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Periodic mesoporous organosilicas derived from amphiphilic bulky polymethylsiloxane

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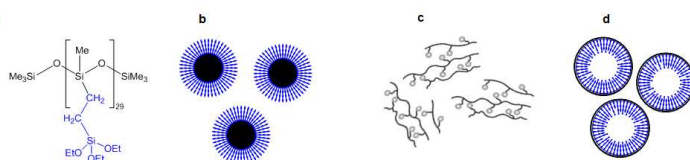
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Novel organosilica materials have been prepared from the newly reported sol-gel processable polymethylorganosiloxane. Under acidic conditions, the intrinsic self-assembling properties of the starting siloxane constitutes an impediment to tune the mesostructure. In contrast, the sol-gel undertaken under basic conditions ensures a monophasic polysiloxane-silica interpenetration, which results in the formation of an MCM-41-type PMOs with well- defined ordered structure.

The successful coupling of the self-assembly of soft-matter and the sol-gel polymerization of inorganic species allowing the tight incorporation of organic and inorganic precursors into well-organized tectonic nanostructures,¹ has been recognized as an historical milestone in the field of mesoporous organosilicas synthesis. These functional hybrid materials become staple tools in a broad range of applications spanning from adsorption, sensing, catalysis to drug-delivery vectors and theranostic agents in advanced nanomedicine.² However, the limited stability issue of these calibrated silicates under hydrothermal or aqueous basic conditions strongly motivated the need to design more stable hybrid alternatives. One of the promising strategies is the chemical alteration of the silica surface either by hydrophobic silanization,³ metal oxides coating⁴ and by walls carbonization/graphitization.⁵ Despite the large spectrum of silicate that can be obtained through this route, mesostructured hybrid materials with high potential of application and commercialization remain highly desirable. Looking for efficient hydrophobic tools and having the most popular polydimethylsiloxane (PDMS) in mind, we were interrogated if these hydrophobic polymers could be incorporated within the walls of uniformly ordered silica-based mesoporous materials.

In this framework, we recently reported the synthesis of poly(triethoxysilyl)ethyl-methylsiloxane⁶ (denoted herein as **PMSi**), a functional system belonging to the PDMS family with additional pendant alkoxyethyl groups (Scheme 1a). The presence of both hydrophobic segments and sol-gel processable functions within the polymer backbone confer to these building-blocks unprecedented solvent-switchable self-assembling properties allowing to direct the antagonistic hydrophobic skeletal and water-sensitive sol-gel groups inside or outside.⁶ Such a behavior is reminiscent to the fabrication of direct or reverse micellar-type assemblies (Scheme 1b and d).

These solvent-switchable properties, the well-established hydrophobicity and the similarities with some “smaller” periodic mesoporous silica (PMOs) precursors prompted us to investigate the preparation of ordered silicates from this soluble, sol-gel processable polymeric **PMSi**.⁷



Scheme 1. Molecular structure of **PMSi** (a) showing the hydrophobic butters (in black color) and the sol-gel region in blue. (b) The self-assembly of **PMSi** in aqueous acidic solution, where the hydrophobic region is located inside to escape interaction with the hydrophilic water solvent. (c) In aqueous basic solution, interconnected branching is observed. (d) In apolar solvent (heptane for instance) the hydrophobic part is located at the external peripheries owing their favorable interaction with the medium.⁶

Recently, many bulky chemical and macromolecular objects including dendrimers,⁸ fatty acids,⁹ polyhedral silsesquioxanes¹⁰ and fullerenes¹¹ have been incorporated into periodic mesoporous organosilicates. However, a close look on these reports indicates that the bulkiness of the starting silane precursors constitutes a general impediment to tune the mesostructure. Beside, none of these macromolecular objects displays self-assembling properties similar to those encountered for **PMSi**. In light of these facts, it appeared of interest to get an insightful understanding on the interplay of this polymer within the micellar assemblies of either octadecyltrimethylammonium bromide (ODTAB) and pluronic P123 aiming at the preparation of MCM-41-type and SBA-15-type PMOs, respectively.

