Poly(silsesquioxanes) derived from the hydrolytic condensation of organotrialkoxysilanes containing hydroxyl groups

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Abstract

Organotrialkoxysilanes containing secondary hydroxyl groups were synthesized by reacting 1 mole of (3-aminopropyl)triethoxysilane (APS) with 1 or 2 mole of phenylglycidylether (PGE). Resulting products, APS–PGE and APS–PGE$_2$, respectively, were subjected to hydrolytic condensation at 50 °C during 24 h. For APS–PGE, the reaction was performed using a molar ratio [H$_2$O]/Si = 3, without addition of an external catalyst. For APS–PGE$_2$, the reaction was catalyzed by HCOOH or NaOH. Resulting poly(silsesquioxanes) (PSSO) were characterized by size exclusion chromatography, Fourier-transformed infrared spectroscopy and matrix-assisted ultraviolet laser desorption/ionization time-of-flight mass spectrometry (UV-MALDI-TOF MS). PSSO derived from APS–PGE and APS–PGE$_2$, catalyzed by HCOOH, exhibited a relatively narrow distribution of polyhedral structures. This constitutes a simple one-step synthesis of polyhedral oligomeric silsesquioxanes (POSS) functionalized with amine and/or hydroxyl groups. The directionality of the reaction pathway towards the formation of polyhedral structures was ascribed to the formation of intramolecular Si–O–C bonds through the reaction of SiOEt or SiOH groups with secondary hydroxyl groups. Intramolecular Si–O–C bonds were found in the structures of APS–PGE and APS–PGE$_2$, and in most of the species of the PSSO obtained from the NaOH-catalyzed reaction of APS–PGE$_2$. A small fraction of surviving Si–O–C bonds was also found in the polyhedral structures of the PSSO derived from the hydrolytic condensation of APS–PGE and APS–PGE$_2$ catalyzed by formic acid. By usual organic reactions transforming hydroxyl groups into other functional groups, it is possible to generate narrow distribution of multifunctionalized POSS starting from an OH-functionalized organotrialkoxysilane.
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1. Introduction

The hydrolytic condensation of organotrialkoxysilanes, RSi(OR$_3'$), performed in the presence of water and an acid or base as catalysts, leads to products that are generically called poly(silsesquioxanes) (PSSO), or silsesquioxanes [1]. These polymers have acquired increasing importance for the synthesis of functionalized organic–inorganic hybrid materials [2]. Species present in a PSSO may vary from perfect polyhedra of formula (RSiO$_{1.5}$)$_n$ (n = even number ≥ 6), denoted as T$_n$ or as polyhedral oligomeric silsesquioxanes (POSS), to partially condensed (but completely hydrolyzed) products of generic formula T$_n$(OH)$_m$, where T = RSiO$_{1.5-m/2n}$. The maximum value of m is equal to $2+n$, representing a linear/branched chain devoid of intramolecular cycles. The structure of a particular n-mer may thus vary from a linear/branched chain (open structure) to a polyhedron (closed structure). A distinctive parameter that characterizes the structure of a particular PSSO is the average fraction of intramolecular cycles (f) present in

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their species [3]. For a generic n-mer, f is given by:

$$f = (2 + n - m)/(2 + n) \quad (\text{for } n = \text{even})$$

or

$$f = (2 + n - m)/(1 + n) \quad (\text{for } n = \text{odd})$$

The average fraction of intramolecular cycles present in a particular PSSO depends on the nature of the organic substituent and on the conditions of the synthesis [3,4]. We recently reported that the hydrolytic condensation of an organotrialkoxysilane with a bulky organic group bearing hydroxyl functionalities, in the presence of both acid and basic catalysts, led to a narrow distribution of perfect and imperfect polyhedra: T_8, $T_9(OH)$, and T_{10}, with traces of $T_7(OH)$ and $T_{11}(OH)$ [5]. The starting silane was the reaction product of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS) with 3 mole of phenylglycidylether (PGE): AEAPS–PGE$_3$, with 3 secondary hydroxyl groups in its structure. The precise directionality of the reaction path towards the generation of three main species was ascribed to the presence of a bulky organic substituent (steric effect promoting intramolecular condensation). However, these previous studies also showed the presence of Si–O–C bonds in the starting OH-functionalized organotrialkoxysilane, produced through reaction of SiOMe groups with secondary hydroxyl groups [5]. The reversible formation of Si–O–C bonds may also take place during the synthesis of the PSSO, through reaction of SiOH groups and OH groups of the organic branches. Extensive intramolecular cyclization through intermediate Si–O–C bonds would favor the formation of cage structures in the resulting PSSO.

The aim of this study was to analyze if the hydrolytic condensation of an OH-functionalized organotrialkoxysilane, with an organic group less bulky than the one used in the previous work [5], could also lead to a narrow distribution of silsesquioxane cages. For this purpose, AEAPS was replaced by (3-aminopropyl)triethoxysilane (APS) as the starting silane. Hydroxyl groups were generated by reacting APS with 1 or 2 mole PGE. PSSO obtained by the hydrolytic condensation of these organotrialkoxysilanes were analyzed by matrix-assisted ultraviolet laser desorption/ionization time-of-flight mass spectrometry (UV-MALDI-TOF MS), to characterize their average fraction of intramolecular cycles.

2. Experimental

2.1. Synthesis of the poly(silsesquioxanes)

Organotriethoxysilanes containing hydroxyl groups were synthesized by reacting 1 mole of APS (Sigma, 98% purity), with 1 or 2 mole of PGE (Aldrich, 99% purity),

to give, respectively, APS–PGE and APS–PGE$_2$. The reaction was carried out in bulk, at 50 °C under vacuum, during 24 h. In these conditions the reaction attained complete conversion [5]. Scheme 1 shows the structure of APS and the two reaction products. The product denoted as APS–PGE is in fact a mixture of the three silanes. Assuming an equal reactivity of primary and secondary amino groups, the reaction product of equimolar amounts of APS and PGE will consist of 25% APS, 50% APS–PGE and 25% APS–PGE$_2$.

