 g (0.003 mol) of **C1G-Cl**, 300 mL of a solution of vinylmagnesium chloride as a 15 wt % solution in THF, and 70 mL of THF. The same workup procedure yielded a yellow oil which was taken up and purified by the addition of 2 g of silica gel and 2 g of active carbon and stirring for 1.5 h. The mixture was filtered and washed with 50 mL of hexane. Removal of volatiles left 19.3 g (95%) of a pure yellow oil: IR (NaCl, cm^{-1}) 3049, 3006, 2923, 2853, 1908, 1592, 1465, 1403, 1129, 1057, 1007, 954, 728; ^{1}H NMR (200 MHz, δ, ppm) 0.48−0.64 (m, 12H), 0.91 (t, 3H), 1.28 (s, 34H), 5.75−5.86 (m, 9H), 6.10−6.22 (m, 18H); ^{13}C NMR (50.32 MHz, δ, ppm) 3.57, 5.27, 12.10, 14.54, 23.12, 24.26, 29.75, 29.80, 30.05, 32.37, 34.29, 134.82, 135.08; ^{29}Si NMR (39.76 MHz, δ, ppm) −18.24 (s, $Si(CH{=}CH_2)_3$), 8.68 (s, core Si). Anal. Calcd for $C_{42}H_{76}Si_4$: C, 72.80; H, 10.98. Found: C, 72.95; H, 11.14.

Preparation of C2G-Cl. The same procedure that was used in the preparation of **C1G-Cl** was used, reacting 7 g (0.001 mol) of **C1G-Vi** with 25 g (0.002 mol) of $HSiCl_3$ in 15 mL of hexane and 5 drops of the xylene solution of Karstedt catalyst. The reaction mixture was stirred at reflux 15 h. After cooling, volatiles were removed at reduced pressure to leave **C2G-Cl** as a yellow oil (19 g, 98%): IR (NaCl, cm^{-1}) 2925, 2854, 1466, 1408, 1261, 1144, 1069, 1007, 725, 580; ^{1}H NMR (200 MHz, δ, ppm) 0.51−0.61 (m, 12H), 0.84−0.92 (m, 23H), 1.24−1.33 (m, 50H); ^{13}C NMR (50.32 MHz, δ, ppm) 2.31, 3.31, 10.50, 14.54, 17.77, 23.11, 24.26, 29.77, 29.88, 30.07, 30.12, 32.34, 34.35; ^{29}Si (39.76 MHz, δ, ppm) 8.33 (s, core Si), 10.87 (s, CH_2-$SiCH_2$), 12.52 (s, $SiCl_3$).

Preparation of C2G-OMe. The procedure used was identical to that used in the preparation of **C1G-OMe**, reacting 28.47 g (0.015 mol) of **C2G-Cl**, 62 mL (0.425 mol) of NEt_3, and 20 mL (0.408 mol) of MeOH in 1.2 L of hexane. The same workup procedure yielded a yellow and viscous oil (24 g, 93%): IR (NaCl, cm^{-1}) 2920, 2839, 1462, 1410, 1254, 1191, 1136, 1087, 831, 777; ^{1}H NMR (200 MHz, δ, ppm) 0.40 (s, 6H), 0.52 (m, 31H), 0.87 (m, 9H), 1.26 (br s, 39H), 3.57 (s, 81H, OMe); ^{13}C NMR (50.32 MHz, δ, ppm) 1.68, 1.90, 3.36, 3.81, 11.19, 14.46, 23.06, 24.40, 29.90, 30.09, 32.30, 34.30, 50.91; ^{29}Si NMR (39.76 MHz, δ, ppm) −41.92 (s, $Si(OMe)_3$), 7.35 (s, core Si), 9.79 (s, CH_2SiCH_2). Anal. Calcd for $C_{69}H_{166}O_{27}Si_{13}$: C, 46.25; H, 9.27. Found: C, 47.20; H, 9.81.

Preparation of Phenyltrivinylsilane (II). The procedure used was identical to that used in the preparation of **I**, reacting 74.0 g (0.350 mol) of phenyltrichlorosilane, 800 mL (1.350 mol) of a solution of vinylmagnesium chloride as a 15 wt % solution in THF, and 500 mL of THF. The mixture was stirred for 1 day at reflux and it was then cooled to room

temperature and poured into a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed twice with water and once with saturated aqueous NaCl and dried over anhydrous $MgSO_4$. The volatile components were removed at low-pressure, leaving a yellow oil. The residual liquid was distilled at reduced pressure to give 52.11 g (80%) of **II** as a clear, colorless liquid: 39.4 °C/10^{-2} mbar; IR (NaCl, cm^{-1}) 3049, 3006, 2923, 2853, 1908, 1592, 1465, 1403, 1129, 1057, 1007, 954, 728; ^{1}H NMR (200 MHz, δ, ppm) 5.83−5.95 (m, 3H), 6.27−6.42 (m, 6H), 7.42−7.62 (s, 5H); ^{13}C NMR (50.32 MHz, δ, ppm) 130.85, 132.43, 136.81, 138.06, 138.90; ^{29}Si NMR (39.76 MHz, δ, ppm) −23.64 (s, $Si(CH{=}CH_2)_3$). Anal. Calcd for $C_{12}H_{14}Si$: C, 77.39; H, 7.85. Found: C, 77.41; H, 7.53.

