Self-Assembly of a Bridged Silsesquioxane Containing a Pendant Hydrophobic Chain in the Organic Bridge

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ABSTRACT: The aim of this study was to synthesize and characterize the self-assembly of a new family of bridged silsesquioxanes containing a pendant hydrophobic chain in the organic bridge. The precursor of this hybrid was obtained by the reaction of glycidoxypropyl(trimethoxysilane) (GPMS) (2 mol) with dodecylamine (1 mol). Polycondensation was produced with formic acid, either in mass or using tetrahydrofuran or isopropanol as solvents. The resulting bridged silsesquioxane was characterized by the presence of both ordered and disordered domains. Experimental evidence obtained from SAXS, WAXS, ^{29}Si NMR, FTIR, HRTEM, and SAED techniques suggested that the basic structure of ordered domains consisted of hybrid organic−inorganic multilayers separated by hydrophobic regions with a thickness equal to the length of a tail-to-tail association of dodecylamine chains in all-trans conformations. To our knowledge, this is the first example of the presence of this kind of structure in a cross-linked hybrid material. A hierarchical organization of ordered domains into semicylindrical shells was observed in a microscopic scale. Because of the presence of pendant hydrophobic chains, the precursor of this hybrid material may be used for the dispersion of hydrophobic molecules or of nanoparticles stabilized by hydrophobic chains.

Introduction

Bridged silsesquioxanes are a family of organic−inorganic hybrid materials synthesized by the hydrolysis and condensation of monomers containing an organic bridging group joining two (or eventually more) trialkoxysilyl or trichlorosilyl groups.[1−11] The organic group, covalently bonded to the trialkoxysilyl groups, can be varied in composition, length, rigidity, and functionalization. It can exhibit self-assembling properties that may direct the formation of a tridimensional hybrid network by a self-organization process in the course of the hydrolysis and polycondensation of the trifunctional silyl groups. This nanostructuring may be used to tune the properties of the hybrid material.[12,13]

Different kinds of organic structures with self-assembly capabilities have been reported in the literature to generate nanostructured bridged silsesquioxanes. Strong hydrogen bonds as those formed among urea groups present in organic bridges, alone or combined with aromatic π-stacking or hydrophobic interactions, produce a variety of self-assembled structures.[13−23] On the other hand, the use of organic surfactant templates has been extensively used to synthesize silica-based materials with well-ordered mesoporous structures.[24−37]

The aim of the present study was to generate nanostructured hybrids by incorporation of the surfactant template as a hydrophobic chain pendant in the organic bridge. To the best of our knowledge, the only previous study of bridged silsesquioxanes with pendant chains (alkyl or perfluorinated) was reported by Ameduri et al.[38] In this study a short bridge composed of 2 C atoms and 1 central Si atom was employed.

Here we will discuss the effect of placing a pendant dodecyl chain in a larger organic bridge. The synthesis of the precursor of the bridged silsesquioxane and the characterization of the self-assembled hybrid network produced by the hydrolysis and condensation of the trialkoxysilyl groups will be discussed. The significance of this study is related to the possibility of using this kind of precursors for the dispersion of nanoparticles stabilized by hydrophobic chains and fixation of the resulting nanostructure by the inorganic polycondensation.

Experimental Section

Materials. Glycidoxypropyl(trimethoxysilane) (GPMS, Dow Corning, 99%; density at 20 °C = 1.07 g/cm³), dodecylamine (DA, Fluka, 98%), formic acid (Cicarelli, 88 wt %, density at 20 °C = 1.20 g/mL), tetrahydrofuran (THF, Cicarelli, 99%), and isopropanol (Cicarelli, 99.5%), were used as received.

