

# One-Step Synthesis of Polyhedral Silsesquioxanes Bearing Bulky Substituents: UV-MALDI-TOF and ESI-TOF Mass Spectrometry Characterization of Reaction Products

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**ABSTRACT:** The NaOH-catalyzed hydrolytic condensation of the reaction product between *N*-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane and phenyl glycidyl ether (PGE) was followed by matrix-assisted ultraviolet laser desorption/ionization time-of-flight mass spectrometry (UV-MALDI-TOF MS) and electrospray ionization time-of-flight mass spectrometry (ESI-TOF MS). After 24 h at 50 °C, main condensation products were a mixture of perfect and imperfect polyhedra: T<sub>8</sub>, T<sub>9</sub>(OH), and T<sub>10</sub>, with traces of T<sub>7</sub>(OH) and T<sub>11</sub>(OH). Every one of these products was composed of a series of peaks in the mass spectra, accounting for the incomplete reaction of PGE with the aminosilane (e.g., T<sub>8</sub> showed the presence of the species containing 24 PGE units arising from the complete reaction of the initial silane, as well as species containing 23, 22, and 21 PGE units). A thermal treatment to 150 °C led to the appearance of extra peaks corresponding to intramolecular dehydration products. Peaks corresponding to the loss of one water molecule from T<sub>9</sub>(OH) and T<sub>7</sub>(OH) were present and could be ascribed to the reaction between SiOH and a secondary OH group. Dehydration products from T<sub>8</sub> and T<sub>10</sub> were observed, as well as species arising from the loss of two water molecules from T<sub>9</sub>(OH) and T<sub>7</sub>(OH). A plausible explanation for the presence of these peaks is the rupture of a Si–O–Si bond in the presence of NaOH, followed by condensation of the resulting fragments with secondary OH groups.

## Introduction

Polyhedral silsesquioxanes, (RSiO<sub>1.5</sub>)<sub>*n*</sub> or T<sub>*n*</sub>, where *n* is an even number and R represents a variety of organic groups, H, Cl, etc., have enormous potential as building blocks for advanced materials.<sup>1</sup> Typical members of this family are the octahedron (T<sub>8</sub>), the decahedron (T<sub>10</sub>), and the dodecahedron (T<sub>12</sub>). These compounds or their precursors may be isolated in low to moderate yields from the hydrolytic condensation of trialkoxy- or trichlorosilanes under strictly controlled conditions.<sup>2–5</sup> One typical precursor is R<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub> or T<sub>7</sub>(OH)<sub>3</sub>. Its reaction with a trichlorosilane leads to a T<sub>8</sub> with one corner attached to an organic group containing a polymerizable or graftable functionality.<sup>6–10</sup> However, cost-effective processes should be devised to synthesize appropriately functionalized silsesquioxanes on a large scale.

A simple route to synthesize mixtures of polyhedral silsesquioxanes in high yield is the hydrolytic condensation of a trialkoxysilane containing a bulky organic substituent.<sup>11</sup> The hydrolytic condensation of the reaction product between *N*-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane and a stoichiometric amount of phenyl glycidyl ether (PGE), using a variety of catalysts (HCl, NaOH, HCOOH), led to a remarkably stable reaction product. Its characterization by SEC, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>29</sup>Si NMR enabled us to infer that the condensation product was a mixture of octahedra (T<sub>8</sub>) and decahedra (T<sub>10</sub>).

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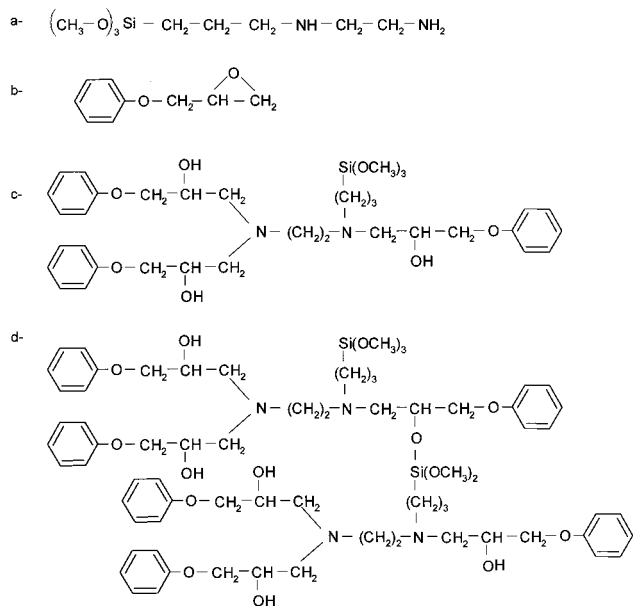
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The aim of this study is to characterize the reaction products in detail, in two different steps of the NaOH-catalyzed hydrolytic condensation, by using matrix-assisted ultraviolet laser desorption/ionization time-of-flight mass spectrometry (UV-MALDI-TOF MS) and electrospray ionization time-of-flight mass spectrometry (ESI-TOF MS). The use of advanced MS techniques for the characterization of silsesquioxanes has been reported in recent publications.<sup>12–18</sup> Hong et al.<sup>12</sup> reported the characterization of highly charged dendrimers with encapsulated cuboid octasilsesquioxanes and molar masses up to about 5500 Da, using ESI MS. Bakhtiar et al.<sup>13,14</sup> reported the mass spectrometric characterization of polyhedral oligosilsesquioxanes and their metal-containing derivatives (with Si–O–M bonds), using atmospheric pressure chemical ionization and turbo ion-spray mass spectrometry. Wallace et al.<sup>15,16</sup> and Eisenberg et al.<sup>17</sup> used MALDI-TOF MS to characterize broad molar mass distributions of incompletely condensed silsesquioxanes. The degree of intramolecular condensation was established for every member of the series of oligomers,<sup>15,16</sup> and key species present in the condensation process were identified.<sup>17</sup> Matejka et al.<sup>18</sup> used ESI MS to characterize the distribution of species present during the hydrolytic condensation of 3-glycidioxypropyltrimethoxysilane. A complex distribution of reaction products was found, including polyhedra and incompletely condensed species.

