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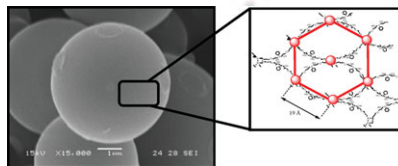
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Full Paper

An original and versatile sol-gel process based on ultrasound-assisted self-assembly of a bridged precursor enables the rapid synthesis of microspheres structured at molecular level. Inorganic domains were arranged into a two-dimensional hexagonal structure leading to the formation of cavities that could be employed as host receptacles to incorporate organic molecules to be used in advanced technologies.

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H. E. Romeo,* M. A. Fanovich, R. J. J.
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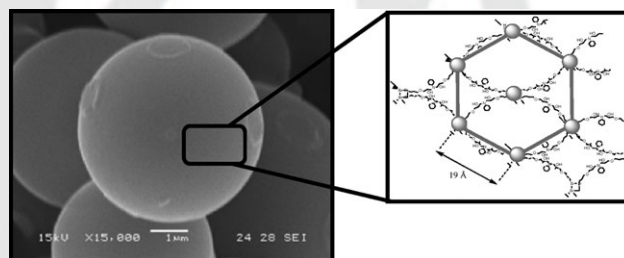
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Fast Synthesis of Nanostructured Microspheres of a Bridged Silsesquioxane via Ultrasound-Assisted Sol–Gel Processing

Hernán E. Romeo,* María A. Fanovich, Roberto J. J. Williams, Libor Matějka, Josef Pleštil, Jiří Brus

Microspheres of a nanostructured bridged silsesquioxane were synthesized by employing ultrasound-assisted self-assembly of a bridged monomer via sol–gel processing. The bridged precursor was synthesized from glycidoxypropyl(trimethoxysilane) (GPMS) (2 mol) and cyclohexylamine (1 mol). The main factor controlling the generation of a stable dispersion of microspheres was the time at which the phase separation of the silsesquioxane was produced during the hydrolytic condensation. An appropriate blend of THF/hexane as a solvent enabled to rapidly generate a stable dispersion exhibiting a low polydispersity. 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.



Introduction

1 The sol–gel processing has been shown to be a powerful
2 method for producing silica-based hybrid materials.^[1–4] In
3 particular, bridged silsesquioxanes are a family of organic–
4 inorganic hybrid materials obtained by the hydrolysis and
5 condensation of monomers containing an organic bridging
6 group covalently bonded to terminal trialkoxysilyl or

trichlorosilyl groups.^[5–7] These bridged hybrids offer the
possibility of producing materials in which the bridging
unit itself exhibits self-assembling properties.^[8,9] Depend-
ing 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,^[10] supramolecular-assembled films,^[11] as well
as mesoporous phenylene-bridged silsesquioxane-based
materials with ordered hexagonal pore structures.^[12,13]
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 such as catalysis, optics, electronics, and biosciences,
among others.^[14]

Different kinds of organic structures with self-assem-
bling capabilities, leading to nanostructured bridged

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silsesquioxanes after hydrolytic condensation, have been reported in the literature. Strong hydrogen bonds as those formed among urea groups, alone or combined with aromatic π -stacking or hydrophobic interactions produce a variety of self-assembled structures.^[15–21]

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,^[22] vigorous stirring of the precursors for long periods,^[23,24] among others, have been reported. C. Ma and Y. Kimura disclosed the preparation of poly(phenylsilsesquioxane)s nanoparticles having an average diameter of 30–110 nm by conducting emulsion polymerization of the phenyltri-chloro hydrolizate.^[25] On the other hand, Liu et al. reported the preparation of nano and microspheres of polysilsesquioxane copolymer by hydrolytic co-condensation of phenyltriethoxysilane with γ -aminopropyltriethoxysilane in the presence of sodium dodecyl sulfate.^[26]

In the last few years, the chemical applications of ultrasound have become an exciting new field of research,^[27] the chemical effects of ultrasound being sorted out into three main areas: homogeneous sonochemistry of liquids, heterogeneous sonochemistry of liquid–liquid or liquid–solid systems, and sonocatalysis. Ultrasonic irradiation differs from traditional energy sources in duration, pressure and energy per molecule because of the cavitation bubble collapse, which means the formation, growth, and implosive collapse of bubbles in the liquid. The application of ultrasonic irradiation to the synthesis of different materials has gained much attention and it is under rapid development.^[28] However, this technique has not been employed yet in the sol–gel reaction of bridged silsesquioxanes with self-assembling capability.