Synthesis of the Precursor. The synthesis was performed in glass tubes (20 mm diameter and 150 mm height), employing a molar ratio GPMS/DA = 2 (in a typical synthesis 3 mL of GPMS were reacted with 1.251 g of DA). The tubes were sealed under nitrogen and placed in a thermostat at 70 °C for 48 h. They were extracted at different times, and the partial extent of reaction was characterized by size exclusion chromatography (SEC). The SEC device consisted of a Knauer K-501 pump, a refractive index detector Knauer K-2301, and a set of Phenomenex Phenogel 5 μ-columns (50A, 100A, and M2). THF was used as a carrier at 1 cm³/min, and the concentration of the precursor solution in THF was 20 mg/cm³.
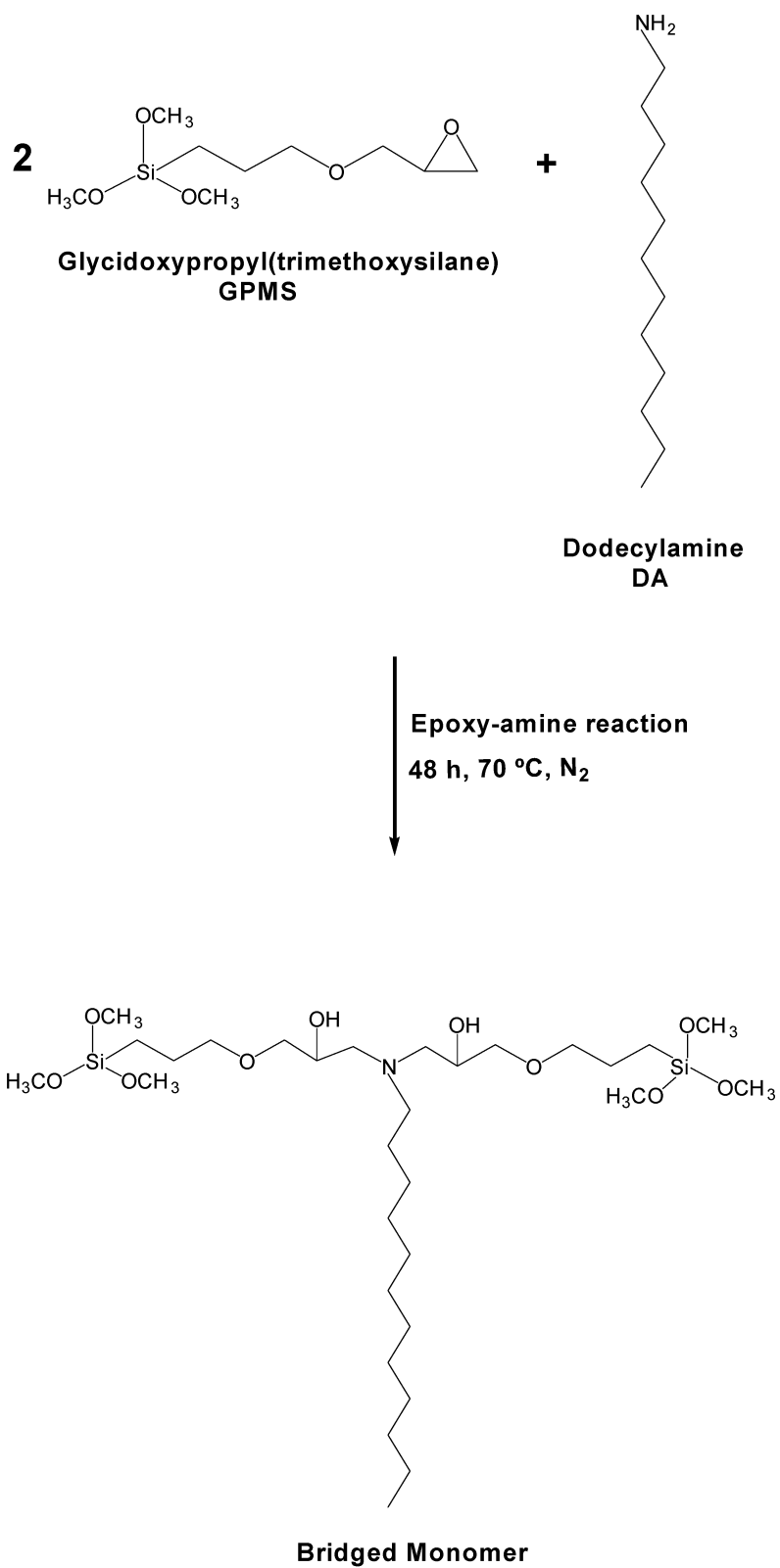
Synthesis of the Bridged Silsesquioxane. The hydrolysis and condensation of the precursor were performed in the same glass tubes employed in the synthesis, using an aqueous solution of formic acid in the following molar ratios: HCOOH/Si = 3, H₂O/Si = 1.05. (In a typical synthesis 1.77 mL of the 88 wt % formic acid solution was added to the precursor synthesized using 3 mL of GPMS and 1.251 g of DA.) The reaction was carried out either in mass or

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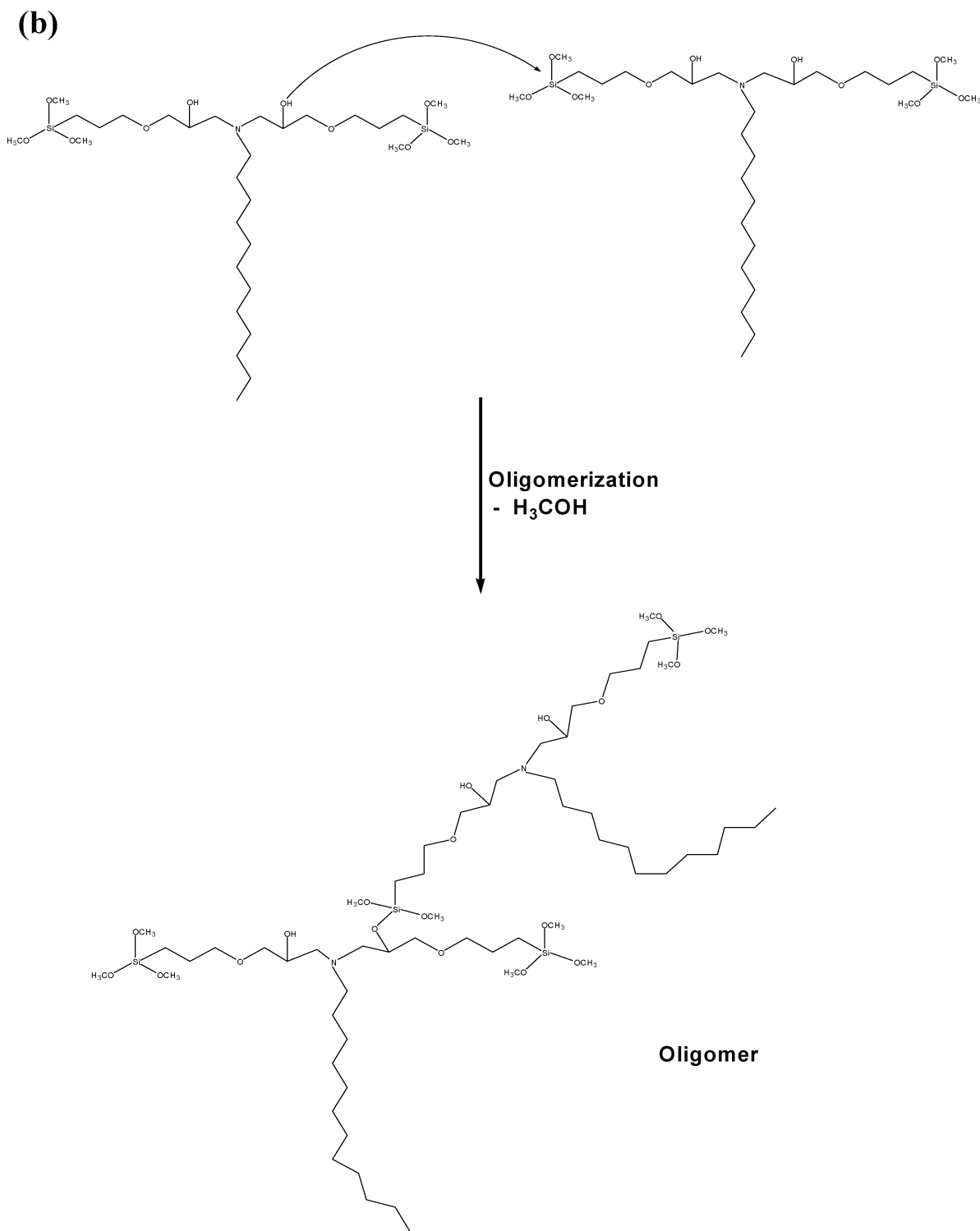[†] INTEMA.
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(a)

