Synthesis and Characterization of Polyhedral Silsesquioxanes Bearing Bulky Functionalized Substituents

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ABSTRACT: A simple route to synthesize polyhedral silsesquioxanes, $(RSiO_{1.5})_n$, by the hydrolytic condensation of modified aminosilanes, is reported. The starting material was *N*-(β-aminoethyl)-γ-aminopropyltrimethoxysilane, a trifunctional aminosilane. It was reacted with a stoichiometric amount of phenylglycidyl ether in sealed ampules at 50 °C for 24 h, leading to the trisubstituted product plus a series of oligomers arising from the intermolecular reaction between methoxysilane groups and the secondary hydroxyls generated by the epoxy−amine reaction. When this product was subjected to hydrolytic condensation using a variety of catalysts (HCl, NaOH, HCOOH) and a thermal cycle attaining 150 °C, polyhedral silsesquioxanes (SSQO) were obtained. Their molar mass was independent of reaction conditions as revealed by size exclusion chromatography. Characterization by ^1H, ^{13}C, and ^{29}Si NMR suggested that the main product was a mixture of polyhedral SSQO with $n = 8$ and 10; i.e., T_8 and T_{10}. Due to the high OH functionality, i.e., 24 OH groups in T_8 and 30 OH groups in T_{10} polyhedra, the synthesized product may be used as a cross-linking unit of very high functionality or as a modifier for several polymeric materials.

Introduction

Polyhedral silsesquioxanes (SSQO), $(RSiO_{1.5})_n$ or T_n, where n is an even number and R = H, Cl, or a variety of organic groups, are a unique class of materials that have begun to occupy a sizable niche in polymer chemistry.[1] They are also referred to as spherosiloxanes because they consist of polyhedral structures that are topologically equivalent to a sphere. Electronic structure calculations performed on a series of silsesquioxane cages $(HSiO_{1.5})_n$ showed that polyhedral SSQO containing triangular faces are significantly less stable than molecules containing only larger rings.[2] Although hexasilsesquioxanes (triangular prisms, T_6) have been synthesized,[3−7] the first member of the series of stable silsesquioxanes is the “cube” (T_8) with O_h symmetry, represented schematically in Figure 1a. Polyhedral structures with $n = 10$ (T_{10}) or 12 (T_{12}) exhibit similar relative stabilities.[2]

There are different strategies for the synthesis of a polyhedral SSQO.[1] The most general route is the hydrolysis and condensation of trialkoxy- or trichlorosilanes.[1,3,4,8] But this path frequently leads to a distribution of different products and a yield of polyhedral SSQO that depends on the nature of the starting silane, solvent, and catalyst, their relative concentrations, the amount of added water, the selected temperature cycle, and the solubility of the final products.[3,4,8]

Precursors of SSQO can be isolated in moderate yields from the hydrolytic condensation of silanes under strictly controlled conditions.[3,4,9,10] A typical one is the incompletely condensed trisilanol, $R_7Si_7O_9(OH)_3$ [$T_7(OH)_3$], shown in Figure 1b. Corner capping of this precursor can be carried out using a variety of trichlorosilane coupling agents.[5,11−13] This leads to an octasilsesquioxane with one corner that may be functionalized with a graftable or polymerizable group. Lichtenhan and co-workers[14−17] have used this approach to synthesize and characterize a variety of linear polymers modified with SSQO building blocks pendent to the polymer backbone.

Feher et al.[18,19] developed a new strategy for preparing functionalized SSQO from fully condensed T_8 frameworks. They used a general and remarkable selective method for effective cleavage of a single framework siloxane linkage, opening the possibility of introducing desired functional groups in the new structure. Some of the resulting hydroxylated species are shown in Figure 1c.

It is now recognized that the SSQO family has an enormous potential as a building block for advanced materials. However, cost-effective methods should be devised to produce appropriately functionalized frameworks on a large scale. During a systematic study of the hydrolytic condensation of different silanes, we found a particular system leading to a mixture of polyfunctionalized SSQO. Of interest was the fact that almost the same distribution of molar masses was obtained using different conditions for the hydrolytic condensation, i.e., changing the type and concentration of catalysts and the thermal cycles. Besides, reaction products were stable after a prolonged heating at 150 °C, giving a strong evidence that polyhedral structures were present. This opens an efficient and direct path to synthesize functionalized SSQO that may be used as

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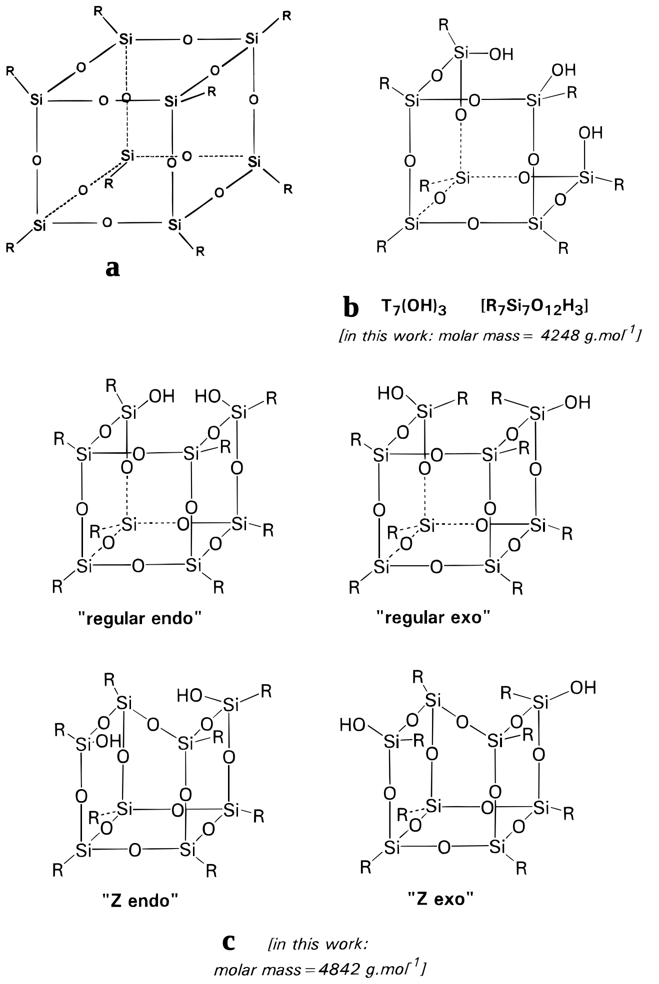