Preparation of P1G-Cl. The procedure used in the preparation of **C1G-Cl** was used in the reaction of 12 g (0.007 mol) of **II** with 50 g (0.004 mol) of $HSiCl_3$ in 45 mL of hexane and 5 drops of the xylene solution of Karstedt catalyst. The reaction mixture was stirred for 30 min at room temperature and 7 h at reflux. The solution was cooled to room temperature, and volatiles were removed at reduced pressure to leave **P1G-Cl** as a colorless oil (35 g, 91%): ^{1}H NMR (200 MHz, δ, ppm) 1.12−1.39 (m, 12H, CH_2), 7.46−7.53 (m, 5H, C_6H_5); ^{13}C NMR (50.32 MHz, δ, ppm) 2.99, 3.61, 9.91, 14.22, 17.63, 17.94, 128.99, 129.09, 130.83, 130.96, 131.63, 132.58, 134.46, 134.86.

Preparation of P1G-OMe. The procedure used was identical to that used in the preparation of **C1G-OMe**, reacting 7 g (0.001 mol) of **P1G-Cl**, 19 mL (0.141 mol) of NEt_3, and 6 mL (0.141 mol) of MeOH in 170 mL of hexane. The same workup procedure yielded 6 g (92%) of **P1G-OMe** as a liquid: IR (NaCl, cm^{-1}) 3048, 2941, 2839, 1462, 1428, 1411, 1256, 1192, 1137, 1087, 999, 820, 782, 701; ^{1}H NMR (200 MHz, δ, ppm) 0.53−1.28 (m, 12H), 3.58 (s, 27H, OMe), 7.29−7.37 (m, 5H); ^{13}C NMR (50.32 MHz, δ, ppm) 1.60, 2.45, 50.86; 127.86, 128.13, 129.09, 129.34, 134.64, 135.03, 136.34, 136.50; ^{29}Si NMR (39.76 MHz, δ, ppm) −41.60, −42.00, −42.37 (s, $Si(OMe)_3$), 3.44 (s, core Si). Anal. Calcd for $C_{21}H_{44}O_9Si_4$: C, 45.62; H, 7.96. Found: C, 45.17; H, 7.46.

Preparation of P1G-Vi. The procedure used was identical to that used in the preparation of **II**, reacting 12 g (0.020 mol) of **P1G-Cl**, 216 mL of a solution of vinylmagnesium chloride at 15% in THF, and 80 mL of THF. The same workup procedure yielded a yellow oil which was taken up and purified by the addition of 2 g of silica gel and 2 g of active carbon and stirring for 1.5 h. The mixture was filtered and washed with 50 mL of hexane. Removal of volatiles left 8.5 g (81%) of **Ph1G-Vi** as a yellow oil: IR (NaCl, cm^{-1}) 3044, 3000, 2933, 2912, 2884, 1911, 1591, 1427, 1403, 1129, 1110, 1055, 1008, 955, 724; ^{1}H NMR (200 MHz, δ, ppm) 0.64−1.50 (m, 12H), 5.46−5.90 (m, 9H), 6.11−6.30 (m, 18H); 7.38−7.50 (m, 5H); ^{13}C NMR (50.32 MHz, δ, ppm) 3.61, 5.20, 128.22, 129.37, 134.83, 134.99, 135.03; ^{29}Si NMR (39.76 MHz, δ, ppm) −17.73 (s, $Si(CH{=}CH_2)_3$), 3.86 (s, core Si). Anal. Calcd for $C_{30}H_{44}Si_4$: C, 69.72; H, 8.52; Found: C, 69.22; H, 8.94.

Preparation of P2G-Cl. A solution of **P1G-Vi** (10.58 g, 0.0205 mol) and 55 g (0.4060 mol) of $HSiCl_3$ in 50 mL of hexane to which two drops of the Karstedt catalyst solution had been added was stirred 30 min at room temperature and 23 h at reflux. Removal of volatile at reduced pressure left **P2G-Cl** as a pale yellow oil (14 g, 90%): ^{1}H NMR (200 MHz, δ, ppm) 0.73−1.47 (m, 48H), 7.46 (m, 5H); ^{13}C NMR (50.32 MHz, δ, ppm) 2.26, 3.00, 14.57, 17.68, 23.11, 24.26, 29.77, 29.88, 30.07, 30.12, 32.34, 34.35.