Glycidoxypropyl(trimethoxysilane)
GPMS

Dodecylamine
DA

Epoxy-amine reaction
48 h, 70 °C, N₂

Bridged Monomer

(b)

Figure 1. Reaction between dodecylamine (DA) and glicidoxypropyl(trimethoxisilane) (GPMS): (a) main reaction and (b) secondary reaction leading to oligomers with covalent Si−O−C bonds.

using THF or isopropanol as solvents. (In a typical synthesis 5 mL of solvent was added to the precursor synthesized using 3 mL of GPMS and 1.251 g of DA.) The tubes were left open and placed in a thermostat at 50 °C for 24 h. Solvents and volatile products were evaporated continuously during the reaction. The product was milled, placed in a Petri dish, and heated in an oven at 110 °C for 3 h. The final hybrid material was a transparent yellow glassy powder.

Characterization of the Bridged Silsesquioxane. Small-angle X-ray scattering (SAXS) measurements were performed on a Kratky camera with a 60 μm entrance slit and a 42 cm sample-to-detector distance. Ni-filtered Cu Kα radiation ($\lambda = 0.154$ nm) was recorded with a linear position-sensitive detector (Joint Institute for Nuclear Research, Dubna, Russia). The experimental (smeared) SAXS curves are presented as a function of the magnitude of the scattering vector $q = (4\pi/\lambda)\sin\theta$ (2θ is the scattering angle).

Wide-angle X-ray scattering (WAXS) spectra were obtained in a powder diffractometer HZG/4A (Freiberger Praezisionsmechanik GmbH, Germany) using Ni-filtered Cu Kα radiation.

1D ^{29}Si MAS NMR spectra were measured using a Bruker Avance 500 WB/US spectrometer at MAS frequency $\omega_r/2\pi = 10$
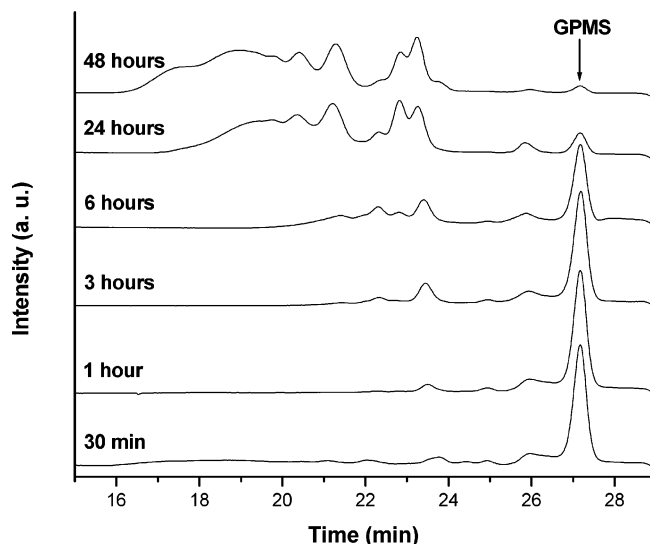
Figure 2. SEC chromatograms obtained at different reaction times during the synthesis of the precursor.
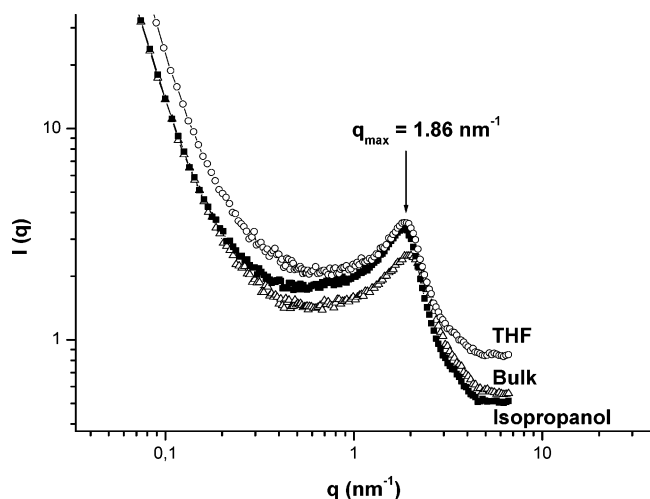

Figure 3. SAXS spectra of the bridged silsesquioxane synthesized in bulk, THF, and isopropanol.

kHz and B_1(^{13}C) field intensity $\omega_1/2\pi = 62.5$ kHz. B_1(^{1}H) field intensity of TPPM (two-pulse phase-modulated) decoupling cor-

responds to $\omega_1/2\pi = 89.3$ kHz. Single-pulse experiments were used with 45° pulse length (2 μs) 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 silsesquioxane with KBr.

High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were performed using an electron microscope JEM-3010. The powder-like particles of the sample were transferred to the microscopic copper grid covered with a thin carbon film and analyzed at 300 kV. Structures were also observed by scanning electron microscopy (SEM, Jeol JXA-8600, gold-coated samples).

Mass density was determined from the mass and volume (measured in water) of a set of three samples.