## Experimental Section

**Synthesis of the Modified Silane.** The starting silane was *N*-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane (Aldrich, 97% purity). Amino groups were capped with phenyl glycidyl ether



**Figure 1.** Chemical structures of (a) *N*-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane; (b) phenyl glycidyl ether, PGE; (c) modified silane obtained by reaction of (a) and (b); and (d) dimer of the modified silane.

(PGE, Aldrich, 99% purity), using about 95% of the stoichiometric value to avoid the homopolymerization of epoxy groups initiated by the tertiary amines present in the silane structure.<sup>11</sup> The reaction was carried out in glass tubes sealed under vacuum and placed in a thermostat held at 50 °C. After 24 h, a complete reaction of PGE was observed.<sup>11</sup> Structures of reagents and reaction products are shown in Figure 1. Apart from the modified silane, a series of oligomers arising from the intermolecular reaction of Si-OCH<sub>3</sub> groups with secondary hydroxyls generated by the epoxy-amine reaction were observed.<sup>11</sup> The structure of a dimer is shown in Figure 1. Oligomers were reconverted into the modified silane monomer in the course of the hydrolytic condensation step.

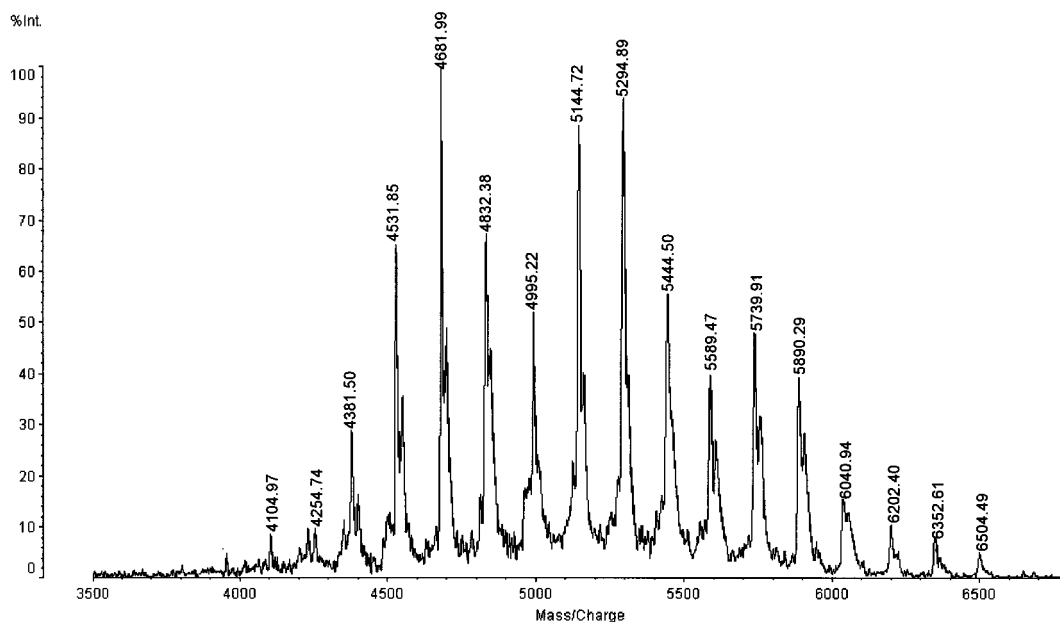
**Synthesis of the Silsesquioxanes.** The hydrolytic condensation of the modified silane was performed in THF solution (40 g of the modified silane in 50 mL of THF), using NaOH as a catalyst (molar ratios NaOH/Si = 0.05, H<sub>2</sub>O/Si = 3). Temperature was held at 50 °C for 24 h, leading to the

silsesquioxane. Its thermal stability was studied by increasing temperature in steps according to the following program: 1 h at 75 °C, 3 h at 100 °C, 3 h at 120 °C, and 1 h at 150 °C. The structures of the silsesquioxanes obtained at 50 °C and after the thermal treatment at 150 °C were characterized by mass spectrometry.