The hydrolytic condensation of both APS–PGE and APS–PGE$_2$ was performed by dissolving 1 g of the corresponding silane in 1.5 ml tetrahydrofuran (THF), adding water and eventually a catalyst, and heating at 50 °C during 24 h, allowing continuous evaporation of volatiles. For APS–PGE, a molar ratio [H$_2$O]/Si = 3 was used, and the reaction was catalyzed by the amino groups of the silane. For APS–PGE$_2$, the hydrolytic condensation was catalyzed by HCOOH 85 wt.% (molar ratios: [HCOOH]/Si = 3, [H$_2$O]/Si = 1.35), or by NaOH (molar ratios: [NaOH]/Si = 0.05, [H$_2$O]/Si = 3). Formic acid acts both as a catalyst and as reactant, promoting the condensation through the formation of sililformates as intermediate species [6].

2.2. Characterization of poly(silsesquioxanes)

Size exclusion chromatography (SEC) was performed with a Waters 510 device, provided with three Styragel columns (HR 3, HR 1 and HR 0.5), and a UV detector (Waters Lambda-Max 481, at 254 nm). THF was used as a carrier at a rate of 1 ml min^{-1}. A solution of about 20 mg of the PSSO in 10 ml THF was prepared, and 0.1 ml were injected in the chromatograph.

Fourier-transformed infrared spectra (FTIR) were recorded with a Genesis II-Mattson device, in the transmission mode, making coatings on NaCl windows.

Matrix-assisted UV-MALDI-TOF MS, was performed using an Applied Biosystems Voyager DE-STR device, equipped with a pulsed nitrogen laser ($\lambda = 337$ nm; pulse width = 3 ns). The selected matrix was 2,5-dihydroxybenzoic acid (gentisic acid, GA; Sigma). Samples were irradiated just above the threshold laser power to obtain molecular ions. Measurements were performed in linear positive-ion modes. Usually 50 spectra were accumulated. Spectra were calibrated using insulin, aprotinin, and α-, β-, and γ-cyclodextrin.

3. Results and discussion

3.1. Reaction between APS and PGE

The reaction of 1 mole of APS with 2 mole of PGE, at 50 °C, was followed by SEC. After 24 h, the monomer and the monoreacted intermediate had completely
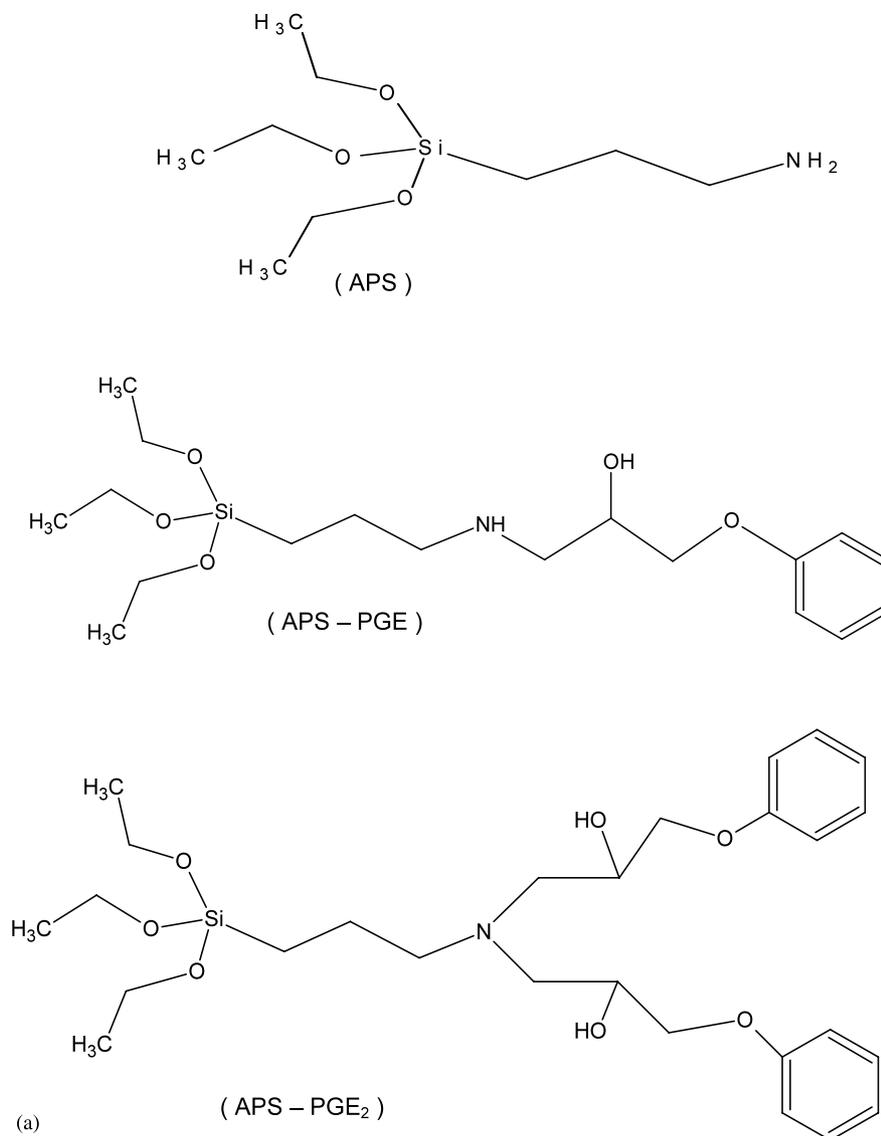
Scheme 1. Chemical structures of the organotriethoxysilanes.

disappeared and APS–PGE$_2$ was the main reaction product. However, a small fraction of higher molar mass species was also recorded. This was ascribed to the formation of dimers, trimers, etc., of APS–PGE$_2$ through the following reaction:

$$Si–(OEt) + C–(OH) = Si–O–C + EtOH$$
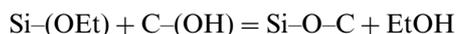
An UV-MALDI MS of the reaction product revealed the following facts.

(a) The main species was APS–PGE$_2$, characterized by the presence of peaks at 522.5 Da (theoretical value = 522.6 Da, ionized with H$^+$), and 544.9 Da (theoretical value = 544.6 Da, ionized with Na$^+$).