Considering the 29 repetitive units of **PMSi** as the unique silica source, we firstly investigated the sol-gel condensation for typical synthesis of MCM-41-type materials using the following composition: 1 Si: 0.21 OTDAB: 0.89 NaOH: 133 H₂O.¹² In parallel, tentative fabrication of SBA-15-type materials has been attempted with the following composition: 1 Si: 0.018 P123: 5.44 NaCl: 5.48 HCl: 187 H₂O, according to the previously reported protocol.¹³ The solid materials obtained after filtration and soxhlet extraction were noticed as **PMSi-SiO₂-base** and **PMSi-SiO₂-acid**, respectively (ESI, S1). These organosiliceous materials were then

subjected to a set of spectroscopic and textural analyses. ^{13}C CP MAS NMR spectrum of the **PMSi-SiO₂-base** showed two strong signals at 1 and 8 ppm, attributed to $\text{CH}_3\text{-Si}$ and $\text{Si-CH}_2\text{-CH}_2\text{-Si}$, respectively (ESI, S2a). Smaller peaks assignable to the residual ODTAB surfactant were also observed between 14 and 53 ppm.¹⁴ Moreover, two weak signals at 18.8 and 59.9 ppm, typical of the ethoxy-bridged silicon ($\text{Si-OCH}_2\text{CH}_3$) were formed in the course of template extraction using HCl/EtOH solution. ^{29}Si one pulse (OP) MAS NMR spectra of these materials display two broad peaks, located at -20 and -66 ppm unambiguously assignable to D^2 [$\text{R}_2\text{-(OSi)}_2$] and T^3 [R-(OSi)_3] Si units, respectively (ESI, S2b). The absence of the signal at -46 ppm, characteristic of C-Si(OEt)_3 in the starting **PMSi**, indicates an advanced extent for the hydrolysis-condensation of these pendant functional groups. Moreover, no resonance corresponding to Q units (region near -100 ppm) has been observed, thereby confirming the preservation of the polymeric skeleton and ruled out the occurrence of any C-Si cleavage during the sol-gel process. The Si/C molar ratios calculated from both elemental analysis ~ 0.7 and thermogravimetric analysis (TGA) ~ 0.8 are in consistency with the theoretical values (0.65).

Having ascertained that the starting **PMSi** polymers have been converted to solid silsesquioxanes, we turned our attention to the assessment of their textural properties. Nitrogen sorption analysis revealed for **PMSi-SiO₂-base** an adsorption-desorption isotherm typical of disordered mesoporous materials with a significant accessible porosity ($S_{\text{BET}} = 396 \text{ m}^2\cdot\text{g}^{-1}$; $V_{\text{meso}} = 0.4 \text{ cm}^3\cdot\text{g}^{-1}$; pore diameter = 51 Å). In contrast, no appreciable ordering or open porosity has been evidenced for **PMSi-SiO₂-acid**. This divergent pattern can be explained by the difference in the supramolecular organization of the starting polysiloxane, where spherical objects can be obtained in aqueous acidic solution (Scheme 1b) while inter-macromolecular branching has been developed in aqueous basic solution similar to those of MCM-41 synthesis (Scheme 1c).⁶ In aqueous acidic solution, the spontaneous formation of well-structured polymethylsiloxane objects induces a fast pluronic template exclusion and hence, an absence of the ordering and porosity. SEM analysis corroborates such suggestive structuring process by the observation of spherical compact beads (Fig. 1a,b). This typical “onion” construction of the microspheres occurs by sequential lipophilic-hydrophilic bilayer growth of individual macromolecular units of the **PMSi** without the need of template (Fig. 1c).¹⁵

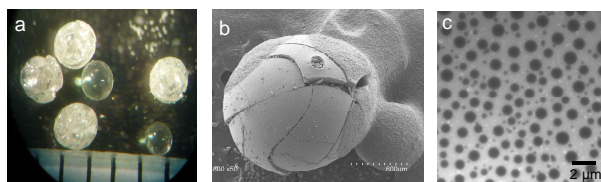


Fig. 1 (a) Optical microscopy image and (b) SEM of **PMSi-SiO₂-acid**. (c) TEM of the pluronic-free material prepared under similar water-acidic sol-gel conditions.⁶

In aqueous basic solution, the entangled network of macromolecular branching (Scheme 1c) do not provoke similar template exclusion and allow some degree of charge matching between hydrolyzed SiO^- intermediates and the ammonium-terminated ODTAB surfactant.

