# NANOSTRUCTURED BRIDGED SILSESQUIOXANES VIA SOL-GEL SYNTHESIS

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**Abstract**

Two types of hybrid materials with different degree of nanoestructuring (a bridged silsesquioxane (BS) and hybrid microspheres (MS)) were obtained from a bridged precursor (P) synthesized by the reaction of glycidoxypropyl (trimethoxysilane) with cyclohexylamine. The polycondensation of P in presence of formic acid produced a hybrid material (BS) exhibiting a short-range order based on elongated organic channels, accommodating the cyclohexyl fragments pending from the organic bridge, bounded by inorganic domains. Also, nanostructured hybrid microspheres (MS) were synthesized from P by employing ultrasound-assisted sol-gel processing. The mild reaction conditions produced the nanostructuring of the silsesquioxane characterized by a fine structure in SAXS spectrum. Inorganic domains were arranged in a two-dimensional hexagonal system leading to the formation of cavities in the microspheres which could be employed as host-guest systems in advanced technologies.

*Key words:* bridged silsesquioxanes; self-assembly; supramolecular structures.

**Resumen**

**Silsesquioxanos puenteados nanoestructurados sintetizados por via sol-gel.** Dos tipos de materiales híbridos con diferente grado de nano-estructuración (un silsesquioxano puenteado (BS) y microesferas híbridas (MS)) fueron obtenidos a partir de un precursor puenteado (P) sintetizado mediante la reacción de glicidoxipropil (trimetoxisilano) con ciclohexilamina.

La policondensación del precursor (P) en presencia de ácido fórmico produjo un material híbrido (BS) que presenta un ordenamiento de corto alcance basado en canales orgánicos alargados, que acomodan grupos ciclohexilo pendientes del puente orgánico, enlazados por dominios inorgánicos. También, a partir del precursor P fueron sintetizadas microesferas híbridas nanoestructuradas (MS) empleando una vía de síntesis sol-gel asistida por irradiación ultrasónica. Las suaves condiciones de reacción produjeron la nanoestructuración del silsesquioxano caracterizado por una estructura fina en el espectro SAXS.

Los dominios inorgánicos presentaron un arreglo bidimensional hexagonal que dio lugar a la formación de cavidades en las microesferas, las que podrían ser empleadas para contener pequeñas moléculas útiles en tecnologías avanzadas.

*Palabras claves:* silsesquioxanos puenteados; autoensamble; estructuras supramoleculares.

## 1. Introduction

Bridged silsesquioxanes are a family of organic-inorganic hybrid materials synthesized by the hydrolysis and condensation of monomers containing an organic bridging group covalently bonded to terminal trialkoxysilyl or trichlorosilyl groups [1-14]. These bridged hybrids offer the possibility of producing materials in which the bridging unit itself exhibits self-assembling properties [15, 16]. Depending on the bridge nature (composition, rigidity, length) and its functionalization, different degree of organization in the final material can be achieved during the hydrolytic condensation of the precursors. In this way,

the bridging group can direct the formation of three-dimensional networks [14], supramolecular-assembled films [17], as well as mesoporous phenylene-bridged silsesquioxane-based materials with ordered hexagonal pore structures [18, 19]. The bridged silsesquioxane family is now recognized to have an enormous potential as a building block for various advanced materials, and their applications can be found in areas as catalysis, optics, electronics and biosciences, among others [20].

A variety of structures and properties have been reported for self-assembled bridged silsesquioxanes. Weak interactions between aromatic units led to birefringent hybrids [21]. Helical morphologies, hollow tubes and spheres were generated from chiral precursors capable of associating through strong hydrogen bonds between urea groups [22, 25, 26]. Highly crystalline hybrid materials were synthesized from a precursor with a diureabenzene group [27] Long-range ordered lamellar structures with a macroscopic organization in compact sheets were obtained by combining the association properties of urea groups by H-bonds and those of long hydrocarbon chains [15, 17, 23, 24, 28]. The self-assembly could also be produced just by the hydrophobic interactions between long alkylene chains [16].

Recently, well-defined spherical micro and nanoparticles have attracted great attention since they have many applications in advanced technologies. Different techniques for preparing these particles at nano and micro scales, via oil/water solvent evaporation method [29], vigorous stirring of the precursors for long periods [28,30], among others, have been reported.