Preparation of P2G-OMe. The procedure used was identical to that used in the preparation of **P1G-OMe** reacting 13 g (0.017 mol) of **P2G-Cl**, 69 mL (0.497 mol) of NEt_3, and 22 mL (0.497 mol) of MeOH in 500 mL of hexane. The mixture was stirred for 15 h at room temperature and 4 h at reflux. The same workup procedure yielded a yellow and viscous oil (25 g, 93%): IR (NaCl, cm^{-1}) 3044, 2941, 2917, 2839, 1460, 1410, 1256, 1192, 1137, 1089, 833, 779, 704; ^{1}H NMR (200 MHz, δ, ppm) 0.44−0.91 (m, 36H), 1.26 (br s, 12H), 3.55 (s, 81H, OMe), 7.29−7.51 (m, 5H); ^{13}C NMR (50.32 MHz, δ, ppm) 1.60, 1.81, 2.79, 3.80, 50.84, 128.07, 129.06, 134.55, 135.01; ^{29}Si NMR (39.76 MHz, δ, ppm) −41.98 (s, $Si(OMe_3)_3$), 2.63 (s, core Si), 9.98 (s, CH_2SiCH_2). Anal. Calcd for $C_{57}H_{134}O_{27}Si_{13}$: C, 42.38; H, 8.30. Found: C, 43.50; H, 8.44.

Preparation of D1G-OMe. Using the procedure described for **C1G-OMe**, the reaction was carried out between 4 g (0.006 mol) of D1G-Cl, 12 mL (0.089 mol) of Et_3N, and 4 mL (0.089 mol) of MeOH in 150 mL of hexane. The some workup procedure yielded a slightly yellow oil: IR (NaCl cm^{-1}): 2941, 2840, 1459, 1411, 1376, 1192, 1136, 1087, 835, 782); ^{1}H NMR (200 MHz, δ, ppm) 0.55 (m, 16H), 3.55 (s, 36H, OMe); ^{13}C NMR (50.32 MHz, δ, ppm) 1.59, 1.88, 50.87; 127.86, 128.13, 129.09, 129.34, 134.64, 135.03, 136.34, 136.50; ^{29}Si NMR (39.76 MHz, δ, ppm) −42.03, (s, $Si(OMe)_3$), 9.99 (s, core Si). Anal. Calcd for $C_{20}H_{52}O_{12}Si_4$: C, 38.46; H, 8.33. Found: C, 39.51, H, 8.57.

Preparation of D2G-OMe. The compound **D2G-Cl** was prepared as described in ref 29. The procedure used was identical to that used in preparation of **C2G-OMe** reacting 19 g (0.009 mol) of **D2G-Cl**, 48 mL (0.344 mol) of Et_3N, and 14 mL (0.3440 mol) of MeOH in 500 mL of hexane. The mixture was stirred for 15 h at room temperature and refluxed for 4 h. The residue was filtered and washed with 250 mL of hexane. The volatile were removed to yield a yellow and viscous oil (15.69 g, 9%): IR (NaCl, cm^{-1}) 2942, 2916, 2840, 1459, 1411, 1250, 1192, 1135, 1087, 835, 775; ^{1}H NMR (200 MHz, δ, ppm) 0.25 (s, 16H), 0.47 (s, 48H), 3.49 (s, 108H, OMe); ^{13}C NMR (50.32 MHz, δ, ppm) 1.51, 1.63 2.92, 3.26, 50.62; ^{29}Si NMR (39.76 MHz, δ, ppm) −42.04 (s, $Si(OMe)_3$), 8.76 (s, core Si), 9.77 (s, CH_2SiCH_2); FAB^+ MS (m/z) 2079 (M + 39, 25), 1958 (three-arm product + 39, 10), 475 ($Si(CH_2CH_2Si(OMe)_3)_3$, 100). Anal. Calcd for $C_{68}H_{172}O_{36}Si_{17}$: C, 40.00; H, 8.43. Found: C, 41.75; H, 8.61.

Hydrolysis and Polycondensation of C0G-OMe. The process of hydrolysis of **C0G-OMe** was carried out according to the following general procedure: 0.060×10^{-3} mol of NH_3 and 1.5 equiv of water were added to 7.59 g (0.020 mol) of precursor in THF, EtOH, or acetone. After several minutes, a white solid precipitated from the solution. The solid obtained in EtOH was filtered, washed with water, and dried in a vacuum at room-temperature, yielding a white powder. The solid melts at 37 °C and is soluble in organic solvents. Spectroscopic analysis: FTIR (KBr, cm^{-1}) 3455, 2920, 2846, 1467, 1194, 1092, 1028, 815, 719; ^{1}H NMR (200 MHz, δ, ppm) 3.58 (s, 1H), 3.57 (s, 2H), 1.26 (br s, 32H), 0.88 (t, 3H), 0.65 (m, 2H); ^{13}C NMR (50.32 MHz, δ, ppm) 9.01, 9.54, 12.40, 23.00, 23.10, 29.68, 29.78, 29.95, 30.11, 32.35, 33.57, 50.87; ^{29}Si NMR (39.76 MHz, δ, ppm) −41.07, −42.14, −49.73, −59.38.