Figure 1. (a) Schematic representation of an octasilsesquioxane, $(RSiO_{1.5})_8$; (b) typical precursor of a SSQO; (c) incompletely condensed "$T_8(OH)_2$" isomers.

cross-linking agents or as modifiers for a variety of polymers. In this paper, the synthesis and characterization of these SSQO will be reported.

Experimental Section

The starting silane was *N*-(β-aminoethyl)-γ-aminopropyltrimethoxysilane. A product from Dow Corning (Z6020, 85% purity) was used in the study of modification and hydrolytic condensation reactions. A product from Aldrich (97% purity) was used to synthesize the final material for NMR characterization.

The aminosilane was modified by reaction with a stoichiometric amount (epoxy/NH) of phenylglycidyl ether (PGE, Aldrich, 99% purity); e.g., 3 mol (450 g) of PGE was used per mole (222 g) of aminosilane. The reaction was carried out in glass tubes sealed under vacuum and placed in a thermostat held at 50 °C. Tubes were removed from the bath at different times and quenched by cooling in an ice bath. Size exclusion chromatography (SEC) of solutions of the reaction products in tetrahydrofuran (THF, 0.02 g L^{-1}) was performed in a Waters device using a refractive index detector and the following Ultrastyragel columns: 100, 500, 10^3, and 10^4 Å. THF was used as eluent at a flow rate of 1 mL min^{-1}.

The hydrolytic condensation of the modified silane was performed in THF solution (40 g of the modified silane in 50 mL of THF), using one of the following catalysts: (a) HCl; molar ratios HCl/Si = 0.05, $H_2O/Si = 3$; (b) NaOH; molar ratios NaOH/Si = 0.1, $H_2O/Si = 3$; (c) HCOOH; molar ratios HCOOH/Si = 0.1, $H_2O/Si = 3$; (d) HCOOH; molar ratios HCOOH/Si = 3, $H_2O/Si = 1.35$. Molar ratios of catalyst and water were calculated by knowing that 672 g of the modified silane contain 1 mol of Si atoms.

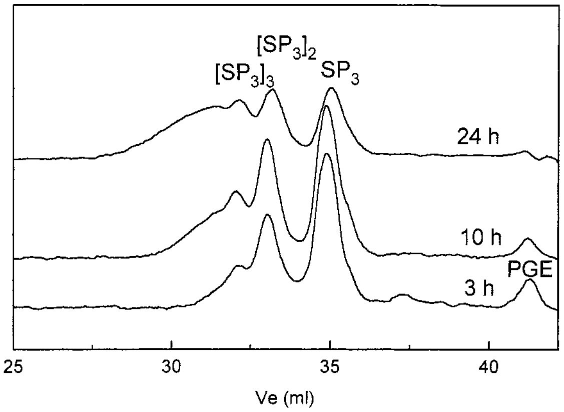


Figure 2. SEC chromatograms of reaction products in the system aminosilane + PGE at 50 °C.

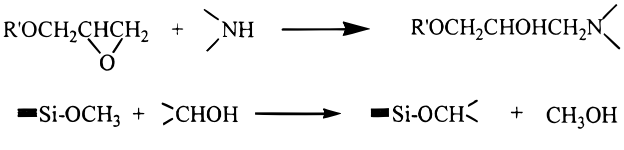
Temperature was held at 50 °C for 24 h. Then, it was increased in steps up to 150 °C. (A typical thermal program was 1 h at 75 °C, 3 h at 100 °C, 3 h at 120 °C, and 1 h at 150 °C; SEC chromatograms of the final material were independent of variations introduced in the duration of different steps.) THF was completely removed during the heating step as revealed by ^1H NMR.

FTIR spectra were obtained in a Bruker IFS 25 device by casting THF solutions onto a NaCl window.

The silsesquioxane synthesized using the aminosilane with highest purity was analyzed by SEC and multinuclear NMR (^1H, ^{13}C, and ^{29}Si). SEC was performed with a Waters device provided with Nucleogel columns 100-5 and 500-5 and refractive index and UV (λ = 254 nm) detectors. High-resolution liquid NMR spectroscopy was carried out with a Bruker DRX400 instrument. ^1H was observed at 400 MHz, ^{13}C at 62.9 MHz, and ^{29}Si at 79.5 MHz. Deuterated chloroform ($CDCl_3$) was used as solvent. Chemical shifts values (δ) are given in ppm with reference to internal tetramethylsilane (TMS). Quantitative $^{13}C\{^1H\}$spectra have been obtained with suppression of the nuclear Overhauser effect and using a delay $D_1 = 10$ s between pulses (pulse angle = 70°). Inverse-gated proton decoupling has also been used to record the $^{29}Si\{^1H\}$ spectra. When not precisely stated, the spectra were recorded at ambient temperature.