The goal of this work was to generate a new family of bridged silsesquioxanes using a precursor synthesized by the reaction of a primary amine (1 mol) with glycidoxypropyl(trimethoxysilane) (GPMS, 2 mol). This kind of bridged precursor introduces a new variable with respect to those previously reported in the literature that is the presence of a pendant organic group (R) in the main organic bridge. Novel nanostructured bridged silsesquioxane and hybrid microspheres were synthesized from this precursor via sol-gel processing without and with ultrasonic irradiation, respectively. The great achievement of our work was to combine the ultrasonic irradiation technique with the self-assembling capability of a bridged precursor to produce microspheres structured at nano scale. The effect of processing variables on the final nanostructuring was analyzed.

## 2. Experimental Part

### Materials

Glycidoxypropyl(trimethoxysilane) (GPMS, Dow Corning, 99%, density at 20 °C = 1.07 g/mL), cyclohexylamine (CA, Merck, 99 %, density at 20 °C = 0.87 g/mL), formic acid (FA, Cicarelli, 88%, density at 20 °C = 1.20 g/mL), tetrahydrofuran (THF, Cicarelli, 99%, density at 20 °C = 0.89 g/mL), and $n$-hexane ($n$-Hex, Sintorgan, 99%, density at 20 °C = 0.66 g/mL), were used without further purification.

### Synthesis of the bridged precursor (P)

The hybrid precursor was synthesized from GPMS and a primary amine, CA (Figure 1) in glass tubes (2 cm diameter and 15 cm height), employing a molar ratio GPMS/CA = 2 (in a typical synthesis 3 mL of GPMS were reacted with 0.78 mL of CA). The tubes were sealed under nitrogen and placed in a thermostat at 70 ºC for 48 h. After that period, the tubes were removed from the thermostat and the reactions were stopped by freezing the tubes. Details of the synthesis were described elsewhere [31].

### Synthesis of the bridged silsesquioxane (BS)

The hydrolysis and condensation of the bridged precursor was performed in a THF solution using an aqueous solution of formic acid in the following molar ratios: HCOOH/Si = 3, $H_2O$/Si = 1.05 (in a typical synthesis 5 mL THF and 1.77 mL of the 88 wt % formic acid solution were added to the precursor synthesized using 3 mL GPMS and 0.78 mL CA). The tubes were left open and placed in a thermostat at 50 °C for 24 h. Solvents and volatile products were continuously evaporated during the reaction. The product was milled, placed in a Petri dish and heated in an oven at 110 °C for 3 h.

### Preparation of the hybrid microspheres (MS)

The hydrolytic condensation of the bridged precursor was accomplished in three different solvents: THF, $n$-Hex, and a mixture of THF/$n$-Hex (1:2 volumetric ratio), using an aqueous solution of FA as catalyst, in the following molar ratios: FA/Si = 3 and $H_2O$/Si = 1.05. In a typical synthesis, 100 mL of a solution containing 3.889 g of the bridged precursor were added to a glass vessel (5 cm diameter x 7.5 cm height) and 1.77 mL of the 88 wt % FA solution were added dropwise with continuous application of ultrasonic irradiation. A 6-mm diameter ultrasonic tip Sonic Vibra-Cell (130W/20kHz) was employed as irradiation source with 50% power

intensity. Solvents and volatile products were continuously evaporated from the open vessel. The process was ended when a white suspension appeared in the reaction medium. The solid was filtered and the remaining solvent evaporated at 80 °C. The resulting powder was placed in a Petri dish and heated in an oven at 110 °C for 3 h. The final product was a fine yellow glassy powder.

*Characterization Methods*

1D $^{29}$Si MAS NMR spectra were measured using a Bruker Avance 500 WB/US spectrometer at MAS frequency $\omega_r/2\pi = 10$ kHz and $B_1(^{13}C)$ field intensity $\omega_1/2\pi = 62.5$ kHz. $B_1(^1H)$ field intensity of TPPM (two-pulse phase-modulated) decoupling corresponds to $\omega_1/2\pi = 89.3$ kHz. Single-pulse experiments were used with 45° pulse length (2 ms) and 60 s repetition delay. The $^{29}$Si NMR scale was calibrated by external standard $M_8Q_8$ (-109.8 ppm; the highest field signal).