The aim of this study was to synthesize novel nanostructured microspheres of bridged silsesquioxanes via ultrasound-assisted self-assembly of a bridged precursor containing a pendant cyclohexyl group in the organic bridge. The effects of both the nature of the reaction solvent on the obtained morphologies and the presence of the pendant group on the final nanostructuration were analyzed. To the best of our knowledge, this is the first report on the combination of the ultrasonic irradiation technique with the self-assembling capability of a bridged precursor to produce microspheres structured at nanoscale.

Experimental Part

Materials

Glycidoxypropyl(trimethoxysilane) (GPMS, Dow Corning, 99%, density at 20 °C = 1.07 g · ml⁻¹), cyclohexylamine (CA, Merck, 99%, density at 20 °C = 0.87 g · ml⁻¹), formic acid (FA, Cicarelli, 88%, density at 20 °C = 1.20 g · ml⁻¹), tetrahydrofuran (THF, Cicarelli, 99%, density at 20 °C = 0.89 g · ml⁻¹), and hexane (Hex, Sintorgan, 99%, density at 20 °C = 0.66 g · ml⁻¹) were used without further purification.

Synthesis of the Bridged Precursor

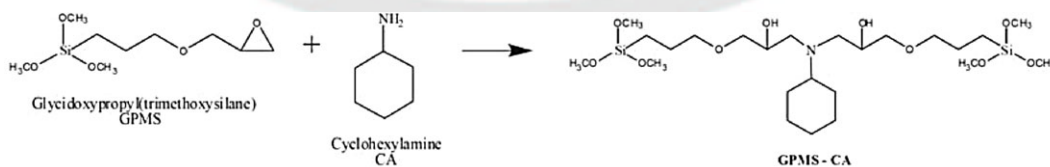
The hybrid precursor was synthesized from GPMS and CA (Scheme 1) in glass tubes (2 cm diameter and 15 cm height), employing a molar ratio GPMS/CA = 2 (in a typical synthesis 3 mL of GPMS were reacted with 0.78 mL of CA). The tubes were sealed under nitrogen and placed in a thermostat at 70 °C for 48 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.^[29]

Preparation of the Hybrid Microspheres

The hydrolytic condensation of the bridged precursor was accomplished in three different solvents: THF, Hex, and a mixture of THF/Hex (1:2 volumetric ratio), using an aqueous solution of FA as a catalyst, in the following molar ratios: FA/Si = 3 and H₂O/Si = 1.05. In a typical synthesis, 100 mL of a solution containing 3.889 g of the precursor (GPMS-CA) were added to a glass vessel (5 cm diameter × 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 (130 W/20 kHz) was employed as an 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 products were fine yellow glassy powders.

Characterization of the Microspheres

Morphologies were observed by scanning electron microscopy (SEM), employing a Jeol JXA-8600 microscope after coating the samples with a thin gold layer.



■ Scheme 1. Stoichiometric reaction between GPMS and cyclohexylamine (CA) leading to the formation of the bridged precursor.

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

5 1D ^{29}Si MAS NMR spectra were measured using a Bruker
6 Avance 500 WB/US spectrometer at MAS frequency $\omega_r/2\pi =$
7 10 kHz and $B_1(^{13}\text{C})$ field intensity $\omega_1/2\pi = 62.5$ kHz. $B_1(^1\text{H})$ field
8 intensity of TPPM (two-pulse phase-modulated) decoupling
9 corresponds to $\omega_1/2\pi = 89.3$ kHz. Single-pulse experiments were
10 used with 45 μs pulse length (2 μs) and 60 s repetition delay.
11 The ^{29}Si NMR scale was calibrated by external standard M_8Q_8
12 (-109.8 ppm; the highest field signal).