**Mass Spectrometry.** Matrix-assisted ultraviolet laser desorption/ionization time-of-flight mass spectrometry (UV-MALDI-TOF MS) was performed using a Shimadzu Kratos, Compact MALDI 4 device with pulsed extraction and tunable time delay capability. It was equipped with a pulsed nitrogen laser ( $\lambda = 337$  nm, pulse width = 3 ns, average power at 20 Hz = 5 mW). The extraction voltage in TOF analyzers was 20 kV, and ions were obtained by irradiation just above the threshold laser power (about 1/3 of the average laser power). Samples were measured in the linear, positive, and negative ion modes. Usually 50 spectra were accumulated.

After exploratory runs using several chemicals—2-(4-hydroxyphenylazo)benzoic acid (HABA), 9*H*-pyrido[3,4-*b*]indole (nor-harmaline), *trans*-3-indoleacrylic acid (IAA), and 2,5-dihydroxybenzoic acid (gentisic acid, GA)—GA was selected as the best matrix leading to high-resolution mass spectra. The sample probe tip was coated with a mixture 8:1 (v/v) of matrix (GA, 10 mg/mL in THF) and analyte (1 mg/mL in THF). Tetrahydrofuran was HPLC grade (Aldrich). Two coatings (0.5  $\mu$ L each) were performed, and solvent was removed by blowing air at room temperature after each one of the coatings. Calibration was performed using solutions of insulin from bovine pancreas (Sigma) and angiotensin I (Sigma) in a 0.1% aqueous solution of trifluoroacetic acid (TFA, Merck) and cyclodextrins (Sigma) in water (Milli-Q grade).

The positive-ion electrospray ionization time-of-flight (ESI-TOF) mass spectra were acquired by directly infusing the polymers solution (0.0004 mg/mL methanol-water 9:1) into the ESI ion source of the Mariner PerSeptive Biosystems ESI-TOF mass spectrometer. The *m/z* range of the mass spectrometer was 500–3000 Da. Methanol-water (9:1) was used as solvent stream. The spray tip potential was +2695.9 V, the nozzle potential was +120.1 V, and the skimmer voltage was +12.01 V. Nozzle temperature was 140 °C. A Harvard PHD 2000 syringe infusion pump at a flow rate of 10  $\mu$ L min<sup>-1</sup> was used for polymer solution introduction. The nitrogen flow rate was 0.4 L min<sup>-1</sup>. The analyzer temperature was kept at 31.7 °C and pressure at 0.55 MPa. The mass calibration was achieved by using angiotensin I (Sigma, 0.0154 mg/mL methanol-water 1:1).



**Figure 2.** UV-MALDI-TOF mass spectrum of the silsesquioxane synthesized at 50 °C.

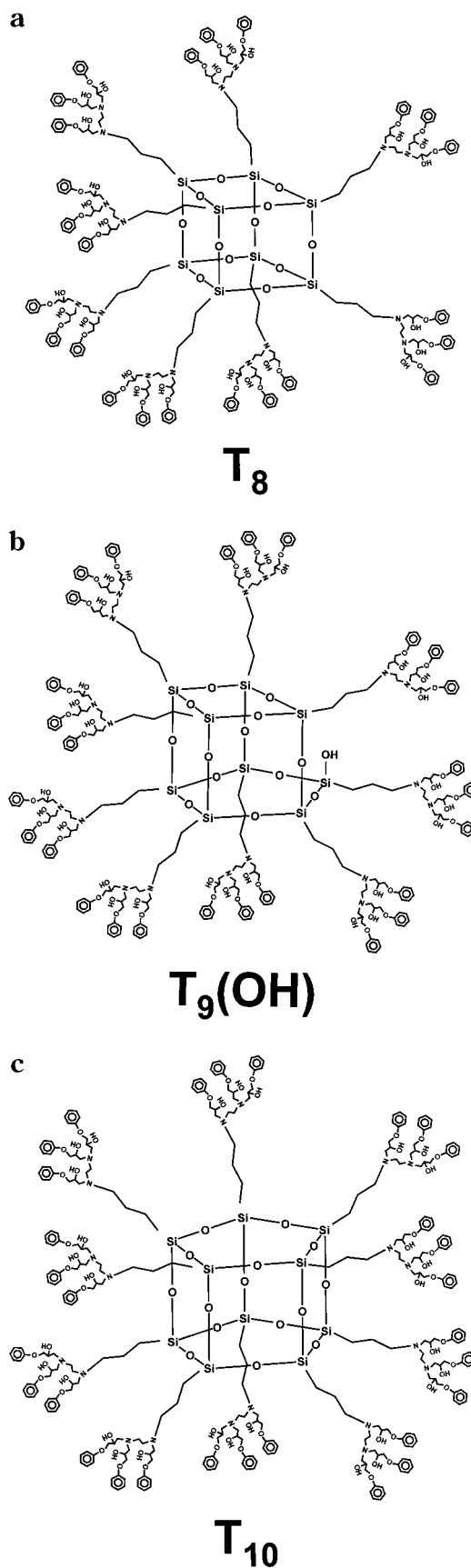
**Table 1. Assignment of UV-MALDI-TOF MS Peaks for the Silsesquioxanes Synthesized at 50 °C and after the Thermal Treatment to 150 °C**