Fourier-transformed infrared (FTIR) spectra were recorded with a Genesis II-Mattson device in the absorbance mode, in the range 400 – 4000 cm$^{-1}$ with a resolution of 2 cm$^{-1}$. Spectra were obtained using pellets of the bridged silsesquioxanes with KBr.

Small-angle X-ray scattering (SAXS) was performed using a pinhole camera (Molecular Metrology SAXS System) attached to a microfocused X-ray beam generator (Osmic MicroMax 002) operating at 45 kV and 0.66 mA (30 W). The camera was equipped with a multiwire, gas-filled area detector with an active area diameter of 20 cm (Gabriel design). Two experimental setups were used to cover the $q$ range of 0.007 – 1.1 Å$^{-1}$ where $q = (4\pi/\lambda)\sin\theta$ ($\lambda$ is the wavelength and $2\theta$ is the scattering angle).

Morphologies were observed by scanning electron microscopy (SEM), employing a Jeol JXA-8600 microscope after coating the samples with a thin gold layer. Transmission electron microscopy (TEM) was performed with microscope JEM 200CX (Jeol, Japan).

TEM microphotographs were taken at acceleration voltage 100 kV, recorded on a photographic film, and digitalized with a PC-controlled digital camera. The samples were dispersed on a carbon film placed over the Cu net. The carbon film was previously coated with glue using a chloroform solution.

## 3. Results and Discussion

*Synthesis of the bridged precursor*

The reaction between GPMS (2 mol) and CA (1 mol) is represented in Figure 1. The epoxy-amine reaction led not only to the desired precur-sor but also to the formation of oligomers produced from Si(OCH$_3$) groups which reacted with the secondary hydroxyls generated by opening of the epoxy ring. In this way, oligomers are formed through covalent Si-O-C bonds [32-33], leading to a viscous solution. However, these Si-O-C bonds may be hydrolyzed along the course of the hydrolytic condensation, particularly when using an acid catalyst. This leads to the regeneration of the main structure depicted in Figure 1 as precursor of the hybrid materials.

*BS and MS characterization*

The conversion attained in the inorganic polycondensation for both BS and MS was investigated by $^{29}$Si NMR. Figure 2 shows the corresponding spectra for both products. The main peaks at -65.8 ppm are characteristic of $T_3$ species: Si-(O-Si)$_3$ [34-37], the two peaks at -59.4 ppm and -55.1 ppm are assigned to $T_2$ structures: Si-(O-Si)$_2$(OH) [38-40], and the smallest peak at -49.6 ppm is attributed to $T_1$ species: Si-(O-Si)(OH)$_2$ [41]. In the spectrum of BS sample the area under the $T_3$ peak was 84% of the total area. This led to a total conversion into Si-O-Si bonds close to 95% (0.84 + (2/3) 0.16) for BS material. The high conversion attained in the inorganic polycondensation indicates that inorganic domains are present as polyhedra or as ladder structures (or blends of both types of structures). For MS sample four signals were obtained from the deconvolution of the $^{29}$Si NMR spectrum. The area under the $T_3$ peak represented 52.4% of the total area, whereas the contribution of the two $T_2$ peaks was 44.4% and the area fraction under $T_1$ was 3.2%. This led to a total conversion into Si-O-Si bonds of 83.1% (0.524 + (2/3) 0.444 + (1/3) 0.032). In this case, the conversion attained is lower than that reached for BS material, for this
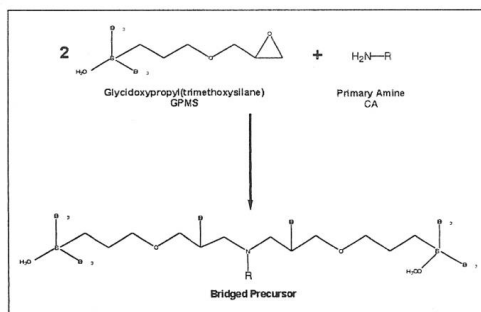