13 Thermogravimetric analyses (TGA) were performed with a
14 Shimadzu TGA-50 thermal analyzer under argon atmosphere at a
15 heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$, from room temperature to 800°C .

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

Results and Discussion

24 Synthesis of the Bridged Precursor

25 The stoichiometric reaction between GPMS (2 mol) and CA
26 (1 mol) was selected in order to synthesize a precursor
27 bearing a pendant cyclohexyl fragment in the organic
28 bridge (see Scheme 1). The epoxy-amine reaction led not
29 only to the desired precursor but also to the formation of
30 oligomers produced from $\text{Si}(\text{OCH}_3)$ groups which reacted
31 with the secondary hydroxyls generated by opening of the
32 epoxy ring. In this way, oligomers are formed through
33 covalent Si-O-C bonds,^[30–33] leading to a viscous solution.
34 However, these Si-O-C bonds may be hydrolyzed along
35 the course of the hydrolytic condensation,^[32] particularly
36 when using an acid catalyst.^[33] This leads to the
37 regeneration of the main structure depicted in Scheme 1
38 as a precursor of the hybrid material.

Preparation of the Hybrid Microspheres

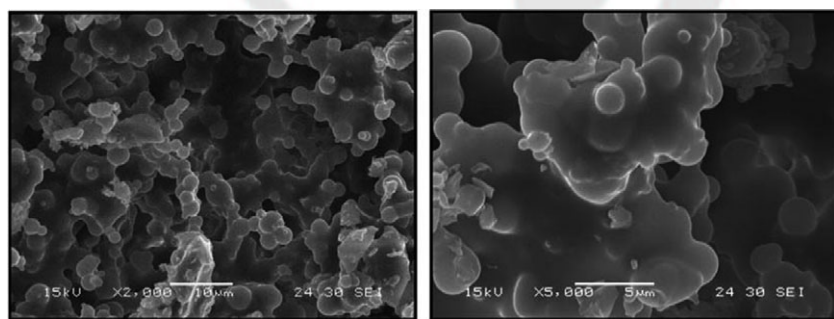
1 It is well known that, depending on the nature of the bridge,
2 the self-assembly of bridged silsesquioxanes can generate
3 structured hybrids. On the other hand, when a reaction-
4 induced phase separation occurs in solution, spherical
5 droplets are generated in the reaction medium to minimize
6 surface tension.^[34] Therefore, an adequate selection of the
7 solvent can produce a dispersion of spherical domains
8 exhibiting a nanostructured morphology.

9 In the present study, the endpoint of the hydrolytic
10 condensation defined by the generation of a white
11 suspension (phase separation) was close to 40 s in Hex
12 and 90 s in the THF/Hex mixture. When pure THF was used
13 as a solvent, no phase separation was observed even after
14 30 min of applying ultrasonic irradiation.

15 The experimental results could be interpreted as
16 follows. When methoxysilyl groups of the bridged
17 precursor are hydrolyzed to silanol groups, an abrupt
18 change of solubility occurs in the nonpolar solvent (Hex).
19 This fact immediately leads to a fast phase separation
20 (microdroplets), which is seen as a white suspension
21 maintained by the ultrasonic irradiation source. As this
22 happens, the inorganic condensation of the hydrolyzed
23 monomers takes place inside the formed microdroplets
24 which continuously incorporate hydrolyzed bridged
25 monomer increasing their size. In this way, the micro-
26 droplets act as microreactors in which the concentrated
27 monomer rapidly condensates. On the other hand, when
28 THF is used as a reaction solvent, the hydrolyzed species
29 are soluble because of the formation of strong hydrogen
30 bonds between Si-OH groups in the precursor and the
31 oxygen atom of the THF molecules. In this case, the
32 inorganic polycondensation of the diluted monomer takes
33 place slowly in a homogeneous solution. The hydrolytic
34 condensation of the precursor in the THF/Hex mixture led
35 to a delayed phase separation compared to the reaction
36 carried out in pure Hex. In summary, the selection of an
37 adequate reaction solvent plays a key role in the synthesis
38 of microspheres structured at the molecular level.