Results and Discussion

Synthesis of the Precursor. The stoichiometric reaction between dodecylamine (DA, 1 mol) and glycidoxypropyl(tri-methoxysilane) (GPMS, 2 mol) was selected to synthesize the precursor bearing a pendant hydrophobic chain in the organic bridge (Figure 1a). But Si(OCH$_3$) groups react with the secondary hydroxyls produced in the epoxy−amine reaction generating CH$_3$OH and leading to the formation of oligomers through covalent Si−O−C bonds (Figure 1b).[39−42]

The consumption of GPMS along its reaction with DA was followed by SEC. While GPMS gave a distinct peak, DA could not be detected under the selected conditions. Figure 2 shows chromatograms obtained at different reaction times. Most of the GPMS was consumed after 48 h reaction, and this time was arbitrarily taken as the end of reaction. The oligomers formed by the inter- and intramolecular condensation through covalent Si−O−C bonds (Figure 1b) appear in the region of higher molar masses. These Si−O−C bonds may be hydrolyzed in the course of the hydrolytic condensation,[41] particularly when using an acid catalyst.[42] This regenerates the main structure depicted in Figure 1a as the building block of the final hybrid material.

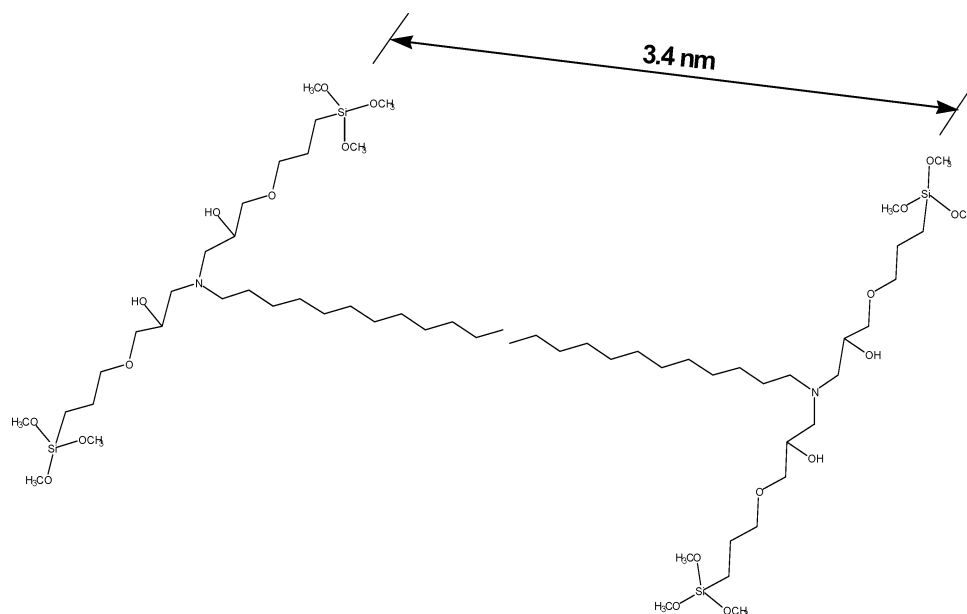**Synthesis of the Bridged Silsesquioxane.** The use of concentrated formic acid (a 88 wt % solution) produced the

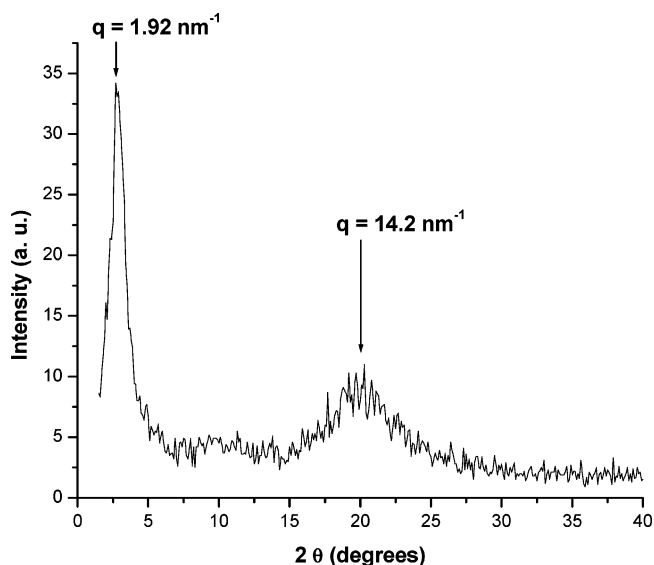**Figure 4.** Tail-to-tail association of two dodecylamine chains.

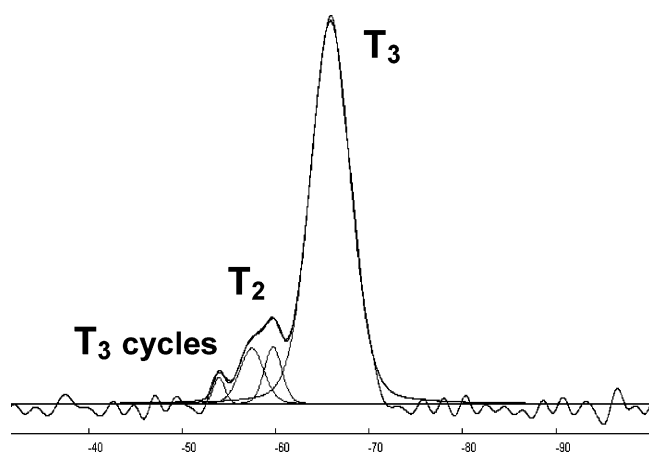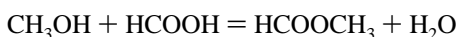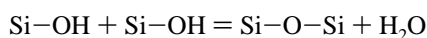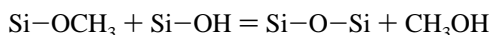**Figure 5.** WAXS spectrum of the bridged silsesquioxane synthesized in THF.

