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This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/148617> since 2016-01-08T11:39:01Z

Published version:

DOI:10.1016/j.micromeso.2014.02.012

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Preparation and physico-chemical characterization of large-mesopore silica thin films templated by block copolymers for membrane technology

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Abstract

Highly selective membranes with controlled porosity can be obtained by growing thin films of mesoporous oxides on an appropriate support. This can be achieved employing organic/inorganic mixed micellar solutions based on metal oxide precursors and commercial templates. In particular amphiphilic block copolymers are very attractive materials as soft-templating agents because they self-assemble into micelles whose morphology and size depend on block composition and solution parameters.

Large-mesopore silica films with narrow pore size distribution and high porosity have been obtained by sol-gel reaction of a silicon oxide precursor (TEOS) and using polystyrene-*block*-poly(ethylene-oxide) (PS-*b*-PEO) copolymers as templates.

In order to modulate size, shape and alignment of the pores, many variables were changed: block copolymer chain length, TEOS/block copolymer ratio, solvent ratio, additives (i.e. polystyrene homopolymer addition). The effect of the different parameters on the porous system was studied by microscopy techniques and gas-volumetric analyses.

Final aim of this work is the preparation of silica membranes to be used as selective gates for controlled dosing and transport of chemical species in solution.

Keywords: block copolymers; mesoporous silica; soft-templating; sol-gel synthesis; membranes.

1. Introduction

Recently, molecular sieves based on mesoporous materials have attracted much attention because their large and tunable porosity is of interest for a number of applications, such as drug delivery, separation and dosing [1-4]. Different approaches have been applied in order to obtain biocompatible, thermally and chemically stable mesoporous materials with finely controlled porosity, narrow pore size distribution and tunable surface chemistry. At present, the sol-gel process carried out in the presence of organic templates and in combination with a spin-coating step is the most facile and versatile method for preparing mesoporous thin films. Conventional procedures for the synthesis of mesoporous silica involve the use of amphiphilic templates [5-7]. Either low molecular weight surfactants and polymers have been used as structure-directing agents in the preparation of organic-inorganic hybrid solutions and they have proved to generate a variety of well-ordered materials by self-assembling processes [8-12].

However, most mesoporous silica membranes that have been proposed till now have pore size limited up to 10 nm, while larger pores are required for application involving large molecules, such as biomolecules [13,14].

To obtain large mesopores we used high molecular weight PS-*b*-PEO copolymers as pore-forming templates. Amphiphilic block copolymers in solution are able to form

various types of aggregates, such as micelles and vesicles, that can be employed to build novel nanomaterials [15,16].

As for common non-ionic surfactants, block copolymers self-assembly mainly depends on the size and chemical nature of the blocks [17,18]. The driving force for self-assembling is the thermodynamic incompatibility of the different blocks in the polymer chains, which brings them to spontaneously segregate in well-defined nanostructures. In particular, when block copolymers are mixed to solvents which are selective for one of the blocks, polymer chains spontaneously aggregate into micelles having different shapes (i.e. spheres, rods, tubes, lamellae). On their turn micelles can self-organize into micellar assemblies with different architectures and degree of order depending on both physical and chemical properties of micellar solutions [19].

Considerable efforts are being made to disclose the self-assembly of different classes of block copolymers in solution. For instance, it is well known that the micelle morphology is solvent-dependent, since the hydrophilic/hydrophobic solvent ratio affects segregation of the polymer blocks and consequently the micelle shape [20,21]. The mesoporous silica films described in this work were obtained by spin-coating mixed micellar solutions containing TEOS as an inorganic precursor, PS-*b*-PEO copolymers as organic structure-directing agents, benzene and ethanol as solvents, and HCl as a sol-gel acid catalyst .

The chemicals listed above are the key compounds of a templating process consisting in three main steps: i) self-assembly of block copolymer templates into micelles, ii) transcription of the micelle arrangement to condensed silica, iii) template removal by thermal treatment in order to obtain the negative replica of the original micellar system [22-24]. The second step of the reported mechanism is crucial, since templates need to be compatible with the generated siliceous network. This way, once block copolymers

and TEOS are mixed together a colloidal solution form, which then evolves towards the formation of an integrated network through a sequence of acid catalyzed hydrolysis and polycondensation reactions [25].

Due to the fast evaporation of solvents during spin-coating, the micelle shape was frozen and transferred from solution to the solid state. Finally, organic templates were removed by a thermal degradation treatment under oxidant atmosphere (i.e. air), leaving an amorphous porous material whose morphology reflects the shape and size of the original micellar system.

Also, as the shape of block copolymer micelles can be modified by addition of core-soluble homopolymers to micellar solutions [26-29], the addition of PS homopolymer to the organic/inorganic sol-gel mixture was investigated. Once homopolymer molecules are incorporated into the micellar system they swell micelles affecting their size, number and shape. In this way spherical micelles can grow turning themselves into rod-like structures and vesicles.

Here, we describe the synthesis and characterization of large-mesopore silica thin films with the final aim to identify suitable conditions for the preparation of membranes. A variety of mesoporous films with different arrangements of pores, and different pore size and shape have been obtained, including silica membranes with pores spanning the membrane from top to bottom.