Characterization of the Hybrid Microspheres

39 SEM images corresponding to the silses-
40 quoxane synthesized in Hex are shown
41 in Figure 1. The presence of fused micro-
42 particles is clearly distinguishable. In this
43 case, phase separation was observed after
44 only 40 s reaction. Presumably, micro-
45 particles generated at low conversions
46 were not gelled and liquid droplets could
47 easily undergo coalescence after filtering
48 and heating for solvent evaporation.



■ Figure 1. SEM micrographs of the hybrid material obtained in pure Hex.

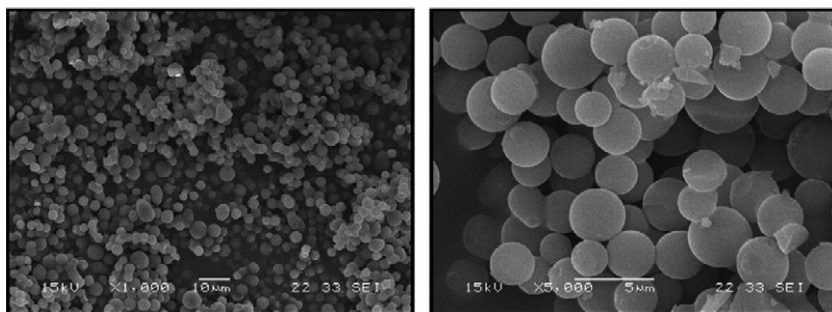


Figure 2. SEM micrographs of the hybrid microspheres obtained in THF/Hex mixture.

Figure 2 shows SEM photographs corresponding to the silsesquioxane synthesized in THF/Hex. In this case, phase separation was observed at a later stage, after 90 s reaction. Possibly the gelation of individual microparticles occurred during this period leaving a small fraction of Si–OH groups at the surface. This could justify the absence of significant coalescence after thermal treatment. Therefore, adjusting the polarity of the reaction medium enabled to delay phase separation and generate a dispersion of individual microspheres of the hybrid material. The distribution exhibited a very low polydispersity with a mean particle size of $3.4 \pm 0.2 \mu\text{m}$ (as obtained by image analysis).

Figure 3 depicts the FTIR spectrum of the microspheres. It confirms the formation of Si–O–Si bonds as well as the retention of the Si–C linkages in the hybrid structure. The small band observed at 914 cm^{-1} corresponds to unreacted Si–OH groups, in accordance to an incomplete condensation.

The type of structures generated during the polycondensation may be inferred from the location of bands characterizing the antisymmetric Si–O–Si stretching

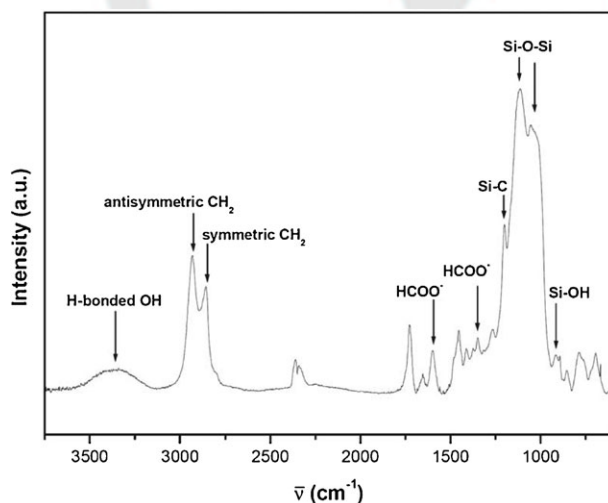


Figure 3. FTIR spectrum of hybrid microspheres.