Results and Discussion

Figure 2 shows SEC chromatograms obtained during the reaction of the aminosilane with PGE. (Chemical structures of the starting reagents are shown in Figure 3a.) After 24 h at 50 °C, PGE was practically exhausted, but the reaction product was not exclusively the trisubstituted silane (SP_3). A series of $(SP_3)_n$ oligomers were formed from the beginning of the reaction; i.e., after the first hour, significant amounts of the di- and trisubstituted silanes were observed together with an incipient amount of $(SP_3)_2$. $(SP_3)_n$ oligomers were produced by the intermolecular reaction of a Si−OCH_3 group with the secondary hydroxyl generated by the epoxy−amine reaction:[20]



$$R'OCH_2\underset{\diagdown O \diagup}{CHCH_2} + \,>NH \longrightarrow R'OCH_2CHOHCH_2N<$$

$$\blacksquare Si\text{-}OCH_3 + \,>CHOH \longrightarrow \blacksquare Si\text{-}OCH< + CH_3OH$$

As an example, the structure of $(SP_3)_2$ is shown in Figure 3b. Intramolecular reactions of this type may also take place.

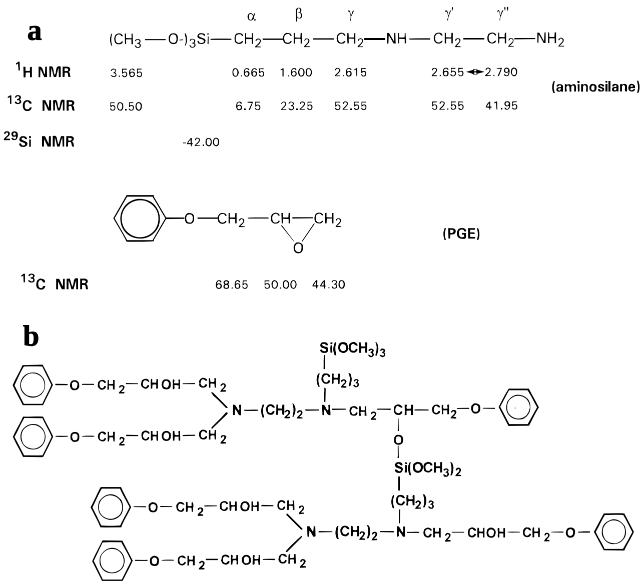


Figure 3. (a) Chemical structures of the starting reagents and their characteristic NMR resonances. (b) Chemical structure of the species $(SP_3)_2$ appearing in the reaction products of aminosilane + PGE at 50 °C.

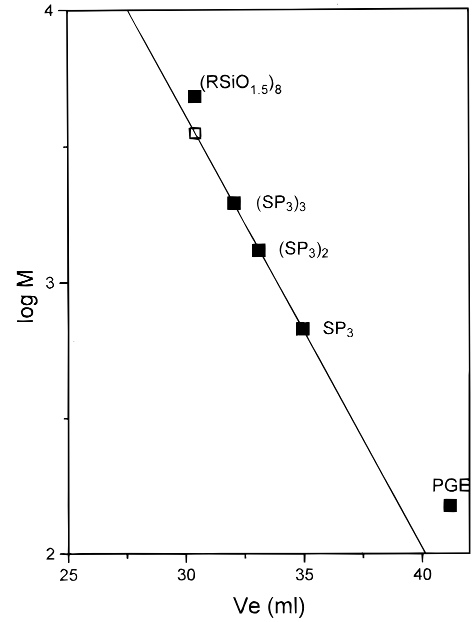


Figure 4. Calibration curve of the set of SEC columns using $(SP_3)_n$ peaks as internal standards: (■) theoretical values; (□) experimental values.

FTIR of samples taken in the course of reaction confirmed the decrease in the intensity of the band at 1191 cm^{-1}, ascribed to CH_3 rocking in $Si-OCH_3$. The presence of methanol was verified by drying the samples and observing the mass loss.

Although gelation is in principle expected during the polycondensation of an A_3B_3 molecule, i.e., the SP_3 containing three OH groups A and three $Si-OCH_3$ groups B, this phenomenon was not observed even after a prolonged heating at 50 °C for 1 week or a postcure step at 120 °C for 7 h. This is probably the result of the high fraction of intramolecular cyclization as well as the attainment of an equilibrium state in the reaction between $Si-OCH_3$ and OH groups.

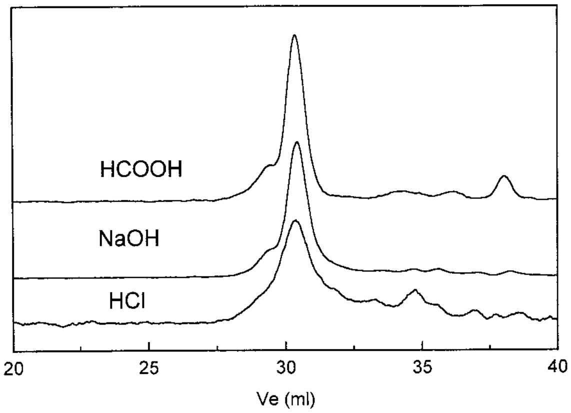


Figure 5. SEC chromatograms of the silsesquioxanes obtained after hydrolytic condensation of the modified aminosilane, $(SP_3)_n$, using different catalysts (RI detection).

Figure 4 shows a calibration curve of the set of SEC columns using $(SP_3)_n$ products as internal standards (PGE lies outside the straight line). Figure 5 shows SEC chromatograms of the mixture of SSQO obtained by hydrolytic condensation of the $(SP_3)_n$ distribution, using different catalysts. The $(SP_3)_n$ oligomers were hydrolyzed and condensed leading to a main reaction product with an elution volume at 30.4 mL whatever the catalyst. A small shoulder is observed at 29.3 mL when using NaOH and HCOOH as catalysts. Also, a small concentration of products with lower molar masses is present.