2. Experimental

2.1 Synthesis and preparation of mesoporous silica thin layers

Silica mesoporous thin films were synthesized by sol-gel reaction of tetraethyl orthosilicate (TEOS $\geq 99.0\%$, Aldrich) in ethanol ($\geq 95.0\%$, Carlo Erba Reagents) under acidic conditions (HCl 37 wt. %, Fluka Chemika). Different sol-gel solutions

were prepared with the TEOS/HCl molar ratio of 3.5. Solutions were stirred at room temperature for half an hour using a magnetic stirrer. Three different types of PS-*b*-PEO block copolymers (PS₁₈₃-*b*-PEO₁₄₅ block copolymers with $M_n = 19000$ -*b*-6400; PS₃₀₈-*b*-PEO₂₅₀ with $M_n = 32000$ -*b*-11000; PS₅₆₇-*b*-PEO₇₀₄ with $M_n = 59000$ -*b*-31000) were purchased from Polymer Source Inc. (Dorval, Canada).

Benzene ($\geq 99.7\%$, Riedel-de-Haën) was chosen as solvent for the preparation of copolymer solutions. Copolymer benzene solutions (1 wt. %) were prepared and stirred for half an hour to ensure complete dissolution of the copolymer.

Micellar solutions (Table 1) were prepared by adding the desired amount of sol-gel solution to the copolymer solution (Scheme 1). Mixed micellar systems containing PS homopolymer were prepared by adding a PS ($M_n=4000$) benzene solution (1 wt.%) (see Table 1).

Final solutions were spin coated onto mica sheets of 1.27 cm x 1.27 cm x 15 mm, at 1000 rpm for 20 sec, using a 8" Desk-top Precision Spin Coating System, model P-6708D vs. 2.0.

After deposition, films were dried in a hood at ambient temperature for at least 12 h in order to reach complete evaporation of solvents. Hybrid films were then transformed into silica nanostructured thin layers by thermal treatments in a furnace under air (400 °C for 2 h, ramp of 2 °C/min).

2.2 Synthesis and preparation of mesoporous silica powders

The same reactants described above were used to prepare silica powders for thermogravimetric analyses (TGA) and N₂ gas-volumetric adsorption at 77K.

In this case the sol-gel solutions were placed in glass Petri dishes, the solvent evaporated, the hybrid film gently scratched and then calcined using the same conditions applied for film preparation (400 °C for 2 h, ramp of 2 °C/min).

The silica mesoporous powders thus obtained were analyzed by HRTEM and compared to mesoporous thin films obtained from the same micellar solutions in order to assess that the morphology of the porous system was the same.

2.3 Physico-chemical characterization

Surface morphology of both hybrid TEOS/PS-*b*-PEO samples and silica thin layers obtained after the block copolymer removal was studied by Atomic Force Microscopy operating in Non-Contact mode (AFM-NC). Analyses were performed in air at room temperature with a Park Systems Instrument, model XE-100. A silicon microcantilever with the reflective side coated with aluminum (force constant 20 N/m and resonance frequency of 265 kHz) and conical silicon tips (radius of curvature less than 10 nm, tip height 15-20 μm, full tip cone angle less than 30°) were used. Scan rates were set between 0.5 and 1 Hz. Topographic (height mode) and viscoelastic (phase-mode) data were recorded simultaneously.

Transmission Electron Microscopy (HRTEM) was used to evaluate the pore size and morphology of mesoporous silica films before and after the removal of the polymer template. Micrographs were obtained by a JEOL 2010 instrument (300 kV) equipped with a LaB₆ filament. For the specimen preparation a few drops of water were poured on the supported silica film. After few seconds the film was gently scratched and separated from the support. Film fragments were then transferred onto holed carbon coated copper grids by lifting the grids onto the water layer. Powdery samples were supported onto holed carbon coated copper grid by dry deposition.

Pore sizes and distributions were calculated by using the software Particule2 on an average of 100 pores.

TGA analyses were performed with a TA Instruments TGA 2050 Thermo-Gravimetric Analyzer in order to monitor the block copolymer degradation and find the best conditions to selectively remove the polymer template avoiding at the same time the collapse of the silica nanoporous structure. Analyses were performed on powdery samples under air flow and using a heating ramp of 2 °C/min from RT to 600 °C. Analyses were also carried out applying the same heating ramp from RT to 400 °C and keeping the final temperature constant for 2 hours.

N₂ adsorption-desorption experiments were carried out by means of ASAP 2020 instrument (Micromeritics) in order to determine specific surface area (BET model) [30] and porosity (DFT model) [31,32] of mesoporous samples. The Density Functional Theory (DFT) was applied in order to examine simultaneously both micro- and mesoporosity of samples. The analyses were performed on powdery samples (ca. 100 mg) outgassed for several hours at 300 °C *in vacuo* (residual pressure 10⁻² mbar) to ensure complete removal of atmospheric contaminants from surface and pores.

3. Results and discussion

3.1 Optimization of the thermal treatment

The self-assembly of PS-*b*-PEO in solution mainly depends on its amphiphilic nature, as for low molecular weight surfactants. In fact, PS-*b*-PEO copolymers are macromolecular non-ionic surfactants with the PEO block being the hydrophilic head and the PS block the hydrophobic tail. Once in a mixed polar/apolar solvent system (i.e. ethanol/benzene) block copolymers self-organize in micelles having a PS core (Figure

1). Around micelles, TEOS can hydrolyze and built up the framework of the final porous siliceous material.