vibrations. For fully condensed silsesquioxanes, the appearance of a single band centered near $1120\text{--}1130 \text{ cm}^{-1}$ may be taken as good evidence for the presence of a polyhedral structure,^[35,36] while the presence of two bands centered near 1040 and $1120\text{--}1130 \text{ cm}^{-1}$ is characteristic of a *cis*-syndiotactic ladder configuration.^[35–37] In our case, two bands located at about 1040 and 1120 cm^{-1} were observed. However, the assignment of these bands to ladder structures should be made with some

caution because complete condensation was not achieved. Most probably, silica domains were organized as imperfect structures exhibiting a large fraction of intramolecular cycles together with a fraction of free silanol groups (one can visualize these structures as imperfect ladders). Two small bands detected at 1350 and 1590 cm^{-1} are indicative of the presence of a small residual fraction of FA as HCOO^- anions, possibly forming salts with tertiary amine groups.^[38] In the range $2850\text{--}2930 \text{ cm}^{-1}$ two well-defined bands could be observed, corresponding to the symmetric and antisymmetric CH_2 stretching modes, respectively. Finally, the broad-band centered at about 3400 cm^{-1} was assigned to C–OH groups including the small fraction of unreacted Si–OH groups.

^{29}Si NMR spectrum provides information related to the condensation degree of the silsesquioxane (Figure 4). Four signals were obtained from the deconvolution of the spectrum. The main peak at -65.8 ppm is characteristic of T_3 species: $\text{Si}(\text{O}-\text{Si})_3$,^[39–42] the two peaks at -59.4 and -55.1 ppm are assigned to T_2 structures: $\text{Si}(\text{O}-\text{Si})_2(\text{OH})$,^[43–45] and the smallest peak at -49.6 ppm is attributed to T_1 species: $\text{Si}(\text{O}-\text{Si})(\text{OH})_2$.^[46] No peaks corresponding to T_0 structures were observed. 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

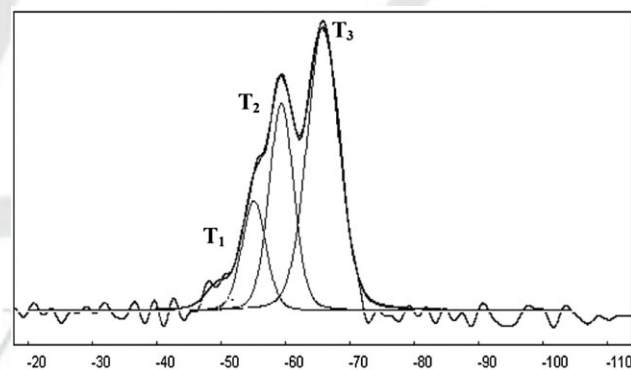


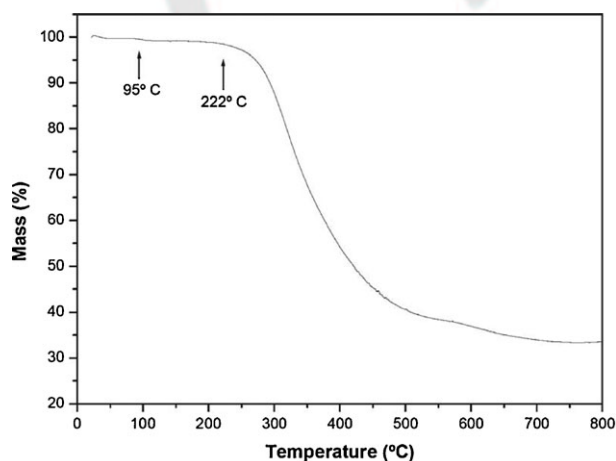
Figure 4. ^{29}Si NMR spectrum of hybrid microspheres.

1 conversion into Si–O–Si bonds of 83.1% ($0.524 + (2/3)$
2 $0.444 + (1/3) 0.032$).