(b) No peaks assignable to the loss of 1 or more EtOH moles from APS–PGE$_2$ were observed, meaning that Si–(OEt) was not involved in the formation of intramolecular loops with C–OH groups pertaining to the organic moiety bonded to the same Si atom.

(c) The dimer present in largest concentration was characterized by peaks at 906.4 and 928.2 Da. These masses may be assigned to the species formed by the loss of 3 mole of EtOH from 2 APS–PGE$_2$ mole (Scheme 2; theoretical mass = 906.1 Da, ionized with H$^+$, and 928.1 Da, ionized with Na$^+$). This means that once a loop is formed there is a high trend to form subsequent loops. It may be speculated that the eight-member ring is formed first leaving the possibility for the other organic branch to form new Si–O–C bonds through intramolecular or intermolecular condensations (dimers with one or two Si–O–C bonds were not present in significant concentrations). The intramolecular condensation through a 16-member ring is indeed possible as shown by the optimized geometry (Scheme 2b). But a second eight-member ring can not be closed due to steric reasons. Trimers and larger molar mass species were
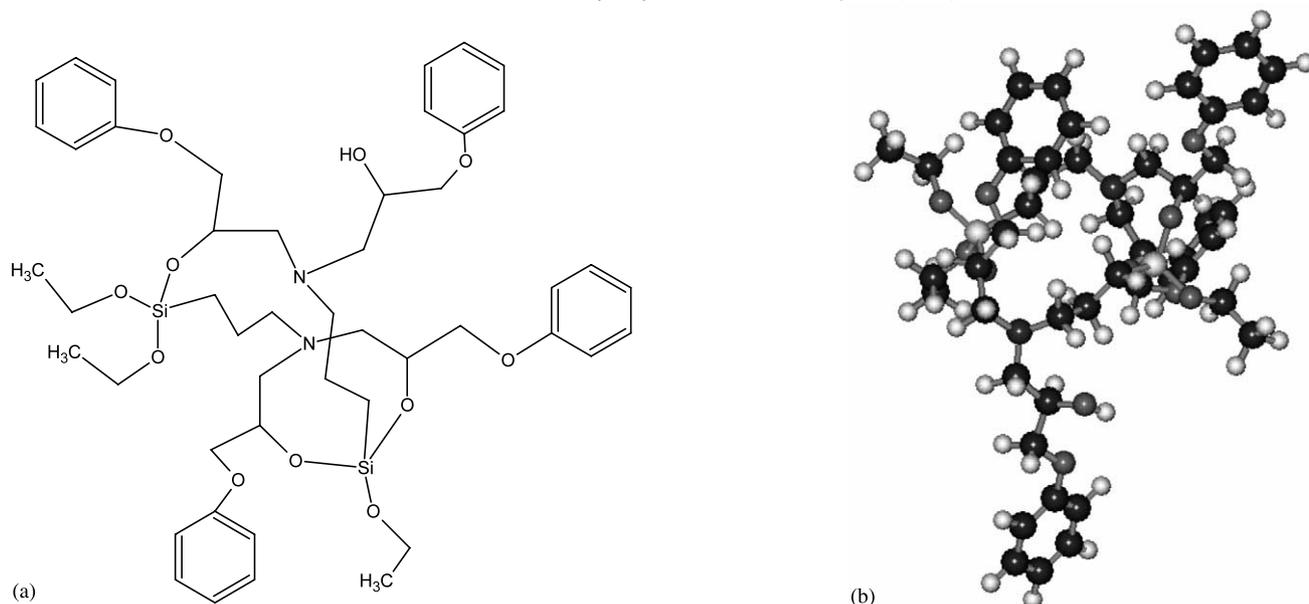
Scheme 2. Chemical structure of the dimer formed during the synthesis of APS–PGE$_2$; (a) schematic representation, (b) optimized geometrical structure (MM+ program of Molecular Mechanics).

also detected in small concentrations, meaning that intermolecular condensations do also take place.

The formation of intramolecular cycles through Si–O–C bonds seems to be a characteristic of organotrialkoxysilanes bearing hydroxyl groups. In the presence of water and an adequate catalyst, Si–O–C bonds will be hydrolyzed leading to a PSSO through condensation of the resulting SiOH groups.

3.2. PSSO derived from APS–PGE

Fig. 1 shows an UV-MALDI-TOF mass spectra of the PSSO obtained by hydrolytic condensation of APS–PGE. Although low-molar-mass products were also present, most of the species were observed in the (m/z) range comprised between 2000 and 4000 Da. Assignment of main peaks is shown in Table 1. Species present in this particular PSSO were perfect polyhedra: T_8, T_{10}, imperfect polyhedra: $T_9(OH)$, $T_{11}(OH)$, and other structures exhibiting a large fraction of intramolecular cycles: $T_9(OH)_3$, $T_{10}(OH)_2$. For every one of these species there is distribution of molar masses that depends on the number of moles of PGE that are covalently bonded to the 3-aminopropyl group. As a 1:1 molar ratio of PGE with respect to APS was used in the synthesis of APS–PGE, the most probable number of PGE moles in a generic species $T_n(OH)_m$, is equal to n. For example, for $T_{11}(OH)$, Table 1 shows the presence of a distribution of species containing from 8 to 15 PGE residues. As an example, Scheme 3 shows an isomer of a T_8 species containing 8 PGE units covalently bonded to the amine groups.

Therefore, the one-step hydrolytic condensation of APS–PGE led to a relatively narrow distribution of POSS, functionalized with both hydroxyls and amino groups. These may be used as building blocks in several types of polymerization reactions.