An estimation of the molar mass of the main product may be obtained by placing its elution volume in the calibration curve of Figure 4. This leads to a molar mass of about 3500 g mol^{-1} while the theoretical value for the octasilsesquioxane (Figure 1a) is 4824 g mol^{-1} and that for the hexasilsesquioxane (T_6) should be 3618 g mol^{-1}. The corresponding point lies above the straight line, consistent with the fact that a polyhedral species will appear at higher elution volumes than a linear or branched species with the same molar mass. Bassindale and Gentle[21] used linear poly(dimethylsiloxane)s (PDMS) standards for SEC analysis of SSQO cubes (T_8) with different organic groups attached to the Si atom. When R was a 1-alkene, molar masses obtained from the calibration curve were remarkably close to the expected molar masses. However, when R was a siloxane, molar masses obtained from the calibration curve were significantly lower than actual molar masses, i.e., 2520 (calculated from GPC calibration) and 3343 (expected). A similar situation seems to be present in our case. It is worth noticing that in our case incompletely condensed SSQO shown in Figure 1c have a molar mass of 4842 g mol^{-1}, whereas the structure shown in Figure 1b has a molar mass of 4248 g mol^{-1}, both being probably not far enough from the exact T_8 value (4824 g mol^{-1}) to be discriminated by SEC.

FTIR spectra showed a strong band at 1121 cm^{-1}, ascribed to a Si—O—Si bond. The observation of a single band lying in the 1120—1130 cm^{-1} range may be taken as a good evidence for the presence of strainless cage structures of the T_8 to T_{14} type.[22] It is however very difficult to distinguish one kind of SSQO cage from another using FTIR (for a T_8 the band is reported at 1121 cm^{-1}; for a T_{10} it is shifted to 1128 cm^{-1}).[22] Strained cycles as those present in a T_6 SSQO show the same band [3] at 1051—1057 cm^{-1}. Therefore, their presence in the reaction products (at least in a significant amount) may be ruled out. A particular issue of the use of concentrated formic acid was the appearance

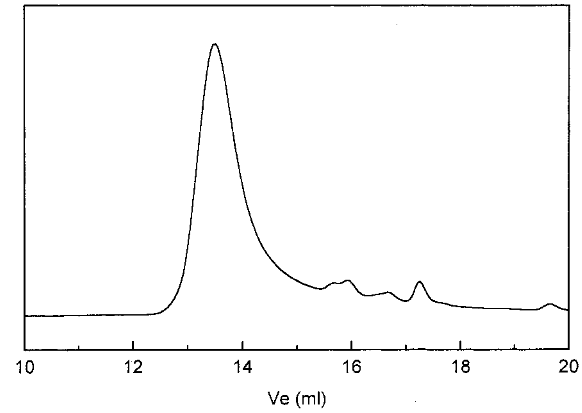


Figure 6. SEC chromatogram of the silsesquioxane obtained starting with a pure aminosilane using formic acid as catalyst (RI detection).

$CH_3—CH_2—NH—CH_2—CH_2—NH_2$

	CH_3	CH_2	NH	CH_2	CH_2	NH_2
^{1}H NMR	1.110	2.790	1.195	[2.645 - 2.660]		1.195
^{13}C NMR	15.15	41.60		52.30	43.80	

(model compound)

Figure 7. Chemical structure of the model amino compound and its ^{13}C NMR characteristic lines in $CDCl_3$.

of an ester band at 1724 cm^{-1}, originating from the partial esterification of secondary hydroxyls.

To characterize the reaction product by NMR, the synthesis was carried out starting from the aminosilane with 97% purity and using formic acid as catalyst. Figure 6 shows the resulting SEC chromatogram obtained with the set of Nucleogel columns.

All ^{1}H, ^{13}C, and ^{29}Si NMR spectra obtained show extremely broad resonances, indicating that the mobility is dramatically constrained as may be expected to occur in a polyhedral species, even for much shorter “arms”.[21] Moreover, in our case the presence of diastereoisomers is expected; this should give a complex number of resonance lines, perhaps not resolved due to broadening originated by restricted mobility. As a matter of fact, whereas the model amino compound shown in Figure 7 shows three different peaks for methylene carbons in the α-position with respect to amino groups (these peaks have equal areas in a quantitative ^{13}C NMR spectrum), after reaction with PGE the spectrum exhibits 16 lines in the range 48.55−59.50 for these carbons, as well as seven lines in the range 66.90−68.60 associated with *C*H−OH resonances (Figure 8). The complex distribution of the respective areas of these lines is connected with the number of diastereoisomers. Furthermore, it has been observed previously by many authors[5,10,19,21,23] that the number and intensity of the peaks corresponding to a given carbon type (for example in the α-position to the Si atom) are the exact image of the type of dissymmetry of the uncompletely or completely condensed SSQO structure. The same remark holds for ^{29}Si resonances. The SSQO investigated by these authors show resonances that remained generally resolved, probably because corresponding substituents were much less bulky than ours and without asymmetric carbons.

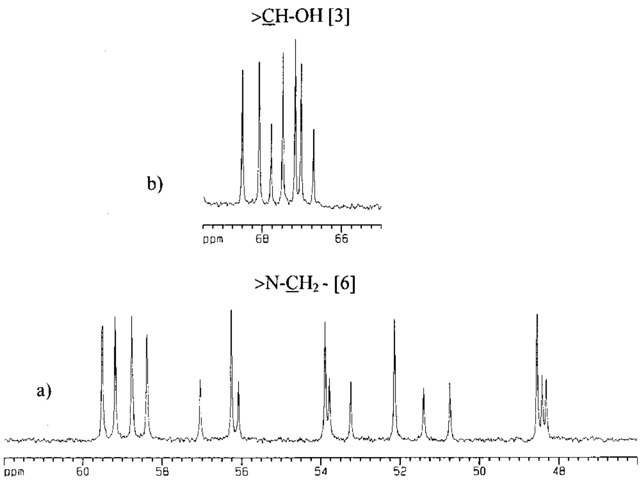


Figure 8. ^{13}C NMR spectrum ($CDCl_3$) of the mixture of diastereoisomers obtained by reaction of the model amine (Figure 7) with PGE: enlargement of (a) $\rangle N{-}\mathit{C}H_2{-}$ and (b) *C*HOH resonance regions.