This positive interplay accounts for the generated open-framework porosity.

Considering the beneficial effect of adding another silica source (tetraethylorthosilicate TEOS for instance) during the preparation of PMOs material to tune the mesostructure, the starting **PMSi** was mixed with the TEOS within the micellar assembly medium. TEOS [Si(OEt)_4] possesses four polymerizable sites thereby acting as a “glue” between several macromolecular units of **PMSi** and as a “relaxing agent” against the stress generated during the charge matching to accommodate the mesostructure. To the best of our knowledge, no report on assembling **PMSi-silica** in tectonic mesostructures has been disclosed. With this aim, **PMSi:TEOS** ratios of 0.14 and 0.19 were used as a silica source for the preparation of **PMSi-SBA-15-bis** and **PMSi-MCM-41-bis**, respectively.^{16,17} After hydrolysis-condensation and soxhlet extraction, the minimum values of Si/C ratios calculated from ^{29}Si OP MAS NMR are in agreement with those obtained from thermogravimetric and elemental analyses (ESI, S3). ^{29}Si and ^{13}C MAS NMR revealed also the formation of a high quantity of SiOEt groups from surface silanols during the surfactant extraction procedure. On the whole, both Q units from TEOS and polymeric polysiloxane were covalently linked within the resulting materials.

X-ray diffraction patterns of **PMSi-MCM-41-bis** and **PMSi-SBA-15-bis** (before extraction of the surfactant template) exhibit the [100], [110] and [200] reflections (with a d_{100} of 42 Å and 106 Å, respectively) typical of 2D hexagonal ordered materials (ESI, S4a-b). Nitrogen physisorption consolidates these results. The sharp increase in the adsorbed volume at narrower P/P_0 values indicates the uniform pores dimension with the isotherm profile of type IV being typical of ordered parent MCM-41- and SBA-15 materials (ESI, S5). A specific surface area of $700 \text{ m}^2\cdot\text{g}^{-1}$ has been measured for **PMSi-MCM-41-bis** with a pore volume of $0.51 \text{ cm}^3\cdot\text{g}^{-1}$ and a pore size of 38 Å. The periodic mesoporous material derived from the SBA-15 synthetic conditions displays an isotherm with a clear H1-type hysteresis loop at high relative pressure, characteristic of large-pore mesoporous materials (pore diameter = 78 Å according to the BdB treatment of the desorption branch). **PMSi-SBA-15-bis** pore wall thickness (48 Å) was higher than that of **PMSi-MCM-41-bis** (12 Å) in agreement with the literature. TEM analysis highlights the intimate organization at the nanoscale of the resulting polysiloxane-silica nanophase. Indeed, a three-dimensional disordered network of short « wormhole-like » mesoporous channels has been observed for **PMSi-MCM-41-bis**, whereas well-ordered channels with a perfect hexagonal structure has been evidenced for **PMSi-SBA-15-bis** (Fig. 2).

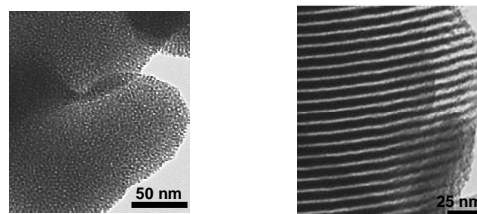


Fig. 2 TEM micrographs of (left) **PMSi-MCM-41-bis** and (right) **PMSi-SBA-15-bis**

One of the most challenging issue in constructing PMOs materials from two or more different silica sources is to ensure the intimate formation of a homogeneous monophasic system rather than a heterogeneous biphasic structure. The homogeneity at the nanoscale is of paramount importance as many bulk properties (anisotropy, conductivity, compartmentalization, hydrophobicity, chirality,...) depend on the degree of periodicity versus clustering of each of the two silica sources. Herein, although textural analyses confirm the nanoscale ordering and the presence of the mesostructure, additional insight is needed to ascertain the location of the polymeric methylsiloxane versus silica within the PMOs framework.