The hydrolytic condensation of unmodified APS, under the same experimental conditions, led to a typical broad distribution of structures (in $T_n(OH)_m$, several values of m were present for a particular n value), extending to the range of large masses. Instead, the hydrolytic condensation of APS–PGE led to polyhedral structures with a relatively narrow distribution of n values. The dramatic change in the reaction path is ascribed to the presence of hydroxyl groups in the structure of APS–PGE, rather than to the increase in the size of the organic moiety. It is possibly that SiOH groups participate in reversible reactions with COH groups pertaining to the organic part attached to another Si atom, forming Si–O–C bonds. After hydrolysis of these bonds, the reaction between two neighboring SiOH groups should be favored thus promoting the formation of closed (polyhedral) structures. An experimental fact supporting this hypothesis may be obtained by analyzing the species present in minor concentrations in the UV-MALDI MS shown in Fig. 1. Among these species we found $T_8(OH)_2$, $T_9(OH) - H_2O$, $T_{11}(OH) - H_2O$, T_{12}, $T_{12}(OH)_2$, $T_{13}(OH) - H_2O$, $T_{13}(OH)$, T_{14}, $T_{14}(OH)_2$, $T_{15}(OH) - H_2O$, $T_{15}(OH)$ and $T_{15}(OH)_3$. Four of these species ($T_n(OH) - H_2O$), are imperfect polyhedra with their only silanol group reacted with a COH group, with the loss of 1 mole of water. This proves that Si–O–C bonds are in fact present in some of the species of the PSSO.

The FTIR spectra of the PSSO in the range of 800–1250 cm^{-1} is shown in Fig. 2 (curve a). Peaks at 1120 and 1079 cm^{-1} are characteristic of v_{as} Si–O–Si in
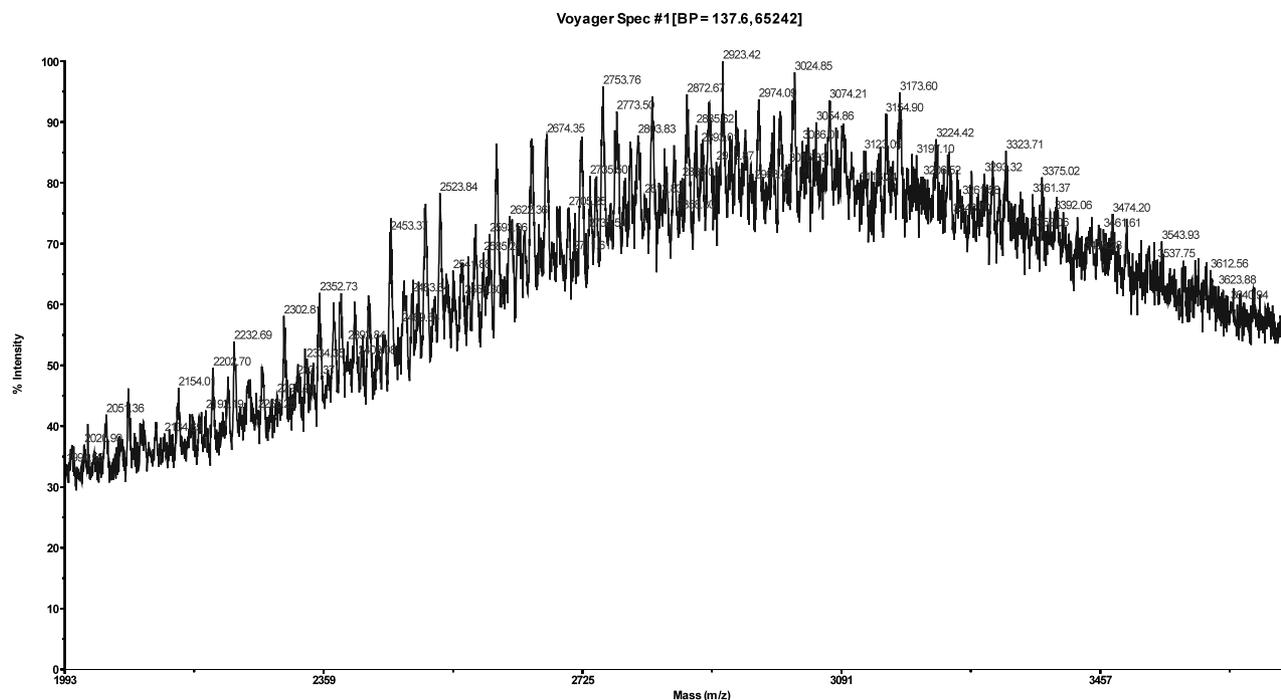
Fig. 1. UV-MALDI-TOF MS of the PSSO obtained by hydrolytic condensation of APS–PGE.

Table 1
Assignment of peaks of UV-MALDI-TOF mass spectra for the PSSO obtained by hydrolytic condensation of APS–PGE

m/z (exp.)	Species	m/z (theor.)	n PGE
2051.4	$T_9(OH)$	2052.9	7
2083.0	T_8	2083.9	8
2154.0	T_{10}	2154.1	7
2202.7	$T_9(OH)$	2203.1	8
2223.0	$T_9(OH)_3$	2221.1	8
2232.7	T_8	2234.1	9
2302.8	T_{10}	2304.3	8
2352.7	$T_9(OH)$	2353.3	9
2373.0	$T_9(OH)_3$	2371.3	9
2382.7	T_8	2384.3	10
2422.2	$T_{11}(OH)$	2423.4	8
2453.4	T_{10}	2454.4	9
2503.0	$T_9(OH)$	2503.4	10
2523.8	$T_9(OH)_3$	2521.4	10
2603.6	T_{10}	2604.6	10
2652.6	$T_9(OH)$	2653.6	11
2674.3	$T_9(OH)_3$	2671.6	11
2722.5	$T_{11}(OH)$	2723.8	10
2753.8	T_{10}	2754.8	11
2773.5	$T_{10}(OH)_2$	2772.8	11
2823.7	$T_9(OH)_3$	2821.8	12
2872.7	$T_{11}(OH)$	2874.0	11
2903.2	T_{10}	2905.0	12
2923.4	$T_{10}(OH)_2$	2923.0	12
3024.8	$T_{11}(OH)$	3024.2	12
3173.6	$T_{11}(OH)$	3174.3	13
3323.7	$T_{11}(OH)$	3324.5	14
3474.2	$T_{11}(OH)$	3474.7	15

m/z, Da; theoretical values correspond to ionization with H^+.

polyhedra and imperfect polyhedra [7], in agreement with the assignments of the mass spectrum.