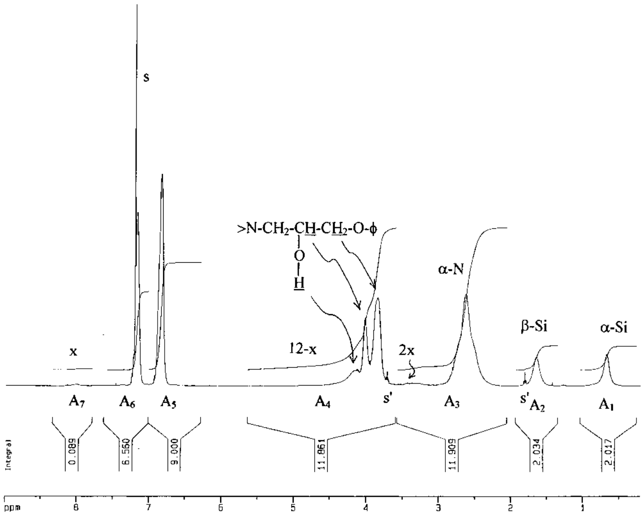


Figure 9. ^{1}H NMR spectrum in $CDCl_3$, at 60 °C, of the silsesquioxane obtained using dilute formic acid as catalyst (s = protonated residue from the deuterated chloroform; s′ = residual THF).

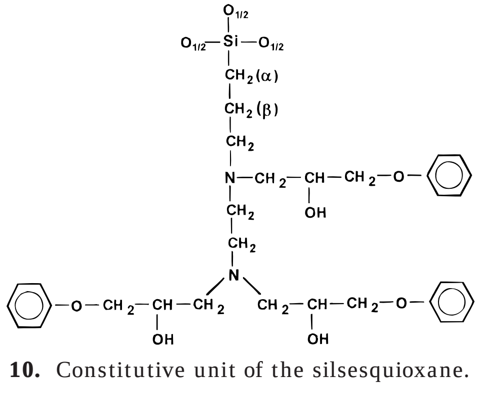


Figure 10. Constitutive unit of the silsesquioxane.

Figure 9 shows the ^{1}H NMR spectrum of the reaction product obtained with HCOOH/Si = 0.1. The constitutive unit (CU) of the expected SSQO is shown in Figure 10. For three aromatic nuclei in the region 6.5−7.5, 1.95 protons are observed at $\delta = 0.670$ corresponding to the CH_2 in the α-position to the Si atom (2 in the CU), 2.01 protons at $\delta = 1.650$ correspond to the β-CH_2 (2 in the CU). The area $A_3 = 12.08$ (12 in the CU) corresponds to all CH_2 in the α-position to the N atom, the major resonance is at $\delta = 2.625$, and a minor one, more deshielded, corresponds to the CH_2 close to a secondary alcohol esterified by HCOOH; its intensity is clearly enhanced when HCOOH/Si = 3. The area $A_4 = 11.87$ (12 in the CU), badly resolved, corresponds to CH_2−O−Ph, C*H*−OH, and CH−O*H* from high to low field. At

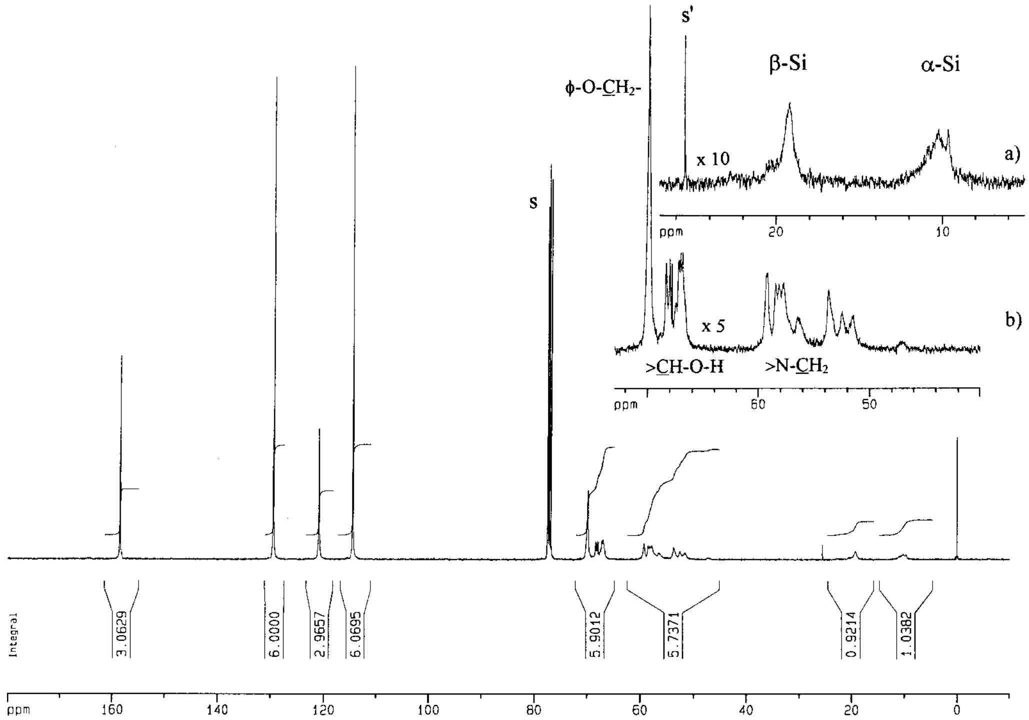


Figure 11. ^{13}C NMR ($CDCl_3$) spectrum of the silsesquioxane obtained with dilute HCOOH (s = $CDCl_3$, s′ = residual THF at δ = 25.45 and 67.75 ppm): (a) enlargement of the resonance region of the methylenic carbons in the α- and β-position to the Si atom; (b) enlargement of the 45−72 ppm region.