Figure 6. ^{29}Si NMR spectrum of the bridged silsesquioxane synthesized in THF.

polycondensation of the precursor through the following reactions:[43,44]

$$Si-OCH_3 + HCOOH = Si-OOCH + CH_3OH$$

$$Si-O-C + HCOOH = Si-OOCH + C-OH$$

$$Si-OCH_3 + H_2O = Si-OH + CH_3OH$$

$$Si-O-C + H_2O = Si-OH + C-OH$$

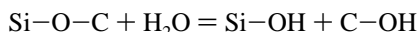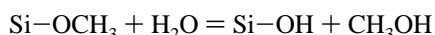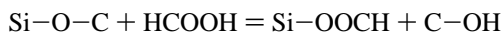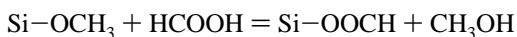$$Si-OOCH + Si-OCH_3 = Si-O-Si + HCOOCH_3$$

$$Si-OOCH + Si-OH = Si-O-Si + HCOOH$$

$$Si-OCH_3 + Si-OH = Si-O-Si + CH_3OH$$

$$Si-OH + Si-OH = Si-O-Si + H_2O$$

$$CH_3OH + HCOOH = HCOOCH_3 + H_2O$$
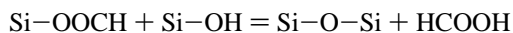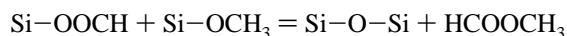
Characterization of the Bridged Silsesquioxane. SAXS spectra of the bridged silsesquioxane synthesized in bulk, in THF, and in isopropanol are shown in Figure 3. A strong correlation peak at $q = 1.86$ nm^{-1} was observed for every case. (A very small shift to higher q values is observed for the
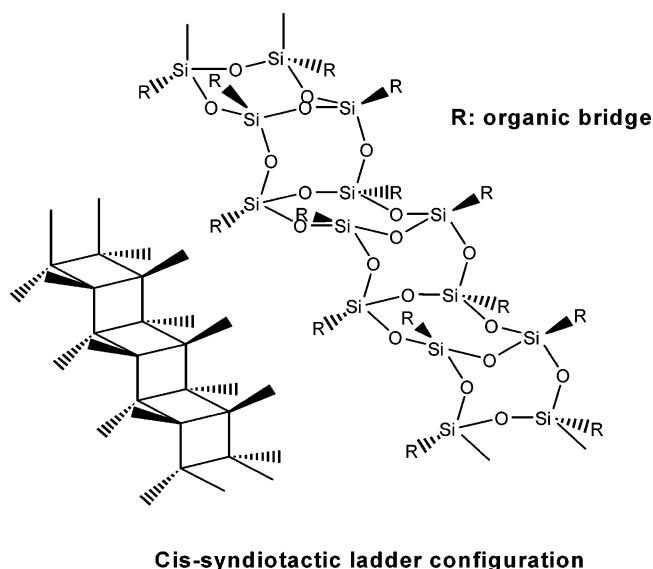

Figure 7. Cis-syndiotactic ladder structure formed by Si−O−Si bonds. Si atoms are located in the vertices, O atoms are located in the lines joining two vertices, and the organic group issuing from every Si atom is omitted.
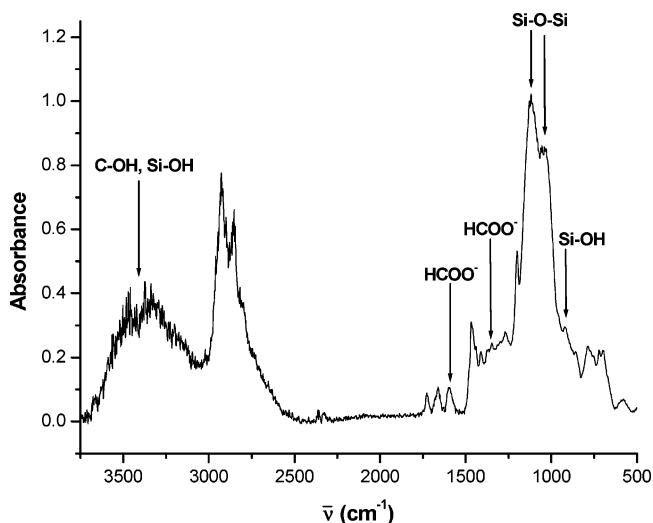

Figure 8. FTIR spectrum of the bridged silsesquioxane.

synthesis in bulk.) The peak represents a correlation length given by $2\pi/q_{max} = 3.4$ nm.

Because of the contrast of electronic densities between the organic and inorganic phases, when a correlation length is found in bridged silsesquioxanes, it is associated with a characteristic distance separating inorganic domains. In the case of self-assembled bridged silsesquioxanes containing urea groups, this characteristic distance was always found equal to the length of the organic bridge.[13,45−49] In our case, the length of the main organic bridge separating two Si atoms (Figure 1a) was calculated using the software ACD Labs/3D Viewer. The resulting value was 1.9 nm, meaning that in the present case the main organic bridge does not determine the characteristic length of the self-assembled structure. Using the same software, it was found that this distance is equal to the length of a tail-to-tail association of two dodecylamine chains with all-trans conformations (Figure 4). No information could be obtained from the scattered intensity in the region of low q values due to the presence of a powder−air interface.

The formation of a bilayer structure composed of a tail-to-tail association of alkyl chains with all-trans conformations has
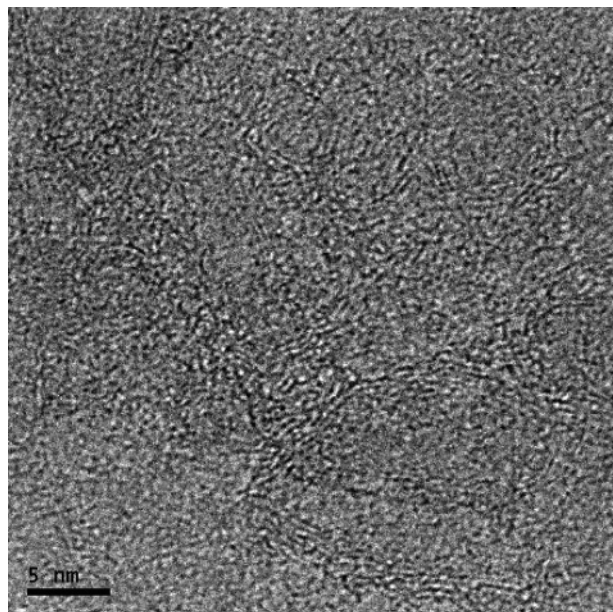
Figure 9. HRTEM micrograph of the bridged silsesquioxane.