3.3. PSSOs derived from APS–PGE$_2$

Size exclusion chromatograms for the PSSOs obtained by the hydrolytic condensation of APS–PGE$_2$ catalyzed by HCOOH or NaOH, are shown in Fig. 3. The PSSO synthesized in the presence of HCOOH exhibited a relatively narrow distribution of reaction products in the region of large masses (low elution times). The NaOH-catalyzed product showed the presence of a narrow peak at large masses, together with a series of peaks corresponding to low-molar mass species. The hydrolytic condensation was clearly less efficient in the presence of NaOH, for the selected concentrations and reaction conditions.

FTIR spectra provide a confirmation of SEC results (Fig. 2, curves b and c). The PSSO synthesized with HCOOH showed the presence of an intense absorption band at 1127 cm^{-1}, together with a band of medium intensity at 1080 cm^{-1}, which are characteristic of polyhedral structures [7]. For the NaOH-catalyzed PSSO, the more intense band in this region was a double peak located at 1047 and 1067 cm^{-1}, with a less intense band at 1128 cm^{-1}. This reveals the presence of a different structure for the species present in this PSSO. Unsymmetrical structures containing internal cyclotrisiloxane rings exhibit characteristic ν_{as} Si–O–Si bands near 990 and 1065 cm^{-1}, in addition to others in the

R₁ : - CH₂ – CH₂ – CH₂ – NH₂

R₂ : - CH₂ – CH₂ – CH₂ – N (CH₂ – CH – CH₂ – O – C₆H₅)₂
                                    |
                                   O H

R₃ : -CH₂ – CH₂ – CH₂ – NH - CH₂ – CH – CH₂ – O – C₆H₅
                                         |
                                        OH
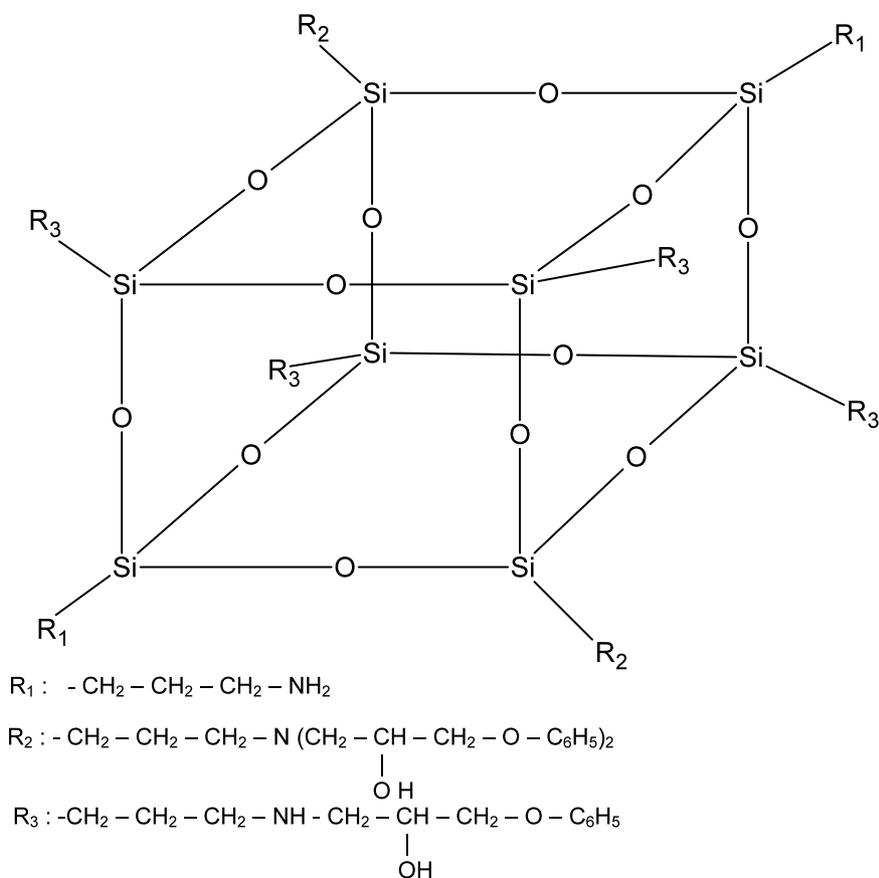
Scheme 3. Chemical structure of a particular isomer of an octahedron (T₈), with 8 PGE residues, present in the PSSO obtained from the hydrolytic condensation of APS–PGE.
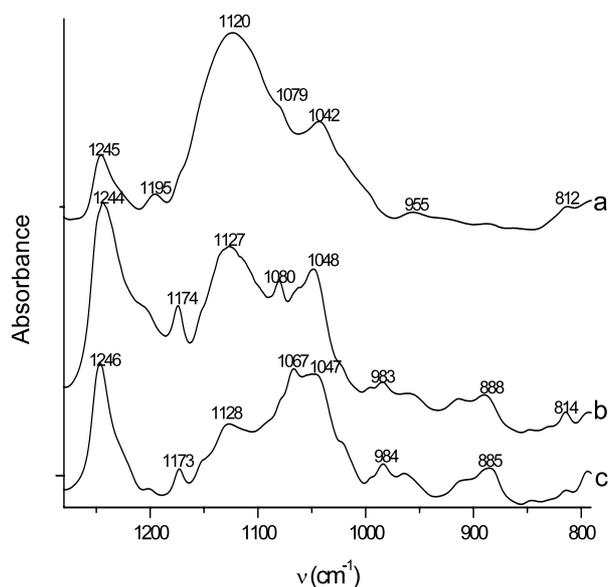
Fig. 2. FTIR spectra in the range of 800–1250 cm⁻¹, of the PSSO obtained by hydrolytic condensation of: (a) APS–PGE, (b) APS–PGE₂ in the presence of HCOOH, (c) APS–PGE₂ in the presence of NaOH.

Fig. 3. SEC chromatograms of PSSOs obtained by hydrolytic condensation of APS–PGE₂, catalyzed by HCOOH or NaOH.

range of 1080–1115 cm⁻¹ [7]. This type of structure might be present in the NaOH-catalyzed PSSO. The

absence of bands at 958 and 1168 cm⁻¹ indicates complete hydrolysis of EtO groups [8]. However, the absence of a band at 930 cm⁻¹ evidences that SiOH groups are not present in significant concentrations [8].