With this aim, specific NMR experiments based on ^1H spin diffusion have been performed to get insight on the spatial proximities between silica and polyorganosiloxane moieties coming from the condensation of Q units, and from D and T units, respectively.¹⁸ Here, 2D ^1H - ^{29}Si HETCOR spectra have been recorded with a mixing time τ_m for ^1H spin diffusion to proceed before the $^1\text{H} \rightarrow ^{29}\text{Si}$ cross-polarization contact time (see ESI, S6 for conditions).^{18b,19} Without ^1H spin diffusion ($\tau_m = 0$ ms) (Fig. 3a and 3c), 2D spectra of both **PMSi-MCM-41-bis** and **PMSi-SBA-15-bis** show similar features. In particular, the ^{29}Si signals of D and T units only give visible correlation peaks with ^1H signals related to alkyl groups (around 1 ppm) and not to silanol related groups in the 4-7 ppm range. When ^1H spin diffusion is activated ($\tau_m = 50$ ms), correlation peaks between ^1H silanol signals and ^{29}Si D and T signals are observed only in the case of **PMSi-MCM-41-bis** (arrows in Fig. 3b), suggesting that silica and **PMSi** moieties are more intimately mixed in this latter material rather than in **PMSi-SBA-15-bis**.

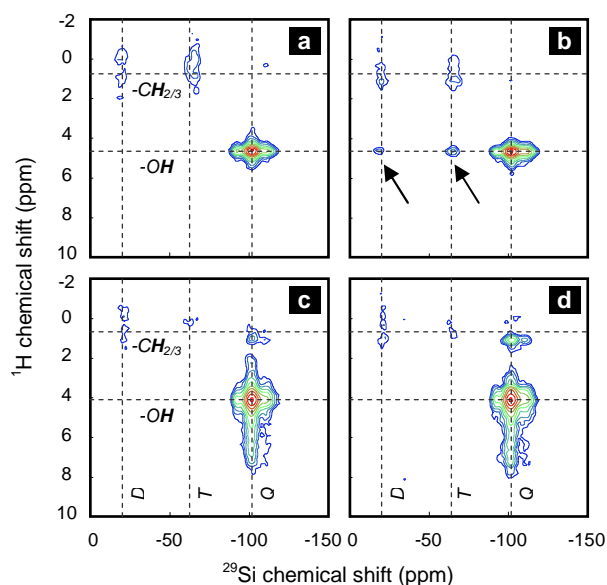


Fig. 3 2D ^{29}Si - ^1H NMR HETCOR spectra of (a,b) **PMSi-MCM-41-bis** and (c,d) **PMSi-SBA-15-bis**. Mixing times are $\tau_m = 0$ ms (a,c) and $\tau_m = 50$ ms (b,d).

Other NMR experiments were consistent with this result. For example, $^{29}\text{Si}\{^1\text{H}\}$ NMR CP-MAS spectra with preliminary ^1H signal selection at ~ 5 ppm only show the signals of Q units for both sorts of materials. But again, when ^1H spin diffusion proceeds before the contact time, ^{29}Si signals for D and T units become visible only

for the **PMSi-MCM-41-bis** materials (ESI, S7). Indeed, hexagonally ordered mesoporous monophasic polyorganosiloxane-silica system are obtained under MCM-synthesis conditions and a less homogeneous, biphasic one under SBA-synthesis conditions. This divergent pattern can be explained by two complementary factors: the supramolecular organization taking place under aqueous acidic (compacted spheres) and aqueous basic conditions (intermacromolecular branching) and the difference in hydrolysis rate of the **PMSi** depending of the experimental conditions; the hydrolysis rate of an alkyltriethoxysilane (**PMSi** for instance) would be much higher than for TEOS in acid medium, while the opposite effect is observed in alkaline medium.²⁰ The spontaneous self-assembly of the **PMSi** in aqueous acidic solution hinders to some extent its homogeneous mixing with the polymerized silicates (coming from TEOS) preferentially located on the surface of the hydrophilic part of the pluronic polymer (Fig. 4 left). The absence of such behavior under basic conditions and the favorable hydrolysis-condensation reaction kinetics allow for better control of the polysiloxane-silica interpenetration, the ensemble takes place near to the hydrophilic part of the micellar ammoniums part (Fig. 4 right).