Fig. 1. Reaction of GPMS (2 mol) with a primary amine (1 mol).
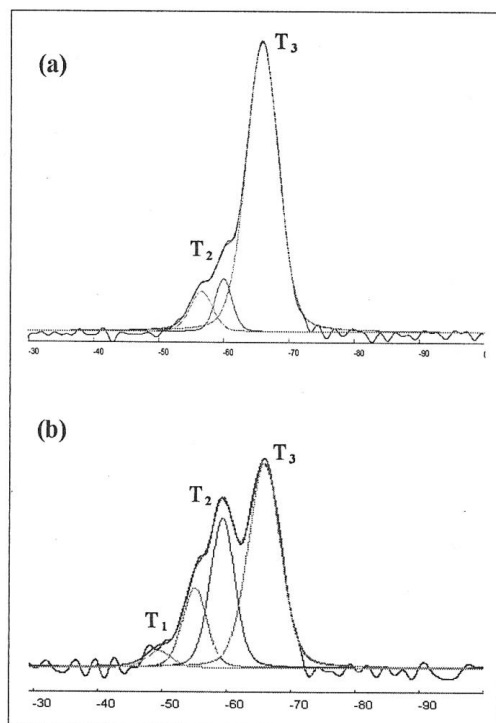
Fig. 2. $^{29}$Si NMR spectra for: a) BS material, b) MS material.



Fig. 3. SAXS spectra of bridged silsesquioxanes BS and MS.
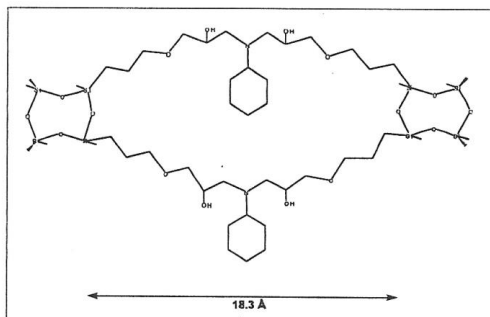


Fig. 4. Minimum conformational energy of two neighbouring organic bridges.

reason, is not possible to ensure that the inorganic structure presents an extended ladder configuration.