assignment	calcd <i>m/z</i>	exptl <i>m/z</i> (50 °C)	exptl <i>m/z</i> (150 °C)
T <sub>7</sub> (OH) (20 PGE) – 2H <sub>2</sub> O	4050.3 (+H <sup>+</sup> )		4051.2
T <sub>7</sub> (OH) (20 PGE) – H <sub>2</sub> O	4068.3 (+H <sup>+</sup> )		4068.2
T <sub>7</sub> (OH) (20 PGE)	4108.3 (+Na <sup>+</sup> )	4105.0	4107.7
T <sub>7</sub> (OH) (21 PGE) – 2H <sub>2</sub> O	4200.5 (+H <sup>+</sup> )		4201.3
T <sub>7</sub> (OH) (21 PGE) – H <sub>2</sub> O	4218.5 (+H <sup>+</sup> )		4218.6
T <sub>7</sub> (OH) (21 PGE)	4236.5 (+H <sup>+</sup> )	4232.8	4237.9
T <sub>7</sub> (OH) (21 PGE)	4258.5 (+Na <sup>+</sup> )	4254.7	4257.0
T <sub>8</sub> (21 PGE) – H <sub>2</sub> O	4362.8 (+H <sup>+</sup> )		4365.6
T <sub>8</sub> (21 PGE)	4380.8 (+H <sup>+</sup> )	4381.5	4382.3
T <sub>8</sub> (21 PGE)	4402.8 (+Na <sup>+</sup> )	4402.7	4400.0
T <sub>8</sub> (22 PGE) – H <sub>2</sub> O	4512.9 (+H <sup>+</sup> )		4513.3
T <sub>8</sub> (22 PGE)	4530.9 (+H <sup>+</sup> )	4531.9	4532.5
T <sub>8</sub> (22 PGE)	4552.9 (+Na <sup>+</sup> )	4552.7	4551.5
T <sub>8</sub> (23 PGE) – H <sub>2</sub> O	4663.1 (+H <sup>+</sup> )		4663.1
T <sub>8</sub> (23 PGE)	4681.1 (+H <sup>+</sup> )	4682.0	4682.2
T <sub>8</sub> (23 PGE)	4703.1 (+Na <sup>+</sup> )	4702.2	4701.2
T <sub>8</sub> (24 PGE) – H <sub>2</sub> O	4813.3 (+H <sup>+</sup> )		4813.5
T <sub>8</sub> (24 PGE)	4831.3 (+H <sup>+</sup> )	4832.4	4832.5
T <sub>8</sub> (24 PGE)	4853.3 (+Na <sup>+</sup> )	4850.4	4851.5
T <sub>9</sub> (OH) (24 PGE) – 2H <sub>2</sub> O	4957.6 (+H <sup>+</sup> )		4956.2
T <sub>9</sub> (OH) (24 PGE) – H <sub>2</sub> O	4975.6 (+H <sup>+</sup> )		4976.6
T <sub>9</sub> (OH) (24 PGE)	4993.6 (+H <sup>+</sup> )	4995.2	4996.1
T <sub>9</sub> (OH) (24 PGE)	5015.6 (+Na <sup>+</sup> )	5017.0	5011.3
T <sub>9</sub> (OH) (25 PGE) – 2H <sub>2</sub> O	5107.7 (+H <sup>+</sup> )		5104.5
T <sub>9</sub> (OH) (25 PGE) – H <sub>2</sub> O	5125.7 (+H <sup>+</sup> )		5125.5
T <sub>9</sub> (OH) (25 PGE)	5143.7 (+H <sup>+</sup> )	5144.7	5145.4
T <sub>9</sub> (OH) (25 PGE)	5165.7 (+Na <sup>+</sup> )	5166.3	5166.4
T <sub>9</sub> (OH) (26 PGE) – H <sub>2</sub> O	5275.9 (+H <sup>+</sup> )		5276.3
T <sub>9</sub> (OH) (26 PGE)	5293.9 (+H <sup>+</sup> )	5294.9	5295.5
T <sub>9</sub> (OH) (26 PGE)	5315.9 (+Na <sup>+</sup> )	5316.2	5315.3
T <sub>9</sub> (OH) (27 PGE) – H <sub>2</sub> O	5426.1 (+H <sup>+</sup> )		5423.9
T <sub>9</sub> (OH) (27 PGE)	5444.1 (+H <sup>+</sup> )	5444.5	5445.7
T <sub>9</sub> (OH) (27 PGE)	5466.1 (+Na <sup>+</sup> )	5465.9	5466.5
T <sub>10</sub> (27 PGE) – H <sub>2</sub> O	5570.4 (+H <sup>+</sup> )		5566.6
T <sub>10</sub> (27 PGE)	5588.4 (+H <sup>+</sup> )	5589.5	5588.9
T <sub>10</sub> (27 PGE)	5610.4 (+Na <sup>+</sup> )	5610.9	5612.6
T <sub>10</sub> (28 PGE) – H <sub>2</sub> O	5720.5 (+H <sup>+</sup> )		5720.7
T <sub>10</sub> (28 PGE)	5738.5 (+H <sup>+</sup> )	5739.9	5739.8
T <sub>10</sub> (28 PGE)	5760.5 (+Na <sup>+</sup> )	5760.5	5761.0
T <sub>10</sub> (29 PGE) – H <sub>2</sub> O	5870.7 (+H <sup>+</sup> )		5869.9
T <sub>10</sub> (29 PGE)	5888.7 (+H <sup>+</sup> )	5890.3	5888.8
T <sub>10</sub> (29 PGE)	5910.7 (+Na <sup>+</sup> )	5911.0	5908.0
T <sub>10</sub> (30 PGE)	6038.9 (+H <sup>+</sup> )	6040.9	6040.4
T <sub>10</sub> (30 PGE)	6060.9 (+Na <sup>+</sup> )	6060.2	
T <sub>11</sub> (OH) (30 PGE)	6201.1 (+H <sup>+</sup> )	6202.4	
T <sub>11</sub> (OH) (31 PGE)	6351.3 (+H <sup>+</sup> )	6352.6	
T <sub>11</sub> (OH) (32 PGE)	6501.5 (+H <sup>+</sup> )	6504.5	
T <sub>11</sub> (OH) (33 PGE)	6651.7 (+H <sup>+</sup> )	6652.1	