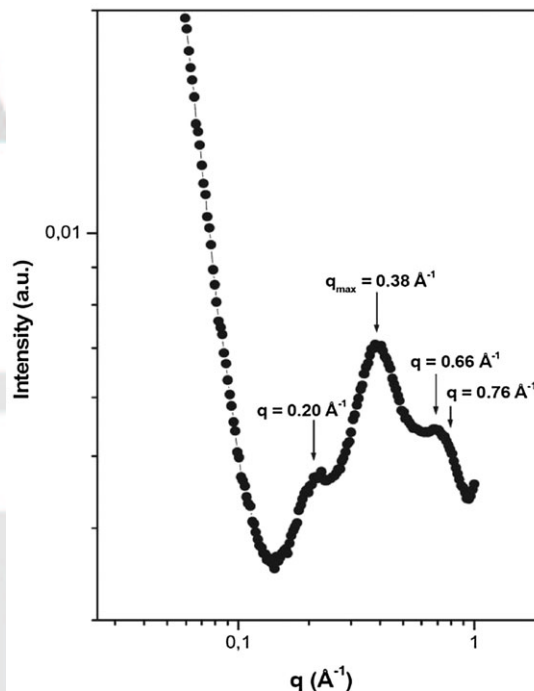
3 Figure 5 shows the TGA thermogram of the micro-
4 spheres. The fast weight loss in the range of 265–650 °C
5 arises from the decomposition of the organic moieties. The
6 mass loss was 67.1% which is in a close agreement with
7 the theoretical organic weight fraction (70%) in the hybrid
8 structure. The mass loss at 95 °C (about 1%) was attributed
9 to the evaporation of adsorbed water. From the obtained
10 thermogram it was possible to infer that the microspheres
11 had a high thermal stability since they began to
12 decompose at about 222 °C.

13 Figure 6 depicts the SAXS spectrum of the microspheres.
14 Due to the contrast of electron densities between the
15 organic and inorganic phases, when a correlation length is
16 found in SAXS spectra, it is associated to a characteristic
17 distance separating inorganic domains. In the case of self-
18 assembled bridged silsesquioxanes, this characteristic
19 distance is frequently found to be equal to the length of
20 the organic bridges.^[15,47] In our system, the appearance of
21 diffraction patterns in the range of 0.14–1.1 Å⁻¹ is
22 indicative of the existence of some degree of organization
23 at the molecular level.

24 In a previous study, we reported the synthesis of a
25 silsesquioxane starting from the same precursor but
26 employing reaction conditions (homogeneous solutions,
27 long times, and high temperatures) that led to a very high
28 conversion in the polycondensation reaction.^[29] In that
29 case, a less defined nanostructuring was observed
30 characterized by the appearance of a single peak in the
31 SAXS spectrum, assigned to the length (19 Å) of the organic
32 bridge. In the conformation of minimum energy, organic
33 bridges were curved to accommodate the cyclohexyl
34 groups in the hybrid structure (as estimated using the
35 software ACD Labs/3D Viewer) leading to the formation of
36 a hybrid material exhibiting a short-range ordering based
37



■ Figure 5. TGA thermogram of hybrid microspheres.



■ Figure 6. SAXS diffractogram of hybrid microspheres.

on elongated organic channels accommodating the
cyclohexyl fragments.

In this work, the q (wave vector) position corresponding to the most intense Bragg peak was found to be 0.38 \AA^{-1} . A second and less intense peak was detected at $q = 0.66 \text{ \AA}^{-1}$, overlapped with a small shoulder located at 0.76 \AA^{-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-dimensional hexagonal structure consisting of cylindrical self-assemblies crystallized in a hexagonal lattice (Figure 7).^[48,49] On this basis, we assigned the most intense peak (0.38 \AA^{-1}), the second one (0.66 \AA^{-1}) and the

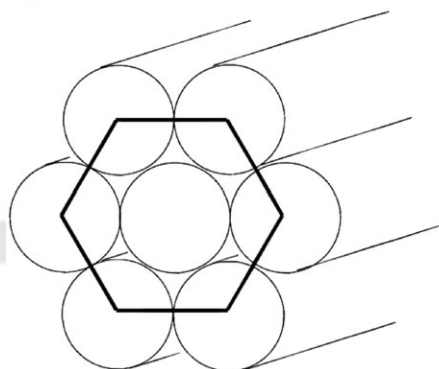


Figure 7. Cylindrical self-assemblies crystallized in a two-dimensional hexagonal array.