Mass spectra provide additional information which is necessary to elucidate the structures of both PSSOs. Fig.

4 shows an UV-MALDI-TOF MS of the PSSO obtained by hydrolytic condensation of APS–PGE_2, in the presence of HCOOH. Table 2 shows the assignment of main peaks, which are present in the region of m/z comprised between 3000 and 5000 Da, in decreasing order of intensities.

Main species present in the PSSO obtained in the presence of HCOOH are polyhedral structures with 8–11 Si atoms, as in the case of the hydrolytic condensation of APS–PGE. Again, the presence of OH groups in the starting organotrialkoxysilane enabled the one-step synthesis of a narrow distribution of POSS. Main species were: T_8, $T_9(OH)$ (the species present in the highest concentration), $T_9(OH) - H_2O$, T_{10}, $T_{10}(OH)_2$, $T_{10}(OH)_2 - 2H_2O$, $T_{11}(OH)$ and $T_{11}(OH) - H_2O$. Both $T_9(OH) - H_2O$ and $T_{11}(OH) - H_2O$ exhibit one intramolecular Si–O–C bond formed by reaction of the SiOH group with an hydroxyl group of one of the organic branches. In the case of $T_{10}(OH)_2 - 2H_2O$, there are two intramolecular Si–O–C bonds formed by reaction of both SiOH groups with hydroxyls of the organic chains. It may be also noticed that although species containing the stoichiometric PGE units were present in the highest concentrations, species lacking 1 or 2 PGE units were also detected. This means that the initial formulation had in fact a slight defect of PGE or that the reaction was not carried out to 100% conversion (although conversion was very close to this value). It is interesting to note that every amino group that was not previously reacted with PGE, formed an amide group by reaction with HCOOH (eliminating 1 water molecule).

Table 2
Assignment of main peaks present in the UV-MALDI-TOF mass spectra of the PSSO obtained by hydrolytic condensation of APS–PGE_2 in the presence of HCOOH

m/z (exp.)	Species	m/z (theor.)	n PGE
3703.2	$T_9(OH)$	3704.9	18
4104.9	T_{10}	4106.4	20
4123.6	$T_{10}(OH)_2$	4124.4	20
3581.1	$T_9(OH)(+HCOOH - H_2O)$	3582.7	17
4506.3	$T_{11}(OH) - H_2O$	4508.0	22
4525.3	$T_{11}(OH)$	4526.0	22
4001.1	$T_{10}(OH)_2(+HCOOH - H_2O)$	4002.2	19
3982.8	$T_{10}(+HCOOH - H_2O)$	3984.2	19
4086.9	$T_{10}(OH)_2 - 2H_2O$	4088.4	20
4403.0	$T_{11}(OH)(+HCOOH - H_2O)$	4403.8	21
4384.5	$T_{11}(OH) - H_2O(+HCOOH - H_2O)$	4385.8	21
3964.3	$T_{10}(OH)_2 - 2H_2O(+HCOOH - H_2O)$	3966.2	19
3684.7	$T_9(OH) - H_2O$	3686.9	18
3283.8	T_8	3285.3	16
3161.7	$T_8(+HCOOH - H_2O)$	3163.1	15
3459.2	$T_9(OH)(+2HCOOH - 2H_2O)$	3460.5	16

Fig. 5 shows the UV-MALDI-TOF MS of the PSSO obtained by hydrolytic condensation of APS–PGE_2, in the presence of NaOH. In this case, the PSSO shows clusters of oligomers containing a particular number of Si atoms: from 2 Si atoms (maximum at 808.0 Da) to 12 Si atoms (maximum at 4890.3 Da). No monomer was detected (peaks at m/z less than 600 Da are due to the matrix or to z values equal to or higher than 2).