Hybrid TEOS/block copolymer films obtained by spin coating micellar solutions (Table 1) were transformed into silica nanostructures by thermal treatment. The degradation of the polymeric component and the formation of a siliceous nanoporous material were investigated by TGA. All the TGA curves obtained from different hybrid films show similar profiles, as that reported in Figure 2a for sample 93TEOS/7PS_{308-b}-PEO₂₅₀. The curve is characterized by three main degradation steps: the first one, complete at around 80 °C, is due to the elimination of water and ethanol residues used in the sol-gel reaction. The second one is caused by the copolymer degradation starting at around 200 °C and mainly occurring in the range 300-400 °C. The thermal profile shows a third step (at T > 450 °C) that in the literature is assigned to condensation reactions of silanol groups forming the more hydrophobic Si-O-Si moieties [33]. Figure 2b shows the degradation profiles of the pure polymer template from RT up to 600 °C (solid line) and up to 400 °C with a final isothermal step at 400 °C for 2 hours (dashed line). Both curves indicate there is no residue at the end of the treatment, meaning that also the thermal treatment at lower temperature for a longer time is able to completely degrade the polymer template. On the base of these data, we chose to perform sample calcination at 400 °C, i.e. a temperature high enough to assure TEOS transformation in a silica network and the burning of organic residues. This way the hydrophobization of siliceous material is avoided as well as the possible collapse of the porous structure [34-35]. In order to be sure that all the organic species were removed, silica samples were leaved in isothermal condition at 400 °C for 2 hours.

As an example AFM micrographs reported in Figure 3 show the surface morphology obtained from a micellar solution containing a TEOS/block copolymer weight ratio of

93:7 (i.e. 93TEOS/7PS₅₆₇-*b*-PEO₇₀₄) before and after thermal treatment. The hybrid film before calcination has a coarse surface characterized by a silicic framework shaped by an assembly of spherical micelles. After calcination a surface with a reversed morphology is obtained, that is with pores instead of protruding micelles.

3.2 Mesoporous silica characterization: internal morphology

Independently from the length of the block copolymer used as soft-templating agent, TEM images show the formation of a homogeneous porous internal system along the thickness of the mesoporous films (Figure 4 for PS₅₆₇-*b*-PEO₇₀₄, Figure 5 for PS₃₀₈-*b*-PEO₂₅₀ and Figure 6 for PS₁₈₃-*b*-PEO₁₄₅).

Samples with the highest TEOS/block copolymer weight ratio (95:5) present spherical pores, homogeneous in size (Table 2), but not regularly distributed (Figures 4A, 5A and 6A).

In order to improve the order of the porous network, increase pore density in the spin-coated films, and modify pore shape, the TEOS/block copolymer weight ratio was progressively reduced.

Reducing the TEOS/block copolymer weight ratio to 93:7, and consequently decreasing the hydrophilic/hydrophobic solvent ratio, the spherical pore morphology is retained and a general improvement of the lateral order is obtained, as observable in Figures 4B, 5B and 6B, and at higher magnification in Figure 7 (a detail of the highly ordered hexagonally packed pores obtained for 93TEOS/7PS₅₆₇-*b*-PEO₇₀₄ sample is reported). Figures 4C, 5C and 6C report TEM micrographs of silica thin layers obtained from the hybrid samples 90TEOS/10PS-*b*-PEO after thermal treatment. All samples present a worm-like nanostructure. This change in the pore shape is given by a change in micelle shape caused by the decrease of the TEOS/block copolymer ratio. Reasonably, by

increasing the hydrophobic weight fraction (block copolymers and benzene) with respect to the hydrophilic one (silica and ethanol), the mixed micellar solution becomes more apolar, and PS-*b*-PEO chains self-assemble in a supramolecular system arranged around a line instead of a dot: this way a minimization of the surface free energy is obtained. Some authors theorize that the sphere-to-cylinder transition is driven by the core-selective solvent (i.e. benzene) by changing the micellar curvature at the interface [25]. Other works propose that elongated nanostructures could derive from the fusion of several spherical micelles along a particular direction [36]. This hypothesis is supported by the spherical shape shown by pore extremities and ramifications, nevertheless at the present state of the research it is not possible to establish which one of the mechanisms proposed is applicable to the systems studied in this paper.

When the TEOS/block copolymer weight ratio reaches the value 88:12, worm-like nanochannels are definitely formed. Using PS₁₈₃-*b*-PEO₁₄₅ as structure directing agent a more inhomogeneous worm-like nanostructure is obtained, with individual spherical pores and spherical end-capped nanochannels (Figure 6D), whereas silica obtained by PS₃₀₈-*b*-PEO₂₅₀ and PS₅₆₇-*b*-PEO₇₀₄ templates are characterized by relatively long and densely packed nanochannels (Figures 4D and 5D). TEM images also show that most nanochannels are parallel to the film surface and even if their length is in the order of micrometers generally they do not span the film from top to bottom.

A further reduction of the TEOS/block copolymer weight ratio to 85:15 (i.e. a further reduction of the hydrophilicity of the reaction medium) results in the formation of a mixed morphology consisting of worm-like pores and some individual nanoparticles (dark areas in Figures 4E, 5E and 6E), indicating that the system is approaching the conditions for reverse micellization. Reverse micelles work as nanoreactors and are able to produce particles with an average diameter of ~ 25-30 nm. The reverse micellization

regime definitively establishes with a TEOS/block copolymer weight ratio of 75:25 and the corresponding samples, obtained after calcination, appear as aggregates of individual silica nanoparticles (Figure 4F, 5F and 6F). As silica nanoparticles were out of this work purposes, lower inorganic/organic weight ratios were not considered. Table 2 reports average pore diameters as observed in TEM micrographs. It is interesting to note that the block copolymer chain length does not affect significantly the pore size of spherical systems (TEOS/copolymer weight ratio of 95:5 and 93:7), while for worm-like systems the diameters of the nanochannels increase as the polymer chain length increases. In particular, samples of the 88TEOS/12PS-*b*-PEO series have diameters ranging from 20 to 42 nm.