ambient temperature, labile exchangeable O*H* protons are deshielded and therefore well resolved; this area corresponds to nearly three protons as expected for a fully condensed SSQO with three secondary alcohol functions for one Si atom. We notice that the resonance area at δ = 8.030 which corresponds to formiate hydrogens (HCOO) is very important when HCOOH/Si = 3 instead of 0.1. In that case 0.92 formiate hydrogens are observed, which means that about 30% of the secondary hydroxyls have been esterified with formic acid. (As one OH is replaced by one HCOO, the number of hydrogens in the CU is not altered by this reaction.) The esterification reaction is reduced to 3% (Figure 9) by using a higher amount of water in the hydrolytic condensation, i.e., a diluted formic acid as the catalyst. Obviously, with NaOH or HCl as catalysts, the OH groups present in the CU remain free. When important esterification occurs, it can be easily evidenced and quantified by the *H*CO−O− resonance ($A_7 = x$) but also by the corresponding CH_2α-N resonance at δ = 3.4 ppm (2x). The corresponding ⟩C*H*−O−CO−H (x) are not resolved from the exchangeable ⟩CH−O*H* (3 − x) observed in the range 4.85−5.3 at ambient temperature.

The ^{1}H NMR spectrum suggests (a) that PGE had completely reacted with amine hydrogens during the synthesis of the precursor, (b) that SiOH groups were not present in significant amounts as no "extra" protons are detected other than the expected quantities, that is to say, for three aromatic nuclei, 2−2−12−12 from high to low field, assigned respectively to α-Si, β-Si, α-N, and all others. In incompletely condensed silsesquioxane frameworks, free SiO*H* protons (sharp resonances) have been previously found at δ = 2.00, 2.09, and 2.38 respectively for "regular exo",[19] "Z exo",[5] and "Z endo"[23] "$T_8(OH)_2$" isomers [Figure 1c], whereas H-bonded SiO*H* (broad resonances) have been found at δ = 4.44 in the range 6−7 and at δ = 7.22 for "regular endo $T_8(OH)_2$"[19] [Figure 1c], "$T_7(OH)_3$"[5,10] [Figure 1b], and "$T_6(OH)_4$".[10]

The quantitative ^{13}C NMR spectrum shown in Figure 11 gives complementary information. Methylenic carbons in the α- and β-position to the Si atom are observed at δ = 10.20 and 19.20, respectively. The integral values (referring to six aromatic nuclei) are 1.04 and 0.92 (one in the CU). The α-Si peak ($\nu_{1/2}$ = 180 Hz) is particularly broad. Its multiplicity, which should originate both from the presence of diatereoisomers and from a possible dissymmetry of the SSQO structures, is not detected. It is probably hidden by the broadening coming from reduced reorientational mobility close to the Si framework. A multiplicity of peaks corresponding to α-N methylenic carbons is observed in the range 45−63 ppm. At lower field, methine ⟩CH−O− (as confirmed by DEPT) is observed, also splitted into many lines (δ = 66.8−69) whereas CH_2−O-ϕ at 69.8 ppm is single and more intense, due to higher reorientational mobility far from the Si framework. Peaks associated with the aromatic carbons appear sharp, meaning that aromatic rings are mobile as expected due to their position at the extremity of the silsesquioxane branches. When using a high HCOOH/Si ratio (3 instead of 0.1), a broad resonance is observed at 160.85 ppm (area = 0.9). This means that 30% of the secondary hydroxyls have been esterified, in excellent agreement with the ^{1}H NMR results. In that case the product slowly evolves (in a few months) in $CDCl_3$ solution: free HCOOH (δ = 169.20) is generated, and the Si framework is also modified as attested by the ^{29}Si NMR spectrum. The same spectra are obtained with HCl/Si = 0.1 and with HCOOH/Si = 0.1.

Figure 12 shows the ^{29}Si NMR spectrum of the silsesquioxane. Four very broad peaks are observed around δ = −64.0, − 65.4, −67.7, −68.2, and a sharper one at −66.45 ppm. Although drawing straight conclusions from such a spectrum is not obvious, some indications of the most probable structures may be obtained. First of all it is convenient to state what kinds of Si are

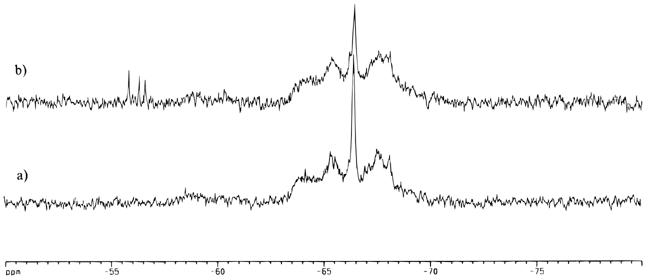


Figure 12. ^{29}Si NMR spectrum (CDCl$_3$) of the silsesquioxane obtained using (a) dilute formic acid and (b) dilute HCl as catalyst.