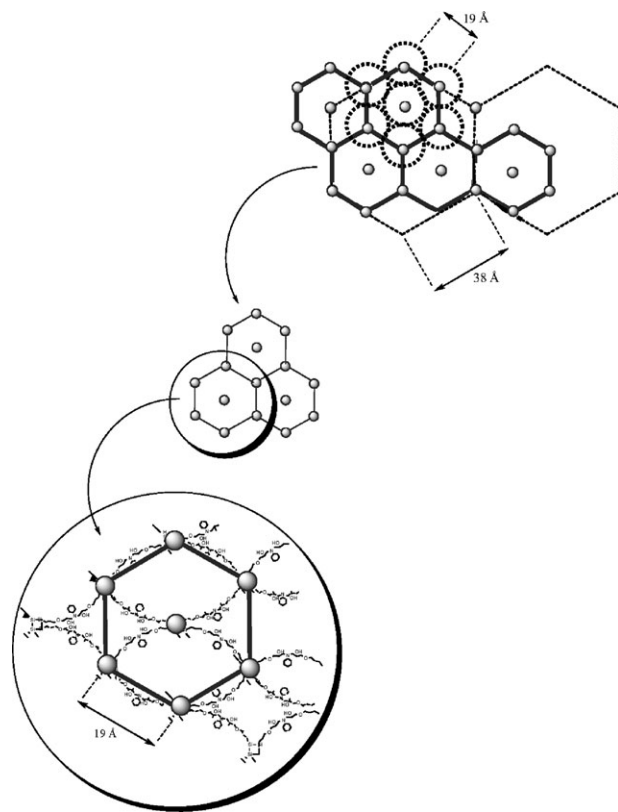


Figure 8. Schematic model representing the hexagonal (2D) arrangement of the nanostructured domains.

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 \AA^{-1}) the distance a was calculated as 19 \AA , which was again attributed to the length of the curved organic bridge. Then, the basic structure could be interpreted as inorganic domains arranged in a hexagonal disposition separated 19 \AA by organic domains (curved bridges). An additional and less intense peak (0.20 \AA^{-1}) was also detected in the spectrum. Based on a hexagonal structure, this pattern corresponds to a distance of 36 \AA which was attributed to the length 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 8. Spheres represent inorganic domains which are the scattering elements (high-electron density centers) of the structure. These domains are arranged into a hexagonal array as shown in the figure. 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 \AA , at the centers of cylinders. The local nanostructure is visualized by the magnification of one small hexagon shown in Figure 8. All inorganic domains are separated by a distance of 19 \AA corresponding to the length of the curved organic bridge.

Basic building blocks are cavities that extend in a direction perpendicular to the plane, with cross sections formed by four organic bridges (shared by two cavities) and four inorganic domains (at the intersection of four cavities). Cavities accommodate pendant cyclohexyl groups (two per cavity in the plane). Therefore, the hybrid material was nanostructured as a set of neighboring cavities in a hexagonal array.

In comparison to the previously reported organic-inorganic material,^[29] the method of synthesis used in this study led not only to a stable dispersion of microspheres but also to a much better nanostructuring of the hybrid material. The high definition of the SAXS spectrum enabled us to propose a more reliable structure for the cavities generated in the microspheres.

Conclusion

A novel and versatile self-assembly process of a bridged precursor assisted by ultrasonic irradiation leads to the formation of nanostructured hybrid microspheres. The main factor controlling the generation of a stable dispersion of microspheres was the time (conversion) at which the phase separation of the silsesquioxane was produced during the hydrolytic polycondensation. Employing a polar solvent like THF did not produce phase separation. A nonpolar solvent like hexane led to a very rapid phase separation that generated a significant coalescence of the original phase-separated domains. Employing an appropriate blend of THF and hexane as a solvent enabled to delay the phase separation and generate a stable dispersion of microspheres exhibiting a low polydispersity. The use of ultrasonic irradiation produced this morphology in a very short reaction time (90 s). The mild reaction conditions employed in the synthesis produced the nanostructuring of the silsesquioxane characterized by a fine structure in the SAXS spectrum. 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).

1 The significance of this work is related to the possibility
2 of employing ultrasonic irradiation-assisted self-assembly
3 of a diversity of bridged building blocks to synthesize
4 nanostructured hybrid microspheres. Bridges containing
5 pendant groups can be employed to generate cavities that
6 can be used as hosts of a diversity of organic molecules.
7 Work in this direction is currently in progress.

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