SAXS spectrum of BS sample is shown in Figure 3. Peak at $q = 0.344$ Å$^{-1}$ was observed, representing a correlation length of $2\pi/q_{max} = 18.3$ Å. This characteristic distance corresponds to the length of the organic bridge estimated using the software ACD Labs/3D Viewer (Figure 4). In the conformation of minimum energy, organic bridges are curved to accommodate the cyclohexyl groups in the structure. The relatively broad peak present in SAXS spectrum evidences the presence of a short-range order in the hybrid material. A scheme of the self-assembled structure of the ordered domains may be proposed, based on the organization of inorganic domains as ladder structures joining curved organic bridges alternatively placed above and below the planes defined by the ladders (Figure 5). Molecular channels result from the self-organization process. The distance between neighbouring organic bridges
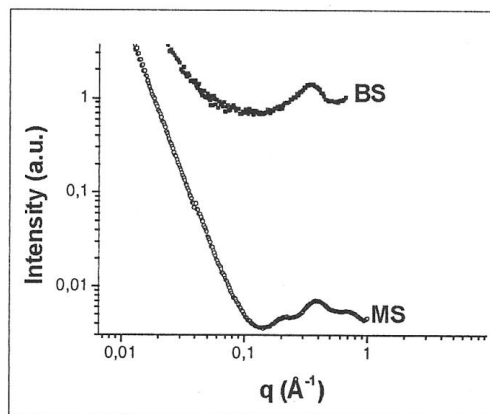
placed in the same surface (upper or lower) of the channel is in the range of 4 – 6 Å (depending on the angle formed by planes of the ladder). This produces a compact organic structure that defines the surface of the channel (e.g., the lateral interchain distance of closely packed alkyl chains is 4.2 Å) [42]. For the MS sample the appearance of diffraction patterns in the range 0.14 – 1.1 Å$^{-1}$ is also indicative of the existence of some degree of organization at molecular level. The $q$ (wave vector) position corresponding to the most intense Bragg peak was found to be 0.38 Å$^{-1}$. A second and less intense peak was detected at $q = 0.66$ Å$^{-1}$, overlapped with a small shoulder located at 0.76 Å$^{-1}$. The relative positions of these diffracted patterns correspond to a $q:\sqrt{3}q:2q$ progression. The series $1:\sqrt{3}:2:\sqrt{7}:3:\sqrt{12}...$ among diffracted peaks is characteristic of a two-dimen-
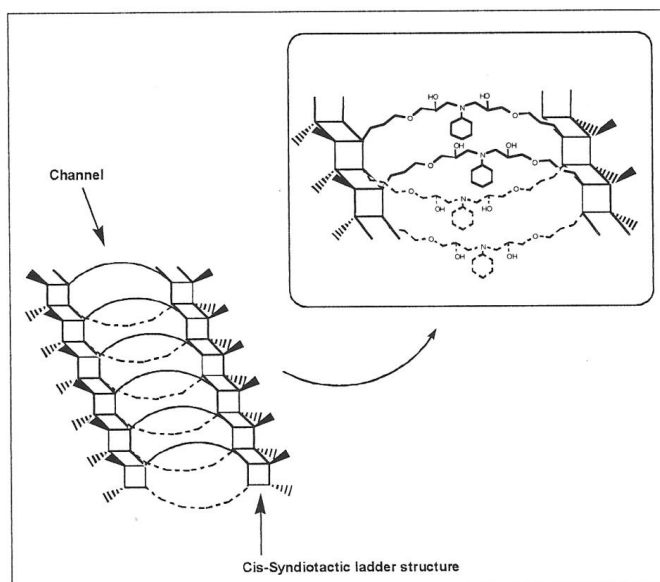
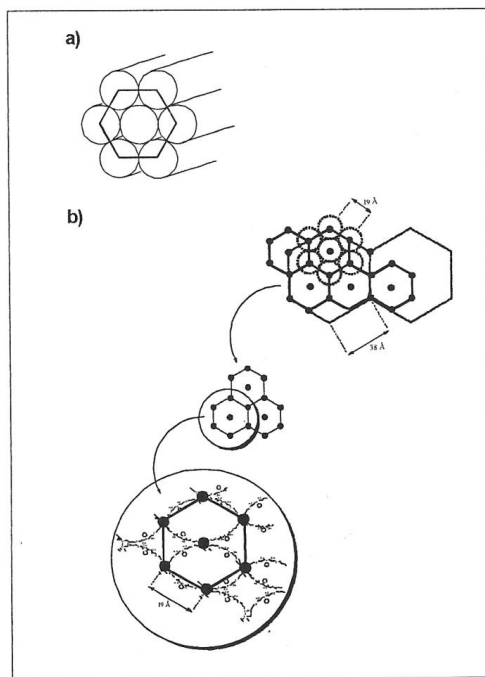Fig. 5. Scheme of the self-assembled structure in BS material.



Fig. 6. a) Cylindrical self-assemblies crystallized in a two-dimensional hexagonal array and b) Schematic model representing the hexagonal (2D) arrangement of the nanostructured domains in MS material.

sional hexagonal structure consisting of cylindrical self-assemblies crystallized in a hexagonal lattice (Figure 6a) [43, 44]. On this base, we assigned the most intense peak (0.38 Å⁻¹), the second one (0.66 Å⁻¹) and the small shoulder to the first, second and third Bragg reflections in accordance to the 2D-hexagonal structure. For a two-dimensional hexagonal structure, the lattice parameter ($a$ = distance between centers of adjacent cylinders) is related to the most intense diffraction peak as follows: $q_{max} = 4\pi/a\sqrt{3}$. From the $q_{max}$ value (0.38 Å⁻¹) the distance $a$ was calculated as 19 Å, which was again attributed to the lengh of the curved organic bridge. Then, the basic structure could be interpreted as inorganic domains arranged in a hexagonal disposition separated 19 Å by organic domains (curved bridges). An additional and less intense peak (0.20 Å⁻¹) was also detected in the spectrum. Based on a hexagonal structure, this pattern corresponds to a distance of 36 Å which was attributed to the lengh of about two organic bridges. In this way, it could be attributed to the first Bragg reflection corresponding to a secondary and spatially less extended hexagonal structure.