not present in significant proportions. SiOH groups have been reported in the region −57 to −61 ppm.[5,10,19,23] Si atoms present in strained triangular cycles show peaks in the region −54 to −58 ppm,[7,24,25] both of them being more deshielded than the Si atom in T$_8$ structures which are found in the region −65 to −67 ppm[26] for different R substituents. For example, with R = C$_6$H$_{11}$ (cyclohexyl), SiOH sites have been observed at $\delta = -56.88$, −57.47, −58.46, and −59.84 ppm for the following T$_8$(OH)$_2$ isomers: "regular exo",[19] "Z endo",[23] "Z exo",[5] and "regular endo",[19] respectively, whereas a peak at −60.16 ppm[5] is observed for the trisilanol T$_7$(OH)$_3$. For the same R, the T$_8$ and T$_6$ single ^{29}Si site is observed at −66.70 and −56.23 ppm,[5] respectively. Relative to the T$_8$ structure, both more strained cycles and SiOH sites are more deshielded. As the spectra obtained do not show any resonance between −50 and −60 ppm, it is possible to conclude that structures of the type T$_x$(OH)$_y$, as well as the strained T$_6$ structure, may be considered negligible. It is worth noticing that with dilute HCl (and not with HCOOH) some very weak and sharp resonances have been observed at −55.80, −56.30, and −56.55 ppm, accounting for the presence of traces of SiOH groups or T$_6$ structure.

For T$_8$ structures with R = (CH$_2$)$_x$CH$_3$, the chemical shift of ^{29}Si has been reported at −66.6 ($x = 5$) and −66.7 ppm ($x = 13$) in CDCl$_3$.[21] The same type of structure with R = (CH$_2$)$_3$NX$_2$ gives ^{29}Si chemical shifts from −66.2 to −66.4 ppm, depending on both the nature of the solvent and the X structure.[27] Therefore, it seems possible to assign the experimental peak at −66.45 ppm to T$_8$ structures. As for the less deshielded ^{29}Si peaks, they can be assigned to the T$_{10}$ structure. This assignment is supported by Rikowski and Marsmann's observations.[26] They prepared T$_{10}$ and T$_{12}$ SSQO cages by partial rearrangement of T$_8$ cubes, in the presence of appropriate catalysts (mainly basic or sometimes neutral salts). For a series of different R structures the chemical shift of the ^{29}Si peak for T$_{10}$ was found to be 1.028 times the one observed for T$_8$. Corresponding shift factors for the experimental peaks at −67.70 and −68.20 ppm, which are 1.017 and 1.026, respectively, are in good agreement with Marsmann's obervations. As for T$_{12}$ structures, which show two different types of Si sites [Si(A) which are part of two 8- and one 10-membered ring and Si(B) which are part of one 8- and two 10-membered rings, with ring strain leading to downfield shift[26]], two peaks with relative intensities 1:2 should be observed, with $\delta T_{12A} = 1.025 \times \delta_{T8}$ and $\delta_{12B} = 1.064 \times \delta_{T8}$.[26] According to this, no evidence of the presence of T$_{12}$ structures would thus be obtained from the ^{29}Si NMR spectrum since no resonance is observed at $\delta = -70.7$ ppm.

Part of the tremendous broadening of the resonances (except that assigned to T$_8$ structure which is surprisingly sharp) is easily attributed to stereochemical differences in the ^{29}Si environment. Rikowski and Marsmann[26] also observed an important broadening and an increased number of peaks when a mixture of two different T$_8$ (two different R and R′ structures) was rearranged. Bassindale and Gentle,[21] who observed multiple and poorly resolved ^{29}Si resonances on T$_8$ obtained by addition of alk-1-enes to T$_8$ (R = H), also explained it by the regiochemistry of the reaction (addition in α and β) causing differences in the bridging oxygen bond angle and therefore in the ^{29}Si chemical shift. An extra broadening factor is the bulky character of the organic Si substituent which is expected to produce a reduced mobility[21] of the Si atom itself and of its close environment (as shown by ^{13}C observation of carbons in the α- and β-position to the Si atom) despite a low overall viscosity of the solutions. Unfortunately, no example of SSQO cages as bulky as our compounds is available at present for comparison and evaluation of the influence of steric hindrance on peak broadening.

Therefore, ^{29}Si NMR data reported here allow to conclude that the hydrolytic condensation of our modified silane leads to a mixture of SSQO cages where T$_8$ and T$_{10}$ constitute an important part. Nevertheless, the low field ^{29}Si resonances at $\delta = -64.0$ and −65.4 ppm remain unassigned.

It is important to emphasize that the behavior found during the hydrolytic condensation of the particular modified silane described in this paper could not be reproduced for other silanes. For example, when γ-(aminopropyl)triethoxysilane was employed and the same steps were performed, a broad distribution of partially condensed products was observed in the SEC chromatograms. This is difficult to explain since no big difference was expected between a trimethoxy- and a triethoxysilane with otherwise similar structures.[9] Besides, when the previous reaction with PGE was not carried out, both aminosilanes led to a broad distribution of products after the hydrolytic condensation step.

Original results presented in this article may be summarized as follows:

(a) A modified silane was synthesized that showed the following unusual behavior: (a1) its hydrolytic condensation using different catalysts and reaction conditions always led to completely soluble products with the same narrow distribution of reaction products, as revealed by SEC; (a2) the reaction products were stable after prolonged treatments at high temperatures (150 °C), whereas under these conditions the hydrolytic condensation of most alkoxysilanes leads to high molar mass products and eventually to gelation.

(b) These stable reaction products are in our opinion a mixture of T$_n$ (polyhedral SSQO), with T$_8$ and T$_{10}$ probably constituting the main species. This statement is supported by the following arguments: (b1) No SiOH characteristic peaks clearly appeared in ^{29}Si NMR spectra, meaning that at least when HCOOH was used as catalyst, T$_x$(OH)$_y$ species were in negligible amounts (besides, products containing SiOH groups are usually unstable to prolonged treatments at high temperatures). (b2) Characteristic peaks of T$_6$ were absent in ^{29}Si NMR spectra. (b3) Peaks in the region expected for T$_8$ and T$_{10}$ were found in the ^{29}Si NMR spectra, but expected peaks for T$_{12}$ were not.