been reported for the products obtained by the hydrolytic condensation of alkyltrialkoxy or alkyltrichlorosilanes (12−18 carbon atoms in the alkyl group).[50−52] For dodecyl chains the distance between inorganic domains in the bilayer structure was reported as 3.7 nm,[52] in close agreement with the experimental distance observed by SAXS and that calculated by molecular models. A similar bilayer arrangement of dodecylamine molecules has been also found in intercalated montmorillonites.[53,54]

Hydrolysis and polycondensation of alkyltrialkoxysilanes (6−18 carbon atoms in the alkyl chain) in a mixture with tetraalkoxysilanes led to multilayered thin films.[52,55,56] However, for these cross-linked materials bilayers exhibiting an all-trans conformation of alkyl chains could not be obtained. For alkyl chains of 8−14 C atoms bilayers with a mixed trans−gauche conformation were observed, whereas for chains of 16 and 18 C atoms interdigitated monolayers were detected.[52] Therefore, to our knowledge this is the first time that bilayers exhibiting an all-trans conformation of alkyl chains are reported in cross-linked organic−inorganic hybrid materials.

The presence of the same correlation distance for the three samples shown in Figure 3 implies that the self-assembly process was not affected to a significant extent by the presence of the selected solvents. The higher q value for the material synthesized in bulk indicates that dodecylamine chains are slightly less extended under these conditions. We did not find any other differences among these samples. Therefore, in what follows only results for the product synthesized in THF will be discussed.

In the WAXS spectrum shown in Figure 5, the strong peak at $2\theta = 2.7°$ corresponds to a scattering vector $q = (4\pi/\lambda)\sin\theta = 1.92$ nm^{-1}; this is the same correlation peak found by SAXS. The peak at $2\theta = 20°$ corresponding to a scattering vector $q = 14.2$ nm^{-1} is an amorphous halo that appears frequently in different types of silsesquioxanes and in amorphous polymers. Harmonics of the strong peak at $q = 1.92$ nm^{-1} could not be find meaning that they were either not present or their intensity was not enough to discern their presence within the fluctuations of the baseline signal (e.g., for a lamellar organization harmonics at $2q$, $3q$, etc., should be present).[20] The range of the structural order may be estimated from the width of the
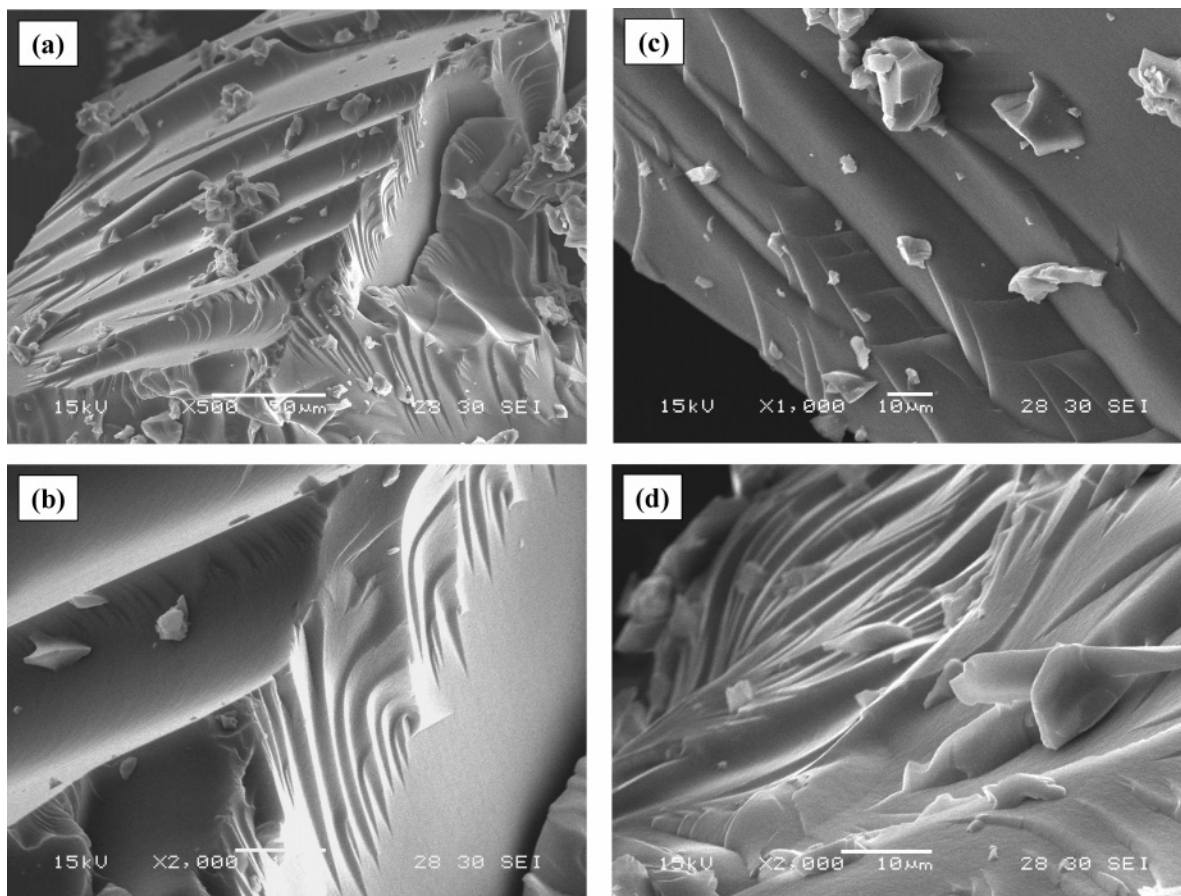