Hydrolysis and Polycondensation of P1G-OMe. The process of hydrolysis of **P1G-OMe** was carried out according to the following general procedure: to 3.73 g (0.006 mol) of **P1G-OMe** in 22 mL of EtOH was added 0.55 mL of a solution 1.1 M of NH_3 in water. The homogeneous solutions were allowed to stand at room temperature. After 6 months, the solvent was eliminated and an oily product was recovered: ^{1}H NMR (200 MHz, δ, ppm) 7.35 (br s, 5H), 3.40 (br s, 19H), 0.84 to 1.28 (br s, 15.5H); ^{13}C NMR (50.32 MHz, δ, ppm) 4.13, 5.17, 11.40, 13.96, 32.50, 48.87, 53.06, 130.30, 130.54, 137.09, 137.48.

Hydrolysis and Polycondensation of C2G-OMe. The preparation of the gels was carried out according to the following general procedure. The solvents, concentrations of the reagents and catalyst are indicated in Table 2. To 4.03 g (0.0023 mol) of **C2G-OMe** in THF, EtOH, or acetone were added 13.5 equiv of water and the catalyst. The homogeneous solutions were allowed to stand at room temperature, and gels were formed within several hours (see Table 2). After curing at room temperature for 7 days, the gels were powdered. The solid was collected, washed with ether, and dried in a vacuum at 100 °C for 24 h, yielding a slightly yellow solid. Spectroscopic analysis of the solids obtained showed similar characteristics: FTIR (KBr, cm^{-1}): 3444, 2922, 2856, 1466, 1411, 1261, 1090, 905, 728; ^{29}Si CP MAS NMR (39.76 MHz, δ, ppm) 9, 0, −47, −56, −65. Some representative spectra are given in Figure 1. In most cases similar intensities of the signals were observed. The gels also showed similar X-ray powder diffraction pattern, with no crystallinity. X-ray powder diffraction shows two broad bands with d spacing of 4.7 and 6.9

Å for the xerogel prepared in EtOH, while one broad band, *d* spacing of 4.8 Å, in the other cases was observed. The surfaces area and pore diameters measures using the N_2 BET technique are listed in Table 3.

Hydrolysis and Polycondensation of P2G-OMe. The gels were obtained as above, using 0.1 M THF, EtOH, or acetone solutions of **P2G-OMe** (0.0023 mol) by addition of 0.608×10^{-3} mol of NH_3 and 13.5 equiv of water. Gelation occurred respectively after 2, 1 or 5 days (Table 2), the gels were treated as described above, and white solids were collected. All samples showed similar spectroscopic characteristics: FTIR (KBr, cm^{-1}) 3422, 2978, 2911, 1420, 1261, 1065, 907, 703; ^{29}Si CP MAS NMR (39.76 MHz, δ, ppm) 9, 3, −48, −56, −65. X-ray diffraction showed two broad bands with *d* spacing of 4.6 and 6.6 Å for the gel obtained in EtOH and one broad band, *d* spacing of 4.9 Å, for gels prepared in THF and acetone. Specific surface areas are listed in Table 3. The hydrophilic character of each materials is indicated in Table 3.

Hydrolysis and Polycondensation of D2G-OMe. The gels were obtained as above, using 3.45 g (1.688 mmol) of precursor in THF, EtOH, and acetone. In this case, an excess of 10% of NH_3 as a 30% solution in water and 18 equiv of water were added to obtain the gels. Transparent gels were formed respectively within 2 h, 30 min, and 1 day. The gels obtained were allowed to stand at room temperature for 7 days. The solids were powdered, washed with ether, and dried in a vacuum at 100 °C for 24 h; white solids were collected. All samples showed similar spectroscopic characteristic: FTIR (KBr, cm^{-1}) 3435, 2930, 2865, 1450, 1261, 1075, 905, 720; ^{29}Si CP MAS NMR (39.76 MHz, δ, ppm) 9, −49, −57, −65. X-ray diffraction showed one broad band, with a *d* spacing of 4.8 Å. The N_2 BET surface areas are shown in Table 3. The hydrophilic materials are presented in Table 3.

Hydrophilic Characterization. Samples of gels (0.1−1 g) have been introduced in a desiccator containing a beaker filled with saturated aqueous solution of sodium bromide. The sample were left in a closed desiccator under reduced pressure (0.1 mmHg) for a period of 24 h and quickly weighted to calculate the variation of weight.

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