## Results and Discussion

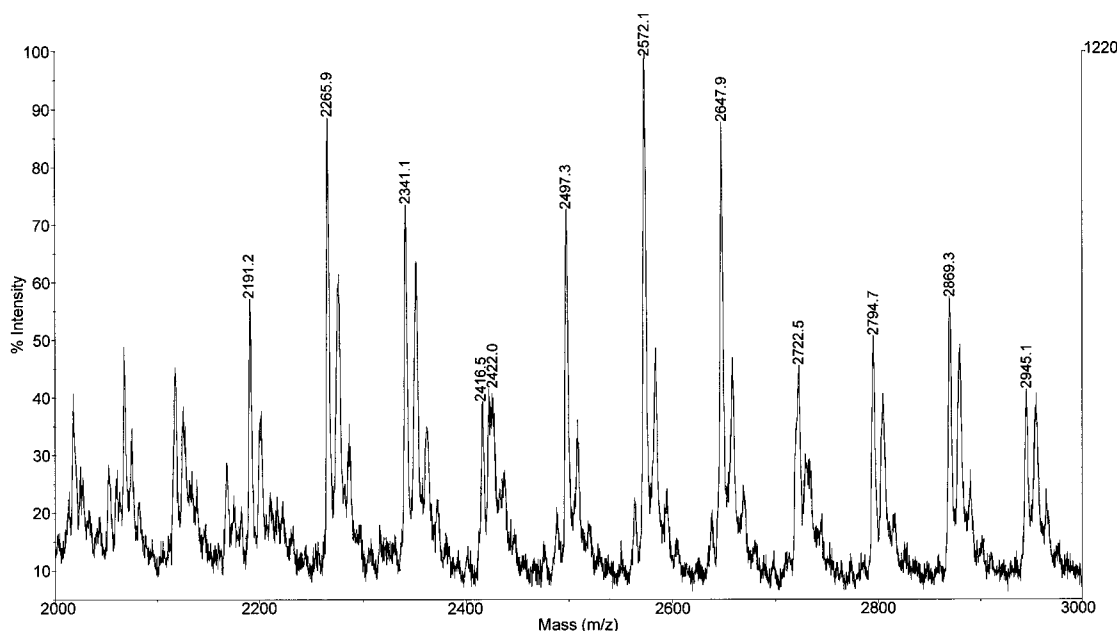
**Silsesquioxane Resulting from the Synthesis at 50 °C.** Figure 2 shows the MALDI-TOF mass spectrum of the product obtained after the step at 50 °C. The following notation was used to indicate the different species present in the silsesquioxane. T<sub>*n*</sub> (*m* PGE) represents a perfect polyhedron with *n* (even number) Si atoms and *m* PGE units covalently bonded to amine nitrogens of the initial silane. This leads to the presence of *m* secondary hydroxyl groups attached to C atoms of the organic chains. The maximum number of PGE units is three per Si atom for the case that every amine hydrogen of the starting silane has been reacted with PGE. This gives a maximum value of *m* equal to 3*n*. But also, species with *m* = 3*n* – 1, 3*n* – 2 and 3*n* – 3, arising from the slight defect of PGE used in the reaction with the aminosilane, were identified (e.g., T<sub>8</sub> species with 21–24 reacted PGE units were identified).