Figure 10. SEM micrographs of the bridged silsesquioxane. The bar corresponds to 50 μm in (a) and 10 μm in (b, c, d).
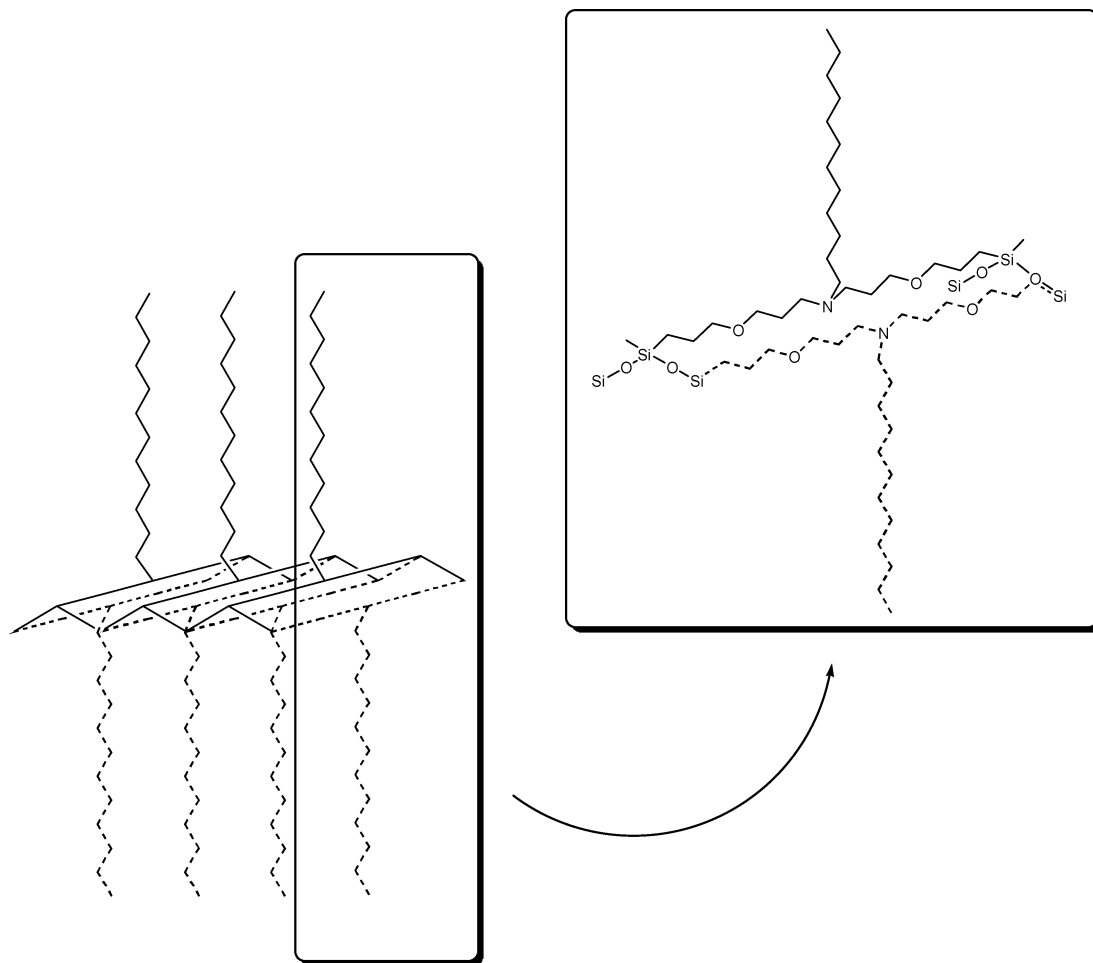
Figure 11. Schematic representation of the basic structure formed in the self-assembly process.

X-ray diffraction peak at half of its maximum, $\Delta q = 0.89$ nm^{-1}. This determines a correlation length (ζ) associated with the repetition of the characteristic distance of 3.4 nm:[21]

$$\zeta = 2\pi/\Delta q = 7 \text{ nm}$$

The ^{29}Si NMR spectrum is shown in Figure 6. The main peak at -65.9 ppm is characteristic of T_3 species: Si$-$(O$-$Si)$_3$, present in either octahedral[41,57−61] or ladder structures.[62,63] Characteristic peaks of decahedra (at about -68 ppm) or dodecahedra (two peaks at about -68 and -71 ppm)[59] were also searched in the deconvolution of the ^{29}Si NMR spectrum. While there was definitively no contribution at -71 ppm, the presence of a peak at -68 ppm could be included in the deconvolution, but only accounting for a 3% of the total area under the main peak. Minor peaks were also present at -53.9, -57.4, and -59.7 ppm, as resulted from deconvolution of the spectrum. Peaks at -57.4 and -59.7 ppm can be assigned to T_2 structures: Si$-$(O$-$Si)$_2$(OH).[57,61,62,64,65] The peak at -53.9 ppm might be assigned to strained T_3 triangular cycles, in comparison with signals at -54.3 ppm reported for the hexahedron with *tert*-butyl groups in the vertices.[66] No T_0 or T_1 structures were present in the ^{29}Si NMR spectrum.

The area under the T_3 peaks represented 86.6% of the total area (84.9% for the main peak and 1.7% for the peak at -53.9 ppm). This led to a total conversion into Si$-$O$-$Si bonds of 95.5% (0.866 + (2/3) 0.134).