3.3 Mesoporous silica characterization: homopolymer addition

In a former work, a small amount of PS solution was used to modify mixed micellar systems containing titanium precursors and to get the transition from spherical micelles to elongated worm-like micelles [37]. This same approach was applied to the nanostructures described in this paper in order to modulate the shape of the micelles first, and then of the silica pores.

Figure 8 shows the effect of PS added into the 93TEOS/7PS₁₈₃-*b*-PEO₁₄₅ sol-gel mixture. Addition of 10 wt.% PS basically enlarges spherical pores, but also a few rod-like pores form. Further increasing the amount of PS (20 wt.%) onion-like structures, deriving from vesicles, appear [38-40]. These results, and others obtained from similar mixed micellar solutions (not reported here), show that in general silica mesoporous films obtained from PS/PS-*b*-PEO micelles have less homogeneous, mixed morphologies, and different types of nanostructures can be found in the same sample.

3.4 Mesoporous silica characterization: surface accessibility

The morphological changes evidenced by TEM micrographs and described in the previous paragraphs are confirmed by AFM analyses. AFM analyses focus on the surface topography of the silica films and provide additional information on pore accessibility. Figure 9A is an example of silica mesoporous film whose pores are accessible to the surface. In contrast, it is clear that accessibility to the porous system is very limited for silica films with nanochannels oriented parallel to the surface (Figure 9B).

In order to further characterize the inner porosity of the mesoporous films and to ascertain the presence of interconnected porosity, thicker samples of larger weight were prepared by casting for nitrogen adsorption analyses and porosity study.

TEM measurements indicated that the casting procedure provided materials with pore morphology and arrangement similar to spin-coated materials only in the case of mesoporous silica films having sphere-like pores (i.e., formulations with TEOS/PS-*b*-PEO weight ratios higher than 90/10), whereas porosity was largely affected by the preparation procedure for all the other cases. For this reason, nitrogen adsorption isotherms were carried out only for spherical pore systems.

All the isotherms obtained are of the IV type, with a hysteresis loop of H2 type (from IUPAC classification) in the relative pressure range 0.5-1. The hysteresis loop and its shape indicate the presence of mesoporosity. The isotherm and the DFT pore size distribution curve of sample 93TEOS/7PS₃₀₈-*b*-PEO₂₅₀ (representative of all the spherical pore systems) are shown in Figure 10. The sample has a very limited adsorbing capacity, a very low specific surface area (ca. 10 m² g⁻¹) and a limited amount of spherical mesopores whose size (about 24 nm) is in good agreement with TEM analyses. Altogether these data indicate that the external surface area is porous and

accessible (as proved by AFM images), whereas the internal porous system is completely not accessible to the adsorptive, meaning that it consists of individual sphere-shaped pores with no interconnections with the surface. Therefore membranes could be obtained only from very thin silica layers with thickness of the same order of magnitude of the spherical micelles used as templates. Examples are shown in Figures 4A, 4B, 6A, 8B, where the sharp color contrast of the TEM micrographs clearly indicates that the whitish spherical pores fully cross the grey silica film.

4. Conclusions

Large-mesopore silica thin films were prepared via a templating strategy based on block copolymer micelles, and they were characterized in order to assess their applicability as selective gates for controlled dosing and transport of chemical species in solution.

Mixed TEOS/PS-*b*-PEO micellar solutions in the range of composition 95:5-75:25 were tested. The length of polymer blocks and the effect of a core-soluble homopolymer were also considered as variables to tune the size, shape and hierarchical organization of the mesopores in the final silica films. As a conclusion, thin mesoporous silica films with tunable porosity were synthesized, but permeability could be achieved only for very thin films with large mesopores spanning the film thickness and deriving from the self-assembly of spherical block copolymer micelles.

Future work will focus on the preparation of such large-mesopore silica thin films on permeable supports for diffusion tests with the aim of proposing this material for membrane technology applications.

5. Acknowledgements

Compagnia di San Paolo and University of Torino are gratefully acknowledged for funding Project ORTO114XNH through “Bando per il finanziamento di progetti di ricerca di Ateneo - anno 2011”.

The authors thank Mrs. Federica Franconieri for technical assistance in TEM measurements.

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Table 1. Compositions (wt. %) of micellar solutions.

Sample name ^[a]	TEOS	PS- <i>b</i> -PEO ^[b]	Benzene	Ethanol	HCl	PS
75TEOS/25PS- <i>b</i> -PEO	2.77	0.92	91.29	4.67	0.34	----
85TEOS/15PS- <i>b</i> -PEO	4.89	0.86	85.39	8.26	0.60	----
88TEOS/12PS- <i>b</i> -PEO	6.08	0.83	82.07	10.27	0.75	----
90TEOS/10PS- <i>b</i> -PEO	7.18	0.80	79.00	12.13	0.89	----
93TEOS/7PS- <i>b</i> -PEO	9.67	0.73	72.07	16.34	1.19	----
95TEOS/5PS- <i>b</i> -PEO	12.38	0.65	64.52	20.92	1.53	----
93TEOS/7PS- <i>b</i> -PEO_ 10PS	9.01	0.68	73.89	15.23	1.12	0.07
93TEOS/7PS- <i>b</i> -PEO_ 20PS	9.01	0.68	73.83	15.23	1.12	0.14

^[a] Sample names refer to the compositions (wt. %) excluding solvents.