T<sub>*n*</sub>(OH) (*m* PGE) represents a polyhedron with *n* (odd number) Si atoms, one SiOH group, and *m* PGE units



**Figure 3.** Schematic representation of T<sub>8</sub>, T<sub>9</sub>(OH), and T<sub>10</sub> structures containing the stoichiometric number of PGE units (24, 27, and 30, respectively).

reacted with amine hydrogens of the initial silane. This gives *m* secondary hydroxyl groups attached to C atoms



**Figure 4.** ESI-TOF mass spectrum in the 2000–3000  $m/z$  range for the silsesquioxane synthesized at 50 °C.

of the organic chains. Species with values of  $m$  equal to  $3n$ ,  $3n - 1$ ,  $3n - 2$ , and  $3n - 3$  were identified.

Table 1 shows the assignment of the main peaks appearing in the mass spectra. Peaks corresponding to the ionization with  $H^+$  and  $Na^+$ , the former being more intense than the latter, could be identified. Three main structures are present:  $T_8$ ,  $T_9(OH)$ , and  $T_{10}$ , with traces of  $T_7(OH)$  and  $T_{11}(OH)$ . Figure 3 shows a schematic representation of  $T_8$ ,  $T_9(OH)$ , and  $T_{10}$  structures containing the stoichiometric number of PGE units (24, 27, and 30, respectively). Mass spectrometry cannot prove that the molecules are regular polyhedra. But these structures are consistent with experimental observations on model compounds and theoretical investigations showing that possible isomers containing  $(Si-O)_3$  rings are significantly less stable than molecules containing only larger rings.<sup>19</sup>

Therefore, the hydrolytic condensation of the particular trialkoxysilane bearing a bulky organic substituent, under mild conditions, leads to a very high yield of polyhedral silsesquioxanes with structures in the  $T_8$ – $T_{10}$  range. Using SEC,  $^1H$  NMR,  $^{13}C$  NMR, and  $^{29}Si$  NMR as characterization techniques, we had postulated that the silsesquioxane was a mixture of  $T_8$  and  $T_{10}$ .<sup>11</sup> The use of UV-MALDI-TOF MS enabled us to confirm the presence of these two polyhedra and to add the species  $T_9(OH)$  which is also present in high concentration.

ESI-TOF mass spectra of the silsesquioxane resulting from the step at 50 °C were obtained in the 500–3000  $m/z$  range. A high number of peaks corresponding to a multiple ionization of reaction products were observed. The range between 2200 and 3000  $m/z$  was relatively clean because only peaks corresponding to double-ionized species ( $z = 2$ ) were present. Figure 4 shows the ESI-TOF mass spectrum in the 2000–3000  $m/z$  range. Every species of generic mass  $M$  is characterized by the presence of three peaks at  $(M + 2H^+)/2$  (high intensity),  $(M + H^+ + Na^+)/2$  (medium intensity), and  $(M + 2Na^+)/2$  (low intensity).

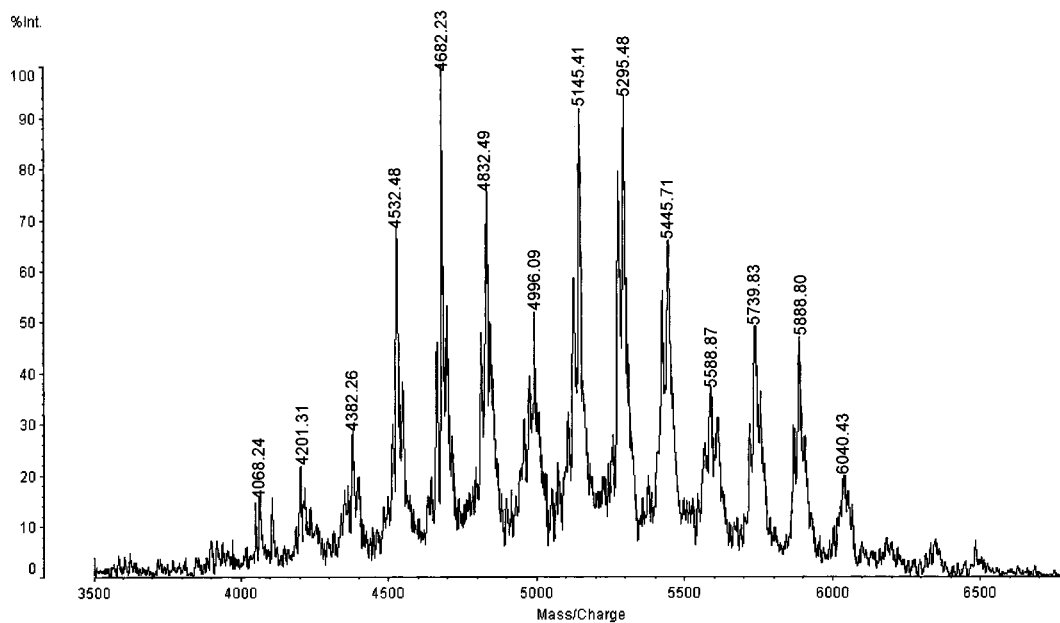
Table 2 shows the assignment of peaks corresponding to species bearing two  $H^+$ . The same products appearing in the MALDI-TOF MS spectra could be identified