The type of structures generated during the polycondensation, either polyhedra or ladders, may be inferred from FTIR spectroscopy observing the location of bands characterizing the antisymmetric Si$-$O$-$Si stretching vibrations. The appearance of a single band centered near 1120$-$1130 cm^{-1} may be taken as good evidence for the presence of a polyhedral structure,[67,68] while the presence of two bands centered near 1040 and 1120$-$1130 cm^{-1} is characteristic of a cis-syndiotactic ladder configuration (Figure 7).[67−69]

Figure 8 shows the FTIR spectrum of the bridged silsesquioxane. The presence of two bands at 1040 and 1118 cm^{-1} evidences the presence of ladder structures formed by Si$-$O$-$Si bonds. The broad band centered at about 3400 cm^{-1} corresponds to the C$-$OH groups and includes a small fraction of unreacted Si$-$OH groups. Two small bands at 1350 and 1590 cm^{-1} evidence the presence of a small residual fraction of formic acid as HCOO$^-$ anions (possibly forming salts with tertiary amine groups).[70]

Figure 9 shows an HRTEM image of the bridged silsesquioxane. A short-range organization in multilayers present in curved and closed structures is observed in some regions of the micrograph. The distance between layers is comprised between 3 and 4 Å. The analysis by SAED revealed a periodicity of 2.8 Å. These values are close to the distance between steps in the inorganic ladder structure, estimated as 3.1 Å (calculated from interatomic Si$-$O distances and Si$-$O$-$Si bond angles).[71] Conformational analysis revealed that the ladder structure exhibits a high flexibility that would enable the self-assembly of organic chains.[72]

Another evidence of the presence of a self-structuring process was obtained from SEM micrographs (Figure 10). Some ordered regions are observed consisting of a self-assembly of semicy-
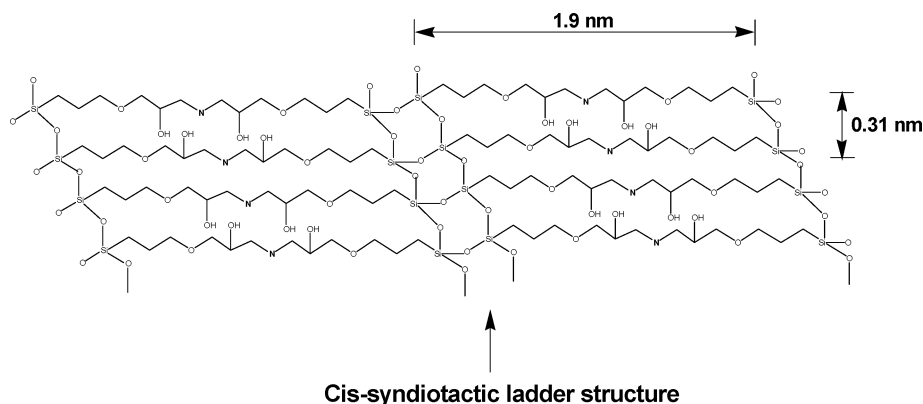
Figure 12. Structure of one of the inorganic−organic hybrid layers.

lindrical shells. There seems to be a relationship between the curved structures observed in HRTEM images and the concentric semicylindrical shells observed at a lower magnification.

In spite of the fact that the inorganic polycondensation was performed at a relatively fast rate, the resulting bridged silsesquioxane exhibited ordered domains extending to the microscopic scale as well as regions without any evident organization. Concerning the ordered regions, experimental results support the following facts: (a) inorganic domains are mainly organized in ladders (FTIR and ^{29}Si NMR); (b) inorganic domains are separated by a characteristic distance of 3.4 nm which corresponds to the length of a tail-to-tail association of two dodecylamine chains with all-trans conformations (SAXS, WAXS); (c) about 95% of Si atoms are present in T_3 structures (^{29}Si NMR); (d) there is a periodicity of about 3 Å in the self-assembled structure (HRTEM, SAED), corresponding to the estimated distance between two organic chains issuing from two adjacent Si atoms. Besides, because of the fact that the distance between adjacent organic chains is shorter than the distance giving a maximum packing density of alkyl chains, adjacent dodecyl chains should be pointing in opposite directions rather than pointing in the same direction.[52,73,74]

A schematic representation of a basic structure satisfying the experimental findings and the steric restrictions is shown in Figure 11. Adjacent dodecyl chains are pointing in opposite directions. The distance between two dodecyl chains pointing in the same direction varies with the O−Si−O angle of the inorganic ladder. A typical angle of 109° places the dodecyl chains at a distance of about 5.4 Å, close to the length of the shorter side of the orthorhombic unit cell of polyethylene (4.945 Å). This means that in the proposed structure dodecyl chains are packed in a one-dimensional array. Clusters of these basic structures are stacked together by a tail-to-tail self-assembly of dodecyl chains exhibiting all-trans conformations (as shown in Figure 4 for a couple of chains).

This organization generates a multilayer structure separated by hydrophobic regions. Each one of the layers is constituted by alternating inorganic ladders and main organic bridges with a periodic distance of 3.1 Å (Figure 12). The theoretical mass density of self-assembled regions should depend on the curvature of the multilayer structure (packing in concentric cylinders is higher than in a lamellar structure). The experimental value was 1.11 ± 0.01 g/cm^3, averaging the densities of both ordered and disordered regions.

Conclusions

A precursor of a bridged silsesquioxane bearing a hydrophobic pendant chain in the organic bridge was synthesized by the stoichiometric reaction of GPMS with dodecylamine. Its

hydrolytic condensation led to a bridged silsesquioxane characterized by the presence of both ordered and disordered domains. Experimental evidence obtained from SAXS, WAXS, ^{29}Si NMR, FTIR, HRTEM, and SAED techniques suggested that the basic structure of ordered domains consisted of a multilayer structure separated by hydrophobic regions with a thickness equal to the length of the tail-to-tail association of dodecylamine chains in all-trans conformations. To our knowledge, this is the first example of the presence of this kind of structure in a cross-linked hybrid material. A hierarchical organization of ordered domains into semicylindrical shells was observed on a microscopic scale.

The significance of this study is related to the possible use of this type of precursors for the self-assembly of nanoparticles functionalized with hydrophobic surfactants, followed by the fixation of the structure during the hydrolytic condensation. Work in this direction is in progress.

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