Voyager Spec #1=>AdvBC(10,0.5,0.1)=>SM5[BP = 177.3, 45046]
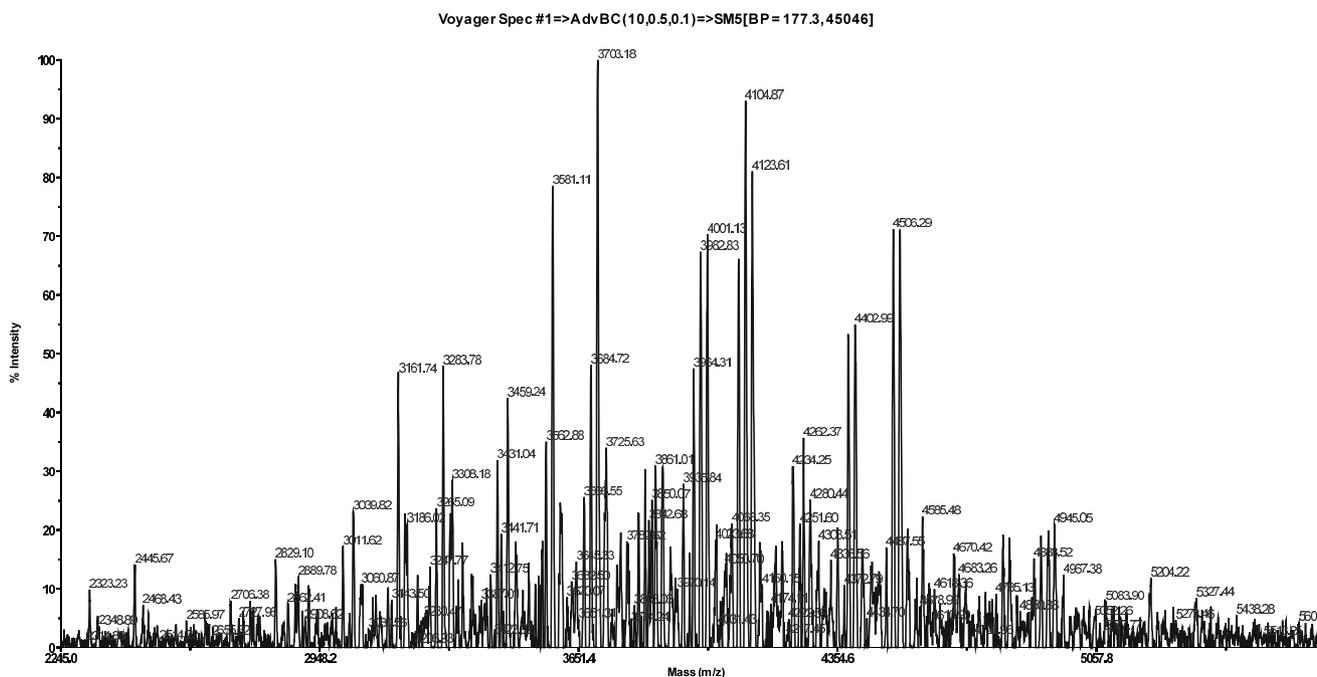
Fig. 4. UV-MALDI-TOF MS of the PSSO obtained by hydrolytic condensation of APS–PGE_2, in the presence of HCOOH.
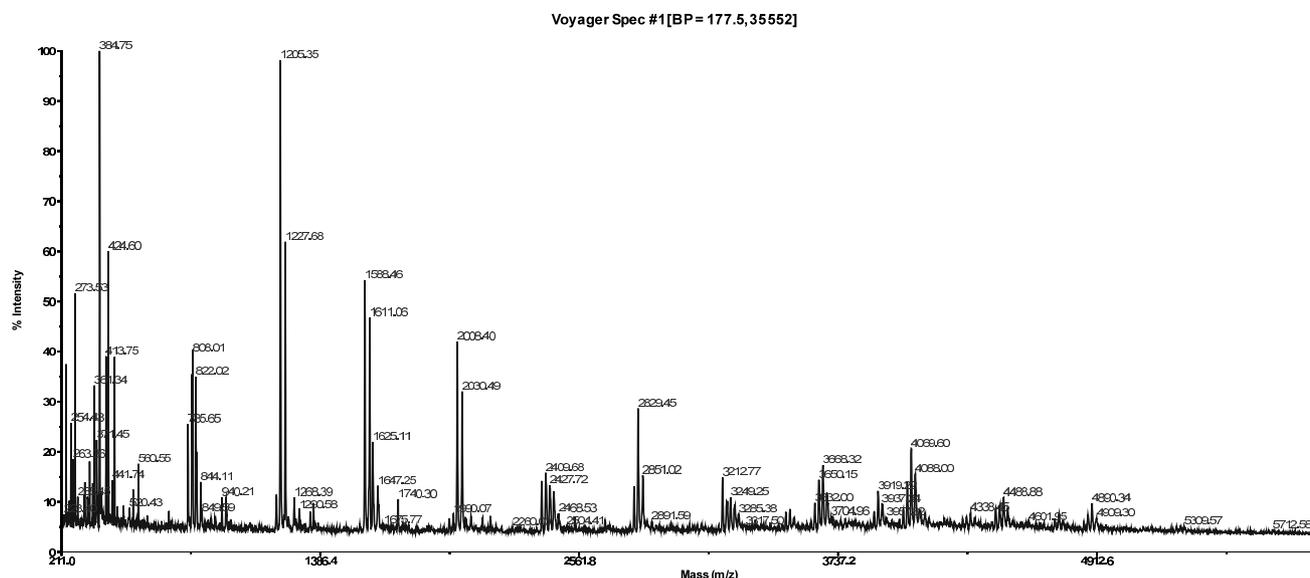
Fig. 5. UV-MALDI-TOF MS of the PSSO obtained by hydrolytic condensation of APS–PGE$_2$, in the presence of NaOH.

Table 3 shows the assignment of the main peak for every cluster. The dimer present in the highest concentration had a mass that could be assigned to $T_2(OH)_4 - 4H_2O$. This corresponds to the formation of the four possible Si–O–C bonds, meaning that this species has no free SiOH or COH residual groups. Scheme 4 shows a possible chemical structure for this dimer exhibiting eight- and ten-member rings (the optimized geometry is shown in Scheme 4b). Notice that SiOH groups have reacted with COH groups pertaining to the organic branch bonded to the other Si atom; this follows from the fact that no intramolecular Si–O–C bonds were found in the monomer during the synthesis of APS–PGE$_2$.

Table 3
Assignment of the main peak of every cluster of species with 2–12 Si atoms, present in the UV-MALDI-TOF mass spectra of the PSSO obtained by hydrolytic condensation of APS–PGE$_2$ in the presence of NaOH (m/z, Da)

m/z (exp.)	Species	m/z (theor. $+H^+$)	m/z (theor. $+Na^+$)
785.6; 808.0	$T_2(OH)_4 - 4H_2O$	786.1	808.0
1205.3; 1227.7	$T_3(OH)_3 - 3H_2O$	1205.6	1227.6
1588.5; 1611.1	$T_4(OH)_6 - 6H_2O$	1589.1	1611.1
2008.4; 2030.5	$T_5(OH)_5 - 5H_2O$	2008.7	2030.7
2409.7	$T_6(OH)_6 - 6H_2O$	2410.2	
2829.4; 2851.0	$T_7(OH)_5 - 5H_2O$	2829.7	2851.7
3212.8	$T_8(OH)_8 - 8H_2O$	3213.3	
3668.3	$T_9(OH)_3 - 3H_2O$	3668.8	
4069.6	$T_{10}(OH)_4 - 4H_2O$	4070.4	
4488.9	$T_{11}(OH)_3 - 3H_2O$	4489.9	
4890.3	$T_{12}(OH)_4 - 4H_2O$	4891.5	

The presence of a significant amount of the completely dehydrated dimer gives evidence of: (a) the competition between the formation of Si–O–Si and Si–O–C bonds during the reaction catalyzed by NaOH, (b) the stability of generated Si–O–C bonds. The reaction path seems to be a typical hydrolytic condensation of Si(OEt) groups, arrested by the total consumption of SiOH groups through intramolecular cyclization with COH groups. The generated oligomers devoid of silanol groups remain stable under the selected reaction conditions.