**Table 2. Assignment of ESI-TOF MS Peaks for the Silsesquioxanes Synthesized at 50 °C and after the Thermal Treatment to 150 °C**

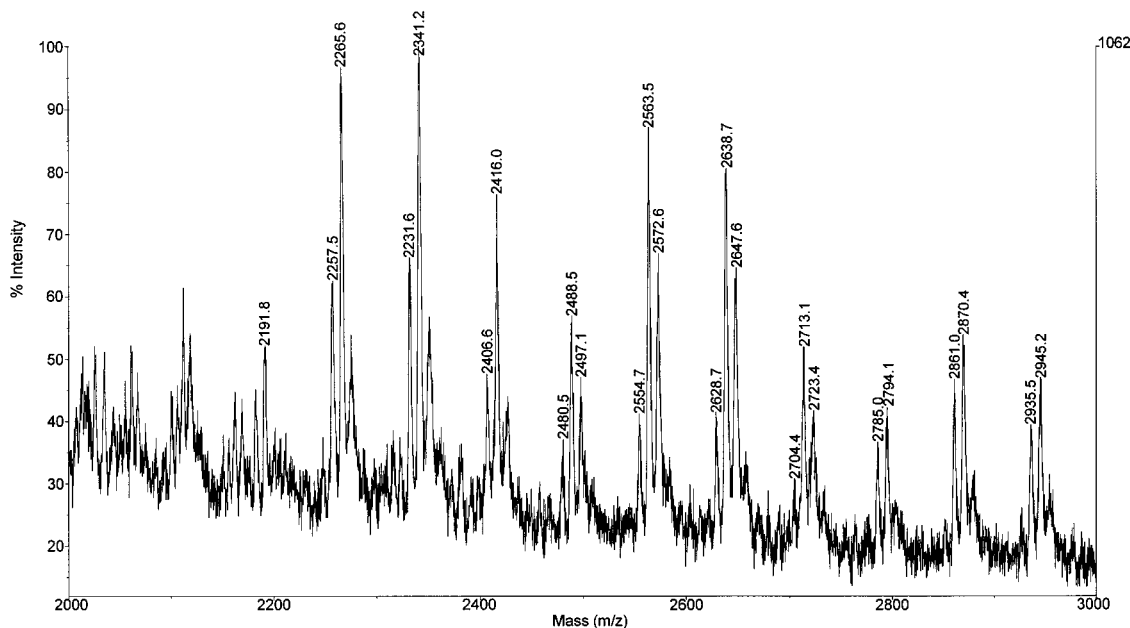
assignment	calcd $m/z$ (+2 $H^+$ )	2 (exptl $m/z$ ), 50 °C <sup>a</sup>	2 (exptl $m/z$ ), 150 °C <sup>a</sup>
$T_8$ (21 PGE)	4381.8	4382.5	4383.7
$T_8$ (22 PGE) – $H_2O$	4513.9		4515.0
$T_8$ (22 PGE)	4531.9	4531.9	4531.2
$T_8$ (23 PGE) – $H_2O$	4664.1		4663.2
$T_8$ (23 PGE)	4682.1	4682.3	4682.4
$T_8$ (24 PGE) – $H_2O$	4814.3		4813.1
$T_8$ (24 PGE)	4832.3	4832.3	4832.1
$T_9(OH)$ (23 PGE)	4844.4	4844.1	
$T_9(OH)$ (24 PGE) – $2H_2O$	4958.6		4961.1
$T_9(OH)$ (24 PGE) – $H_2O$	4976.6		4977.0
$T_9(OH)$ (24 PGE)	4994.6	4994.6	4994.2
$T_9(OH)$ (25 PGE) – $2H_2O$	5108.7		5109.3
$T_9(OH)$ (25 PGE) – $H_2O$	5126.7		5127.0
$T_9(OH)$ (25 PGE)	5144.7	5144.2	5145.2
$T_9(OH)$ (26 PGE) – $2H_2O$	5258.9		5257.3
$T_9(OH)$ (26 PGE) – $H_2O$	5276.9		5277.4
$T_9(OH)$ (26 PGE)	5294.9	5295.7	5295.3
$T_9(OH)$ (27 PGE) – $2H_2O$	5409.1		5408.7
$T_9(OH)$ (27 PGE) – $H_2O$	5427.1		5426.2
$T_9(OH)$ (27 PGE)	5445.1	5445.0	5446.8
$T_{10}$ (27 PGE) – $H_2O$	5571.4		5569.9
$T_{10}$ (27 PGE)	5589.4	5589.3	5588.3
$T_{10}$ (28 PGE) – $H_2O$	5721.5		5722.1
$T_{10}$ (28 PGE)	5739.5	5738.6	5740.9
$T_{10}$ (29 PGE) – $H_2O$	5870.7		5871.0
$T_{10}$ (29 PGE)	5889.7	5890.2	5890.4

<sup>a</sup> Calculated from experimental  $m/z$  data ( $z = 2$ ), as 2 ( $m/z$ ).