^[b] Three different types of commercial PS-*b*-PEO block copolymers were selected:

PS₁₈₃-*b*-PEO₁₄₅; PS₃₀₈-*b*-PEO₂₅₀; PS₅₆₇-*b*-PEO₇₀₄.

Table 2. Average pore sizes from HRTEM measurements.

Sample name	PS₅₆₇-<i>b</i>-PEO₇₀₄^[a]	PS₃₀₈-<i>b</i>-PEO₂₅₀	PS₁₈₃-<i>b</i>-PEO₁₄₅
88TEOS/12PS- <i>b</i> -PEO	42 ± 8	30 ± 5	20 ± 4
90TEOS/10PS- <i>b</i> -PEO	32 ± 6	33 ± 5	17 ± 3
93TEOS/7PS- <i>b</i> -PEO	23 ± 3	23 ± 3	29 ± 3
95TEOS/5PS- <i>b</i> -PEO	25 ± 3	27 ± 3	28 ± 4

^[a] Diameters are reported in nm ± SD (or Standard Deviation).

Figure captions

Figure 1. Formation of block copolymer micelles and their assembly in the silica matrix.

Figure 2. Thermogravimetric and differential thermogravimetric curves of a 93TEOS/7PS₃₀₈-*b*-PEO₂₅₀ film (a). Thermal degradation of PS₃₀₈-*b*-PEO₂₅₀ from RT up to 600 °C (solid line) and from RT up to 400 °C with a final isothermal step of two hours at 400 °C (dashed line) (b).

Figure 3. AFM micrographs of 93TEOS/7PS₅₆₇-*b*-PEO₇₀₄ thin film before (A) and after (B) block copolymer thermal removal.

Figure 4. TEM micrographs of calcined films templated by using PS₅₆₇-*b*-PEO₇₀₄ and decreasing the TEOS/block copolymers weight ratios: 95/5 (A), 93/7 (B), 90/10 (C), 88/12 (D), 85/15 (E), 75/25 (F). All the micrographs were collected at the same magnification.

Figure 5. TEM micrographs of calcined films templated by using PS₃₀₈-*b*-PEO₂₅₀ and decreasing the TEOS/block copolymers weight ratios: 95/5 (A), 93/7 (B), 90/10 (C), 88/12 (D), 85/15 (E), 75/25 (F). All the micrographs were collected at the same magnification.

Figure 6. TEM micrographs of calcined films templated by using PS₁₈₃-*b*-PEO₁₄₅ and decreasing the TEOS/block copolymers weight ratios: 95/5 (A), 93/7 (B), 90/10 (C), 88/12 (D), 85/15 (E), 75/25 (F). All the micrographs were collected at the same magnification.

Figure 7. TEM micrograph of 93TEOS/7PS₅₆₇-*b*-PEO₇₀₄ calcined silica sample at high magnification. The hexagon drawn evidences the spatial organization obtained.

Figure 8. TEM micrographs of 93TEOS/7PS₁₈₃-*b*-PEO₁₄₅ calcined samples with addition of 0 % (A), 10 % (B) and 20 % (C) of PS homopolymer. All the micrographs were collected at the same magnification.

Figure 9. AFM micrographs of calcined silica films: 93TEOS/7PS₅₆₇-*b*-PEO₇₀₄ well-ordered spherical porous system (A) and 88TEOS/12PS₃₀₈-*b*-PEO₂₅₀ horizontally oriented worm-like channel system (B).

Figure 10. N₂ adsorption-desorption isotherms at 77 K (A) and DFT pore size distribution curves of 93TEOS/7PS₃₀₈-*b*-PEO₂₅₀ silica powder (B). Dark symbols refer to the adsorption branch of the isotherm, empty symbols to the desorption branch.