One point that merits further discussion is the assignation of peaks distributed in a very narrow region (from −63.5 to −68.5 ppm), in the ^{29}Si NMR spectrum shown in Figure 12a. Although its high-field part could be assigned to T_8 and T_{10} polyhedra, the extreme broadening of the resonance was only partly explained by the presence of diastereoisomers in the organic group attached to the Si atoms. (Proof of this was presented in Figures 7 and 8 on the basis of previous broadening observed by other authors[21,26] in similar situations.) The very bulky character of the substituent used in the frame of this work allows to expect an extra broadening of the individual resonances, but both broadening factors should hold in the same manner for different POSS structures; therefore, it remains troublesome that, compared with $\delta = -66.45$ ppm (T_8), both higher- and lower-field resonances are broader. The presence of low-field resonances (−67.7 and −68.2 ppm) and the above remark are two reasons for suspecting the presence of some other POSS structures than the major T_8 and T_{10}. To completely solve this matter, it would be necessary to relie on the organic synthesis of the proposed bulky structures starting from H_8T_8 or $H_{10}T_{10}$ (which would require multiple synthesis steps and purifications) or to try to separate the mixture of reaction products using HPLC. Both possibilities are beyond the scope of this presentation. With a view to reduce the importance of these undesired structures, some modifications of the experimental procedure have to be explored in the future.

The functionalized mixture of SSQO cages may be used as a cross-linking agent or as a modifier for several types of polymers. The octasilsesquioxane has a total of 24 OH groups, i.e., three OH groups per branch (although when the hydrolytic condensation was performed in the presence of a concentrated formic acid solution, about 30% of OH's were converted into the corresponding formiates). The functionalized SSQO may be used for example as a nanoscopic filler acting as a cross-linking unit in polyurethane formulations. (The SSQO could be dissolved in oligomeric glycols.)

Conclusions

We have reported a simple route to synthesize functionalized polyhedral silsesquioxanes bearing bulky substituents. A trifunctional aminosilane was reacted with a stoichiometric amount of phenylglycidyl ether (PGE). When the addition was completed, apart from the trisubstituted product, a distribution of oligomeric species, arising from the intermolecular reaction of methoxysilanes with generated OH groups, was observed. But when this product was subjected to hydrolytic condensation using a variety of catalysts (HCl, NaOH, HCOOH), a mixture of silsesquioxane cages, $(RSiO_{1.5})_n$, was obtained with T_8 and T_{10} being the main products of the synthesis. Due to their high OH functionality, these spherosiloxanes may be used in several types of polymer formulations.

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References and Notes

(1) Provatas, A.; Matisons, J. G. *Trends Polym. Sci. (Cambridge, U.K.)* **1997**, *5*, 327 and references therein.
(2) Earley, C. W. *J. Phys. Chem.* **1994**, *98*, 8693.
(3) Brown, J. F.; Vogt, L. H. *J. Am. Chem. Soc.* **1965**, *87*, 4313.
(4) Brown, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 4317.
(5) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741.
(6) Behbehani, H.; Brisdon, B. J.; Mahon, M. F.; Molloy, K. C. *J. Organomet. Chem.* **1994**, *469*, 19.
(7) Unno, M.; Alias, S. B.; Saito, H.; Matsumoto, H. *Organometallics* **1996**, *15*, 2413.
(8) Voronkov, M. G.; Lavrent'yev, V. I. *Top. Curr. Chem.* **1982**, *102*, 199.
(9) Feher, F. J.; Newman, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 1931.
(10) Feher, F. J.; Budzichowski, T. A.; Blanski, R. L.; Weller, K. J.; Ziller, J. W. *Organometallics* **1991**, *10*, 2526.
(11) Shockey, E.; Lichtenhan, J. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 525.
(12) Otonari, Y. A.; Lichtenhan, J. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*, 513.
(13) Feher, F. J.; Weller, K. J.; Schwab, J. J. *Organometallics* **1995**, *14*, 2009.
(14) Lichtenhan, J. D.; Otonari, Y. A.; Carr, M. J. *Macromolecules* **1995**, *28*, 8435.
(15) Haddad, T. S.; Lichtenhan, J. D. *Macromolecules* **1996**, *29*, 7302.
(16) Lichtenhan, J. D. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 10, pp 7768−7778.
(17) Lichtenhan, J. D.; Haddad, T. S.; Schwab, J. J.; Carr, M. J.; Chaffee, K. P.; Mather, P. T. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 489.
(18) Feher, F. J.; Soulivong, D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 491.
(19) Feher, F J.; Soulivong, D.; Eklund, A. G. *Chem. Commun.* **1998**, 399.
(20) Serier, A.; Pascault, J. P.; Lam, T. M. *J. Polym. Sci. A: Polym. Chem.* **1991**, *29*, 1125.
(21) Bassindale, A. R.; Gentle, T. E. *J. Mater. Chem.* **1993**, *3*, 1319.
(22) Brown, J. F.; Vogt, L. H.; Prescott, P. I. *J. Am. Chem. Soc.* **1964**, *86*, 1120.
(23) Feher, F. J.; Soulivong, D.; Nguyen, F. *Chem. Commun.* **1998**, 1279.
(24) Feher, F. J.; Soulivong, D.; Lewis, G. T. *J. Am. Chem. Soc.* **1997**, *119*, 11323.
(25) Smolin, Y. I.; Shepelev, Y. F.; Ershov, A. S.; Hoebbel, D.; Wieker, W. *Kristallografiya* **1984**, *29*, 712.
(26) Rikowski, E.; Marsmann, H. C. *Polyhedron* **1997**, *16*, 3357.
(27) Feher, F. J.; Wyndham, K. D. *Chem. Commun.* **1998**, 323.

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