Every species present in the highest concentration in the corresponding cluster, could be assigned to $T_n(OH)_m - mH_2O$ (Table 3). This means that all silanol groups form intramolecular cycles with hydroxyl groups, in agreement with results arising from the FTIR spectrum. The number of free hydroxyl groups is $2n - m$. The fraction of intramolecular Si–O–Si cycles is low for the tetramer ($f = 0$) up to the octamer ($f = 0.2$), indicating the presence of an 'open' Si–O–Si skeleton. But it increases significantly for the high-molar-mass oligomers (e.g. $f = 0.67$ for the decamer and $f = 0.71$ for the dodecamer). Table 3 also shows that Na^+ ionization was significant for the species containing a small number of residual hydroxyl groups (for the dimer, the intensity of the peak corresponding to Na^+ ionization was higher than the peak arising from H^+ ionization).

4. Conclusions

The presence of hydroxyl groups in the organic part of organotrialkoxysilanes has a significant influence on

(a)

(b)
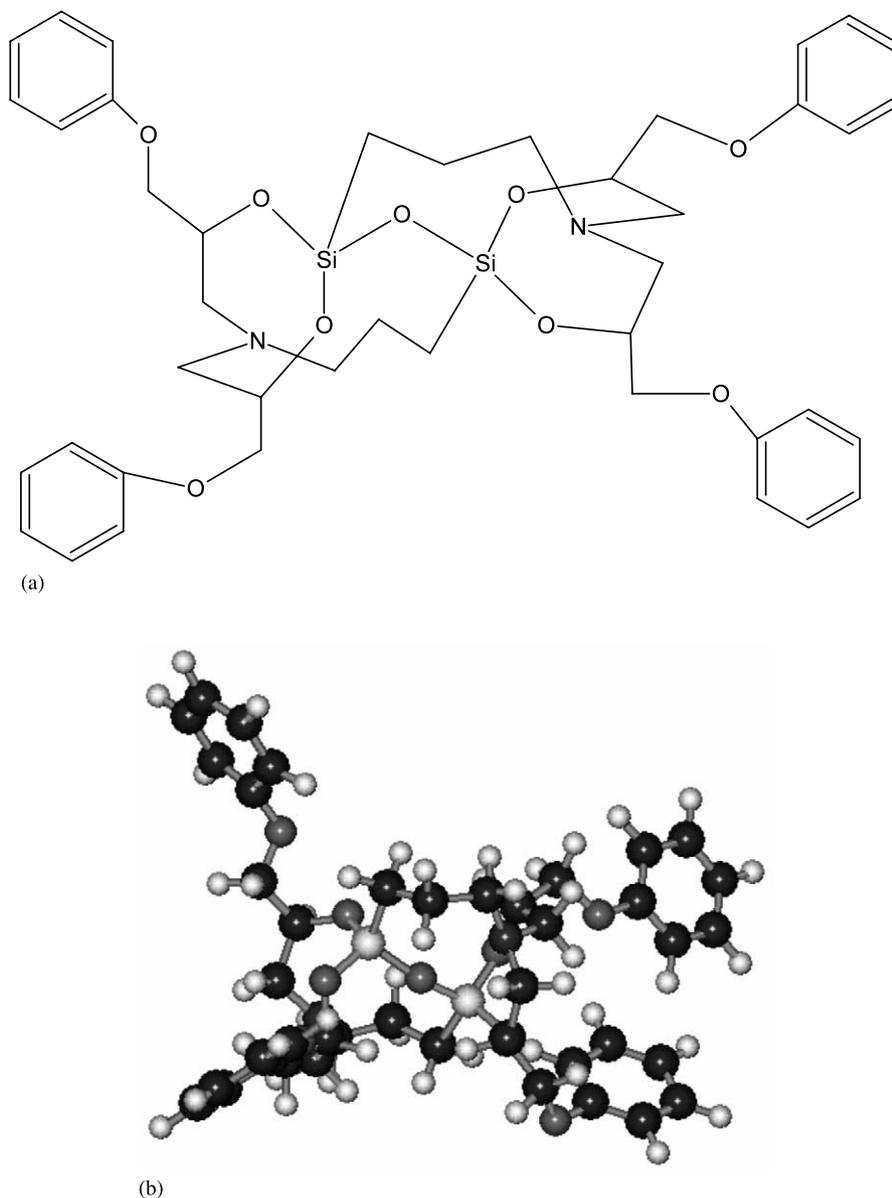
Scheme 4. Chemical structure of the dimer formed during the hydrolytic condensation of APS–PGE$_2$, in the presence of NaOH; (a) schematic representation, (b) optimized geometrical structure (MM+ program of Molecular Mechanics).

the course of its hydrolytic condensation. This is due to the formation of Si–O–C bonds through the reaction of SiOH (or SiOEt) groups with the hydroxyl functionalities of an organic moiety bonded to a neighboring Si atom, producing intramolecular cycles. Depending on the catalyst and reaction conditions, Si–O–C bonds may be stable or may be hydrolyzed leading to more stable Si–O–Si bonds. In the last case, the resulting PSSO exhibits a narrow distribution of polyhedral structures, an interesting finding that makes it possible the one-step synthesis of OH-functionalized POSS. The directionality effect towards the generation of closed structures, is possibly derived from the continuous reversible formation of intramolecular cycles through Si–O–C bonds. This argument was supported by the presence of species exhibiting these cycles in the resulting PSSO (e.g. $T_{11}(OH) - H_2O$ represents an imperfect polyhedron of 11 Si atoms with the only residual SiOH group reacted with an hydroxyl, generating an intramolecular Si–O–C bond).

Under reaction conditions where Si–O–C bonds were stable (for the NaOH-catalyzed reaction), the resulting PSSO exhibited a distribution of low-molar-mass oligomers with a large fraction of stable intramolecular cycles formed through Si–O–C bonds. In this case, the SiOH+COH reaction became competitive with the SiOH+SiOH reaction, provoking an arrest of the molar mass increase due to depletion of SiOH groups.

The significance of this study is related to the possibility of generating narrow distributions of functionalized

silsesquioxane cages, by the hydrolytic condensation of OH-functionalized organotrialkoxysilanes. After the synthesis, hydroxyl groups may be transformed into different functional groups through typical organic reactions leading to a variety of multifunctional silsesquioxane cages. These products may be used as building blocks of silsesquioxane-modified polymer networks.

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