Figure 1

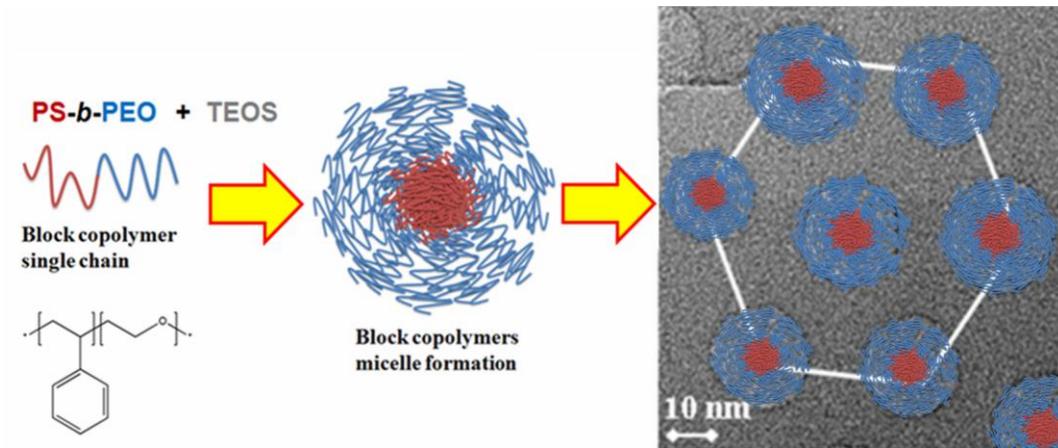


Figure 2

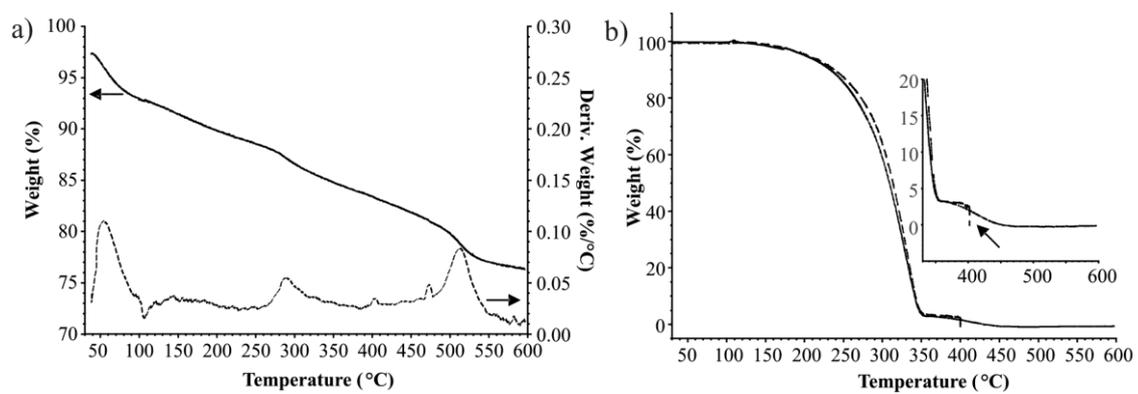


Figure 3

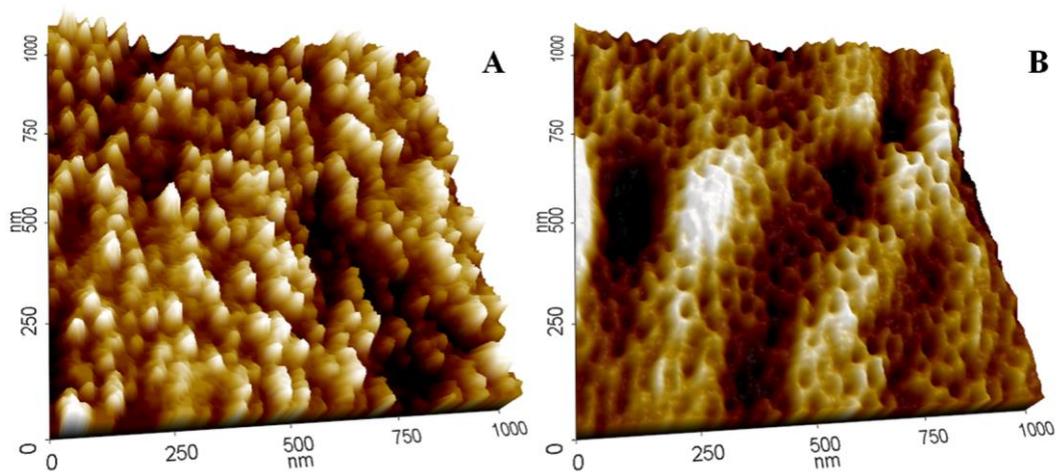