with a much better precision. (The difference between experimental and predicted masses is less than 1 Da for every species.) The only difference is the appearance of  $T_9(OH)$  (23 PGE) superimposed in the cluster of double-ionized peaks of  $T_8$  (24 PGE). Inspection of the region between 2000 and 2200  $m/z$  showed the presence of peaks ascribed to triple-ionized species with 10 and 11 Si atoms superimposed with double-ionized species with seven Si atoms. Species with 12 or more Si atoms, which should have appeared as triple-ionized products in the 2200–3000  $m/z$  range, were not present, in agreement with results obtained with MALDI-TOF MS. Small peaks corresponding to the loss of one water



**Figure 5.** UV-MALDI-TOF mass spectrum of the silsesquioxane after the thermal treatment to 150 °C.



**Figure 6.** ESI-TOF mass spectrum in the 2000–3000  $m/z$  range for the silsesquioxane after the thermal treatment to 150 °C.

molecule from  $T_9(\text{OH})$  (24–26 PGE) are present in the ESI-TOF mass spectrum at  $2(M + 2\text{H}^+) = 4976.0$ , 5126.3, and 5276.6 (theoretical values = 4976.6, 5126.7, and 5276.9). These species could not be detected by MALDI-TOF MS. Although it cannot be discarded that they were effectively present in the reaction product, they may have also formed during the infusion of the solution into the ESI ion source through the nozzle at 140 °C.

The combination of MALDI-TOF MS and ESI-TOF MS enabled us to assess that the silsesquioxane resulting from the one-step synthesis at 50 °C was mainly composed of a mixture of  $T_8$ ,  $T_9(\text{OH})$ , and  $T_{10}$  polyhedra, with minor amounts of  $T_7(\text{OH})$  and  $T_{11}(\text{OH})$ .

**Silsesquioxane Resulting from the Heating up to 150 °C.** Figure 5 shows the MALDI-TOF mass spectrum of the silsesquioxane obtained after the thermal treatment to 150 °C, and Table 1 shows the

assignment of the main peaks. While the species observed in the original silsesquioxane are present after the thermal treatment, new structures generated by intramolecular rearrangements could be identified. Species  $T_8$  and  $T_{10}$  generate new structures arising from a loss of one water molecule. Species  $T_7(\text{OH})$  and  $T_9(\text{OH})$  generate two sets of new structures arising from the loss of one and two water molecules. Possibly the same occurs for the traces of  $T_{11}(\text{OH})$  that could not be resolved with enough precision.

Figure 6 shows the ESI-TOF mass spectrum in the 2000–3000  $m/z$  range for the silsesquioxane heated to 150 °C. The assignment of peaks is shown in Table 2. The presence of species derived from the loss of one water molecule from  $T_8$ ,  $T_9(\text{OH})$ , and  $T_{10}$ , and the loss of two water molecules from  $T_9(\text{OH})$ , is confirmed.

The loss of the first molecule of water in  $T_7(\text{OH})$  and  $T_9(\text{OH})$  is probably due to the intramolecular reaction

between the SiOH group and a secondary alcohol to give a C–O–Si bond. The loss of the water molecule in T<sub>8</sub> and T<sub>10</sub>, and the second water molecule in T<sub>7</sub>(OH) and T<sub>9</sub>(OH), requires a different explanation. A plausible mechanism is the rupture of a Si–O–Si bond, in the presence of NaOH, followed by condensation with two secondary alcohols, giving two C–O–Si bonds and deleting one water molecule. Cage rearrangement of silsesquioxanes in the presence of NaOH has been reported.<sup>20</sup>

### Conclusions

A trialkoxysilane containing a bulky organic substituent was synthesized by the reaction between *N*-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane and phenyl glycidyl ether (PGE). Its NaOH-catalyzed hydrolytic condensation was followed by UV-MALDI-TOF and ESI-TOF mass spectrometry. After 24 h at 50 °C, main condensation products were T<sub>8</sub>, T<sub>9</sub>(OH), and T<sub>10</sub>, with traces of T<sub>7</sub>(OH) and T<sub>11</sub>(OH). Every one of these products was composed of a series of peaks in the mass spectra, accounting for the incomplete reaction of PGE with the aminosilane (e.g., T<sub>8</sub> showed the presence of a species containing 21–24 PGE units). A thermal treatment to 150 °C led to the appearance of extra peaks corresponding to intramolecular dehydration products. Peaks corresponding to the loss of one water molecule from T<sub>9</sub>(OH) and T<sub>7</sub>(OH) were present and could be ascribed to the reaction between a SiOH group and a secondary OH group. But also dehydration products from T<sub>8</sub> and T<sub>10</sub> were observed, as well as species arising from the loss of two water molecules from T<sub>9</sub>(OH) and T<sub>7</sub>(OH). A plausible explanation for the presence of these peaks is the rupture of a Si–O–Si bond followed by the condensation with secondary OH groups.

The synthesized polyhedral silsesquioxanes are high-functional polyols that may be used as building blocks for a variety of thermosetting polymers.

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