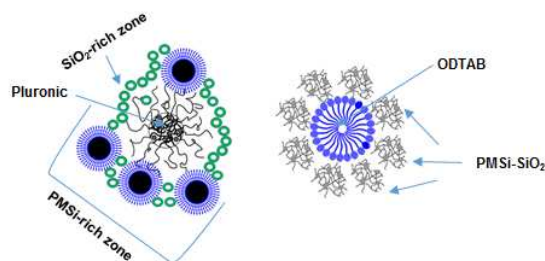


Fig. 4 Schematic illustration of the formation of a biphasic system for SBA-15-type PMO (left) and a monophasic one for MCM-41-type PMOs (right).

Herein, under optimized synthetic conditions, hydrophobic **PMSi** and hydrophilic silica were successfully coupled within the same tectonic mesostructure. Work is in progress to explore the presence of the hydrophobic **PMSi** within these novel PMOs in catalysis and for host-guest interactions.

Experimental

Synthesis of PMSi-SiO₂-base material. The ODTAB surfactant (1.185 g, 3.10^{-3} mol) was dissolved in an aqueous solution of sodium hydroxide (0.5 g in 33.7 g H₂O) and stirred for 5 h at room temperature before adding a **PMSi** precursor (2.71 g, 0.36 mmol, $M = 7412$). The molar composition of the gel was: 1 SiO₂/0.21 ODTAB/ 0.89 NaOH/ 133 H₂O. The mixture was vigorously stirred at room temperature for 14 h and under static conditions at 95 °C for 24 additional hours. The solid was washed with ethanol and dried in air. Surfactant was removed using a Soxhlet apparatus with a mixture of ethanol and concentrated 37 wt % HCl and subsequent drying at 55 °C in air.

Synthesis of PMSi-SiO₂-acid material. Pluronic P123 (1.2 g, 0.21 mmol, $M = 5800$ g) and sodium chloride (3.5 g) were dissolved in aqueous acidic solution (5 cm³ of concentrated 37 wt % HCl in 34 cm³ H₂O) and stirred for 4 h at room

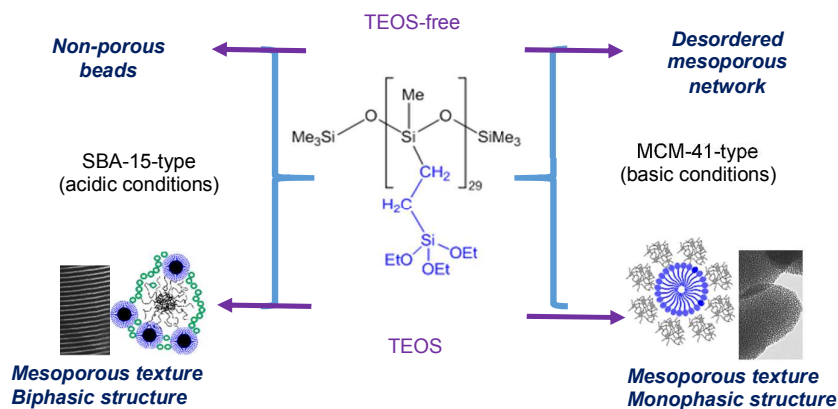
temperature before adding a **PMSi** precursor (3 g, 0.4 mmol). The molar composition of the gel was: 1 SiO₂/0.018 P123/ 5.44 NaCl/ 5.48 HCl/187 H₂O. The mixture stirred at 40 °C for 24 h, followed by aging the suspension at 80 °C for another 24 h under static conditions. The solid was washed with ethanol before surfactant extraction using a Soxhlet apparatus and subsequent drying at 80 °C in air.

Notes and references

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- The lower **PMSi**/TEOS ratio in SBA-15-type compared to MCM-41-type is explained by the currently higher wall thickness of SBA-15-type due to the acidic sol-gel conditions compared to those of MCM-41-type materials.
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Depending on the synthetic conditions (surfactant, acid, base, presence or absence of TEOS), the sol-gel polymerization of functionalized polyorganosiloxane affords various textured silica-based materials.