Figure 4

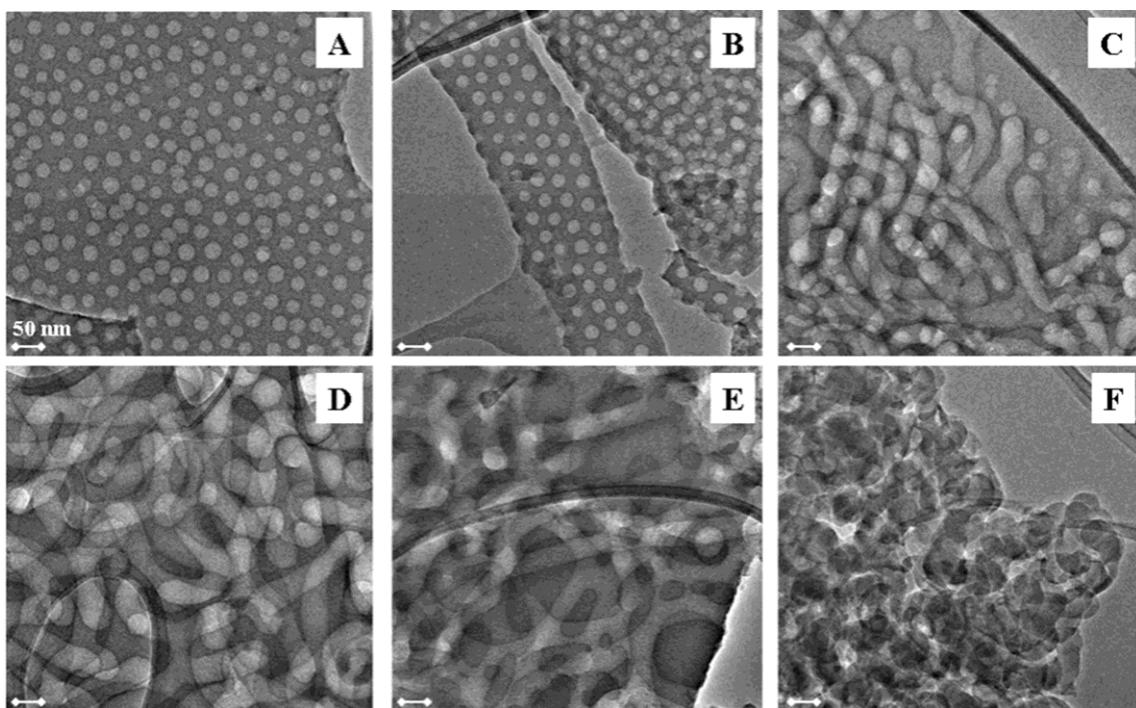


Figure 5

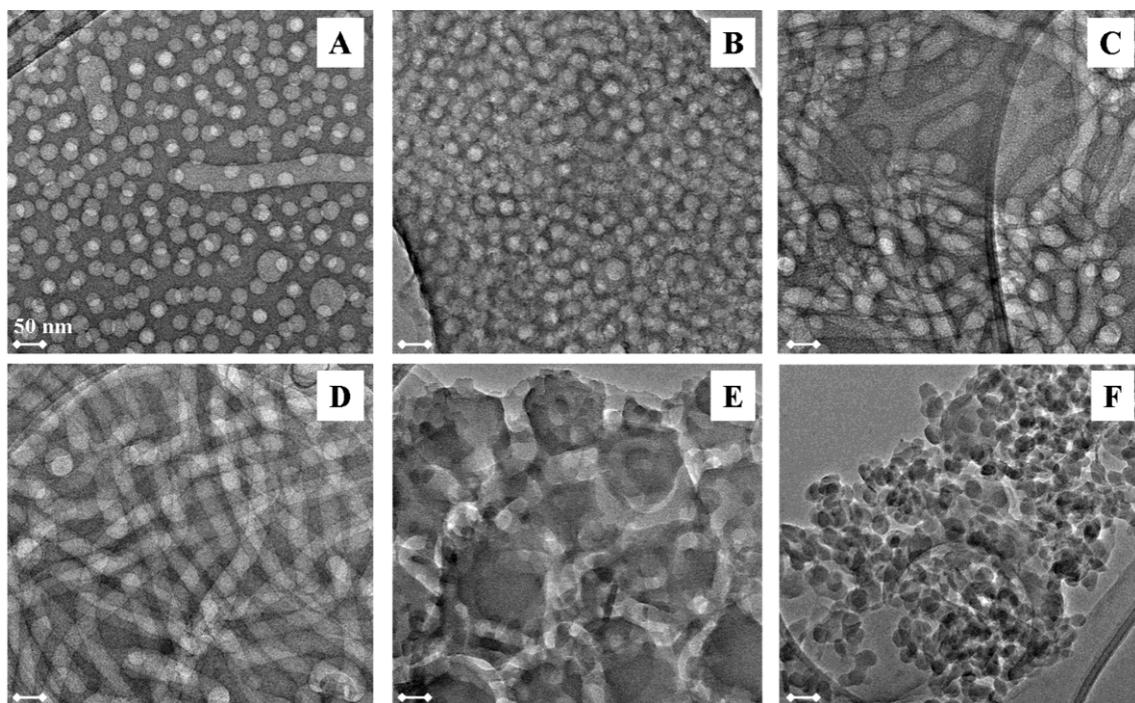


Figure 6

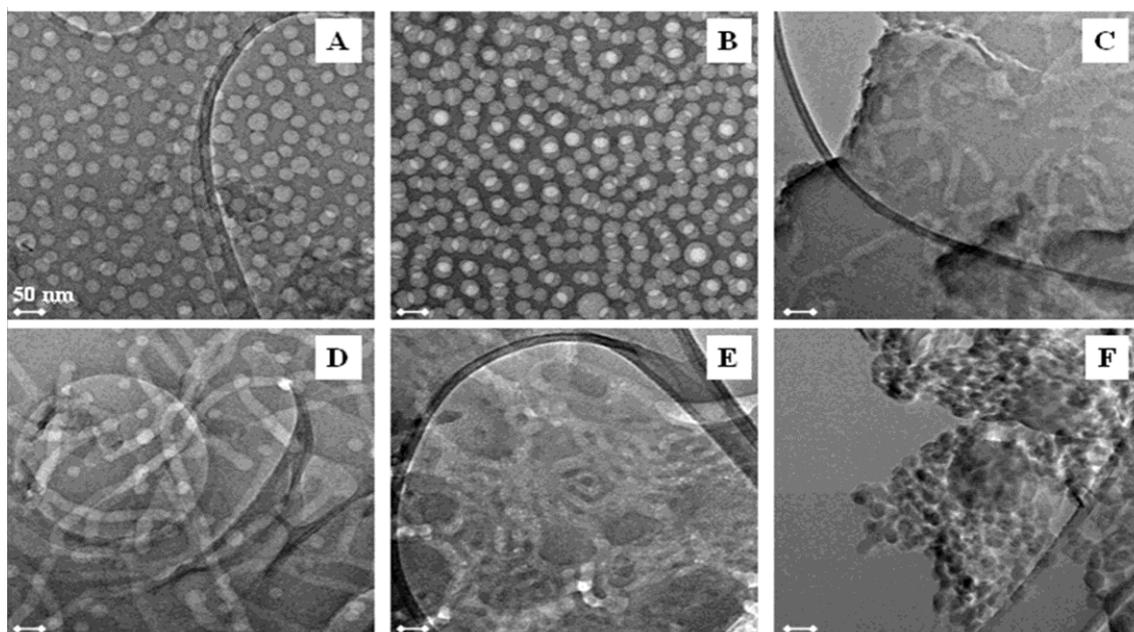


Figure 7