A schematic model representing the hexagonal array and the calculated distances of the nanostructured domains is shown in Figure 6b. Spheres represent inorganic domains which are the scattering elements (high-electron density centers) of the structure. These domains are ar-
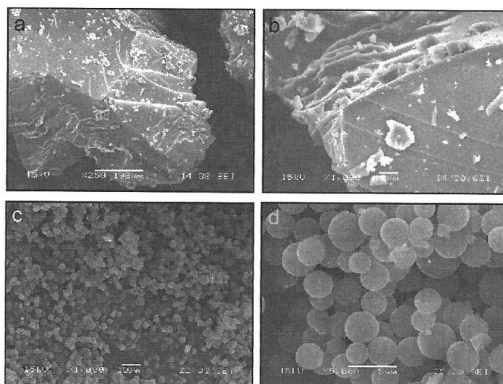
Fig. 7. SEM micrographs of a), b): BS material; c), d) MS material.
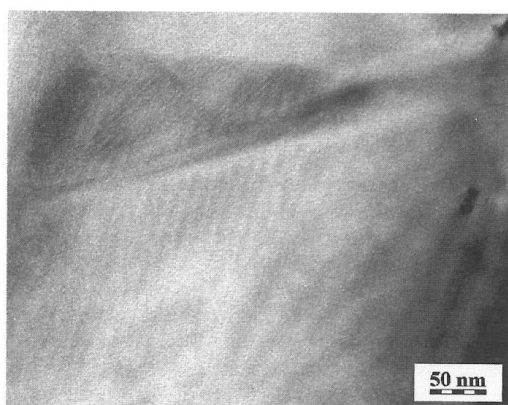


Fig. 8. TEM image of the MS bridged silsesquioxane.

ranged into a hexagonal array as shown in the Fig. Dashed circles and small hexagons have been traced to visualize the hexagonal system. Big and dashed hexagons intend to show the secondary hexagonal arrangement arose from the extension of the basic structure. All inorganic domains have a similar hierarchy in the structure meaning that similar structures of dashed circles and hexagons can be shifted by arbitrarily selecting a set of inorganic domains separated by 19 Å, at the centers of cylinders. The local nanostructure is visualized by the magnification of one small hexagon shown in the Figure 6b. All inorganic domains are separated by a distance of 19 Å corresponding to the lengh of the curved organic bridge. The ultrasound assisted sol-gel synthesis led to a much better nanostructuration of the hybrid material

in comparison to the material obtained without this irradiation (BS sample). The high definition of the SAXS spectrum enabled us to propose a more reliable structure for the cavities generated in the microspheres.

Figure 7 shows SEM photographs corresponding to the obtained materials. The BS material was a compact solid that did not exhibit any measurable porosity (mass density: 1.20 g/mL) (Figure 7a and 7b). On the other hand, the MS material (Figure 7c and 7d) is formed by spherical microparticles with low coalescence. The size distribution exhibited a very low polydispersity with a mean particle size of $3.4 \pm 0.2$ mm (as obtained by image analysis).

Figure 8 shows a TEM image of the BS. Small ordered regions with a lamellar structure co-exist with regions that do not exhibit any particular feature in the image. The characteristic thickness of a lamella lies in the range of 50-100 Å involving the stacking of a few basic units.

## 4. Conclusions

Bridged silsesquioxanes obtained by the hydrolytic condensation of a bridged precursor synthesized by the stoichiometric reaction of glycidoxypropyl (trimethoxysilane) with cyclohexylamine exhibit a nanostructuration as evidenced by SAXS and TEM.

For the hybrid material synthesized without ultrasonic irradiation (BS sample), at least a fraction of inorganic domains is self-organized as cis-syndiotactic ladder structures as evidenced by $^{29}$Si NMR spectra. Organic bridges extending between two ladders are curved to accommodate the cyclohexyl groups in the structure. This leads to the formation of elongated organic channels bounded by inorganic ladders. The repetition of this structure leads to a foil of alternating inorganic ladders and organic channels in BS material.

Moreover, a novel and versatile self-assembly process of a bridged precursor assisted by ultrasonic irradiation leads to the formation of nanostructured hybrid microspheres. In MS material, inorganic domains were arranged in a two-dimensional hexagonal system. Basic building blocks were cavities with cross sections formed by four organic bridges (shared by two cavities) and four inorganic domains (at the intersection of four cavities).

The presence of hydroxyls, tertiary amines and ether groups in the organic channels makes these hybrids excellent hosts of small organic molecules capable of forming H-bonds. Work in this direction is currently in progress.

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