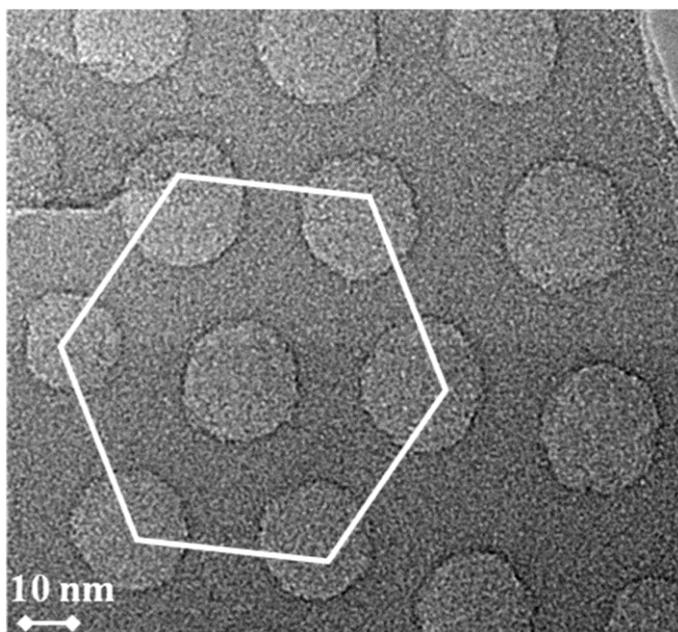


Figure 8

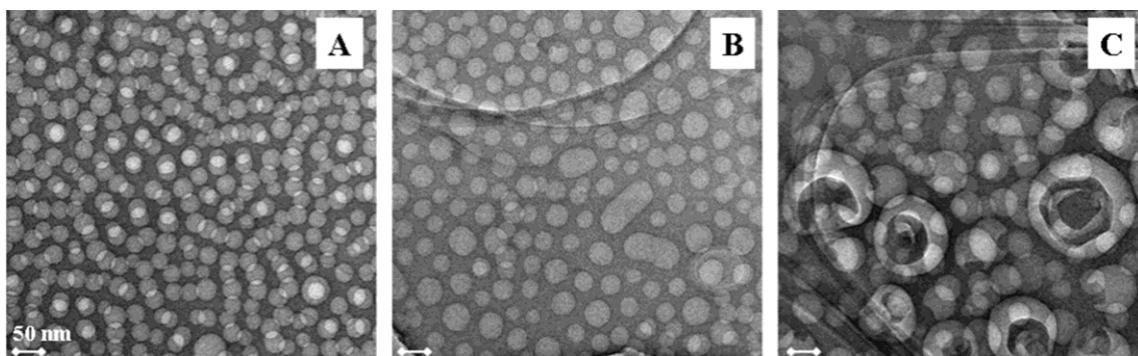


Figure 9

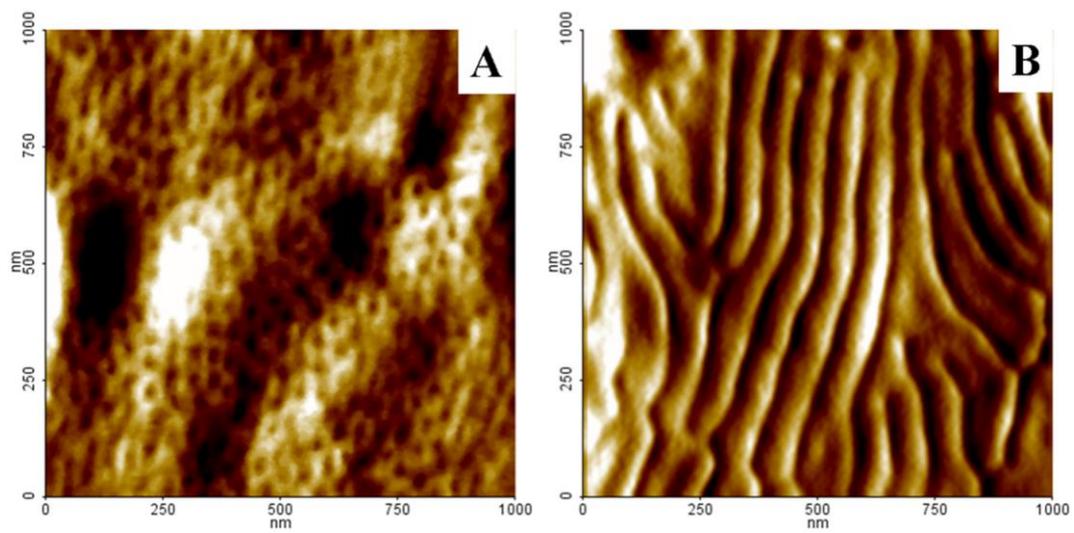


Figure 10

