Supplementary Information

Complete shape retention in the transformation

of silica to polymer micro-objects

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1. SEM micrographs of silica forms
2. X-ray diffraction pattern, adsorption measurements and 2D (1H-29Si) Lee-Goldburg HETCOR
NMR spectrum of ‘morphological’ silica
3. SEM micrographs of nanocomposite forms
4. BET adsorption curve, benzene absorption measurements and thermal analysis of the
nanocomposite
5. Dynamic Light Scattering of silica, nanocomposite and polymer objects
6. 2D Lee-Goldburg HETCOR NMR of the nanocomposite
7. TEM images of the nanocomposite.
8. SEM micrographs of selected polymer forms
9. Optical images and fluorescence micrographs of the plastic objects after different times of DNA
diffusion
10. Manipulation of a tubular polystyrene micro-object by the electron-beam irradiation as shown
by SEM microscopy
11. SAXS and Molecular weight distribution plot of the polystyrene objects
12. 13C solution NMR spectrum and microstructure of the polystyrene objects
13. $^{13}$C CPMAS fast NMR and 2D ($^{1}$H-$^{29}$Si) HETCOR NMR spectra of polymethylmethacrylate nanocomposite and thermal analysis of both the nanocomposite and the polymethylmethacrilate objects.

**Discussion of the experimental conditions and the mechanism for the formation of morphological silica.**

The conditions for the formation of varied silica morphologies depend on parameters like the nature of the surfactant, the silica precursors, counterions and their concentrations and also pH, ionic strength and temperature. The reactions are generally performed under quiescent conditions, following the initial stirring together of the reagents. Under quiescent conditions and in acidic solution it is possible to obtain three families of monoliths: fibers, gyroids and spheres. The growth process of shapes can be described as starting from a nucleation of seeds that are constituted by liquid-crystal templates of condensing silica and surfactant. The final shape has its origins in the topological defects present in the primary seeds, as the seeds induce the formation of the disclination defects. The director field grows concentrically and coaxially around the defect line. For a better understanding of silica object growth the elasticity theory has been recalled. The stresses, both radial and longitudinal, induced by the silica condensation on the gel material explain the objects’ curvature. Of the several variables governing the process pH is one of the most relevant; it influences the surface charge on the seed, the deposition of silicate micelles onto the preformed seed and growing mesophase, and the formation rate of the silica aggregate. In our studies we used cetyltrimethylammonium chloride as the surfactant template and tetraethylorthosilicate as the silica source. Gyroid shapes are formed with 3.5 HCl moles per 100 moles of H$_2$O. Acidic conditions create protonated silicates in the head-group region of the micelles and modulate the positive charge distribution on the surface of the silicate precursors. In addition, charge repulsion between colloidal particles is dominated by the acidity of the solution. Under the high acidic condition, the silicate micelles deposit over the preformed layers in a planar arrangement. This arrangement creates gyroidal shapes containing an architecture of concentric channels coiling around the main axis.

An aqueous solution of cetyltrimethylammonium chloride, hydrochloric acid (7 moles of HCl per 100 moles of H$_2$O) and formamide (10.2 moles of formamide per 100 moles of H$_2$O) was prepared and left to age for 48 hours, TEOS was then added and after 3 days in a quiescent state the silica objects formed. The use of formamide in the synthesis is applied to produce, upon acid hydrolysis, ammonium chloride and formic acid. This results in a $\sim$ 1.9 pH solution and an ionic strength that favors tubular formation. Low acidity and a high ionic strength medium favor a slow condensation rate and polymerization-induced differential contraction of silicate micelle rods. Monodispersited silica fibers could be obtained at low temperature. Indeed it is the environmental solution of the silicate liquid-crystal seed that predetermines the defect and director field pattern, the surface mesostructure and the charge of the seed. The seeds are formed by a step-by-step aggregation and the anchoring of silicate micelles over the preformed nascent morphology. Disclination defects, considered the cause of the formation of curved morphologies on the micron scale, are generated in the precursor unpolymerized silicate phase which is liquid-crystal-like. In the MCM-41 material, disclinations are observed with the director $\textbf{n}$ along the channels. The $\pm \pi$ disclination defect involves a large strain field with channel bending. Indeed, close to the core region, where the bending is more acute, the defect becomes more stressed, and this leads to channel breaking into short lengths. On the outer region of the curvature there is the formation of dislocations. If one recalls the concepts developed in the liquid crystal field, the consequences of the presence of line defects can reach the scale of a few microns and explain the generation of the curved shapes. In fact, defect stabilization in liquid crystals requires less energy than in crystalline solids and the
lower energy favors the formation of defects with large dimensions and strong distortions of the initial director fields. Viscosity in liquid crystal material is low, and small forces that are locally active during the silica growth can induce deformation of the elastic medium. Thus generated morphologies reach an energy minimum even in the presence of curvatures, unlike the situation with a conventional crystal.

In the particular case of our morphologies, the discoids and toroids are generated from a $+2\pi$ disclination rotated along the transverse axis in the $ab$-plane.$^a$)

References


Figure 1. SEM micrographs of single objects showing gyroidal and tubular shapes of mesoporous silica, synthesized under quiescent conditions. Scale bars correspond to 2 $\mu$m.
Figure 2. a) Powder X-ray diffraction pattern of MCM-41 (Bruker D8 Advance), where the sharp peak is due to the regular repetition of 3.04 nm of mesochannels in the hexagonal packing. b) BET adsorption curve of nitrogen at 77K with the typical profile of an MCM-41 silica from which a surface area of 1192 m²/g was measured. c) 2D ($^1$H-$^{29}$Si) HETCOR NMR spectrum of silica particles recorded under fast magic angle spinning conditions and Lee-Goldburg proton
homonuclear decoupling; the magnetic correlations between hydrogens and silicon atoms of the silanol groups on the channels walls are mainly shown in the contour plot.

Figure 3. SEM micrographs of single objects showing gyroidal and tubular shapes of polystyrene/MCM-41 nanocomposites. The nanocomposite adduct, that serves as a mediator for information transcription, assumes the architecture of a geometrical solid of micrometric dimensions. Scale bars correspond to 2 µm.
Figure 4. a) BET adsorption curve of nitrogen at 77K of polystyrene/MCM-41 nanocomposite, showing a surface area of 612 m$^2$/g (BET method) and a total pore volume of 0.28 cm$^3$/g and b) benzene adsorption curve of the nanocomposite, compared to MCM-41. The decrease of the surface area in the nanocomposite is a proof of the presence of the polymer in the channels. c) Differential scanning calorimetry of the bulk polymer and of MCM-41/polymer nanocomposite, where the flat trace, evidenced in the circle, indicates the absence of the glass transition. DSC showed no trace of the glass transition, because a collective motion is impeded in polymer chains confined to low-dimensionality spaces. d) Thermogravimetric analysis (TGA) showed PS degradation in the nanocomposite (20% weight-loss) at a temperature as high as 500°C, since the surrounding silica-case provides protection to the polymer chains. Specific density measured by He picnometry (1.91 g/cm$^3$, compared to 2.1 g/cm$^3$ of MCM-41) is congruent with the polymer inclusion (the polymer shows a specific density of 1.02 g/cm$^3$). In addition, the presence of polymer inside the matrix reduces the XRD peak-intensity at 3.05 nm due to the reduced nanophase electron density contrast in the material.
Figure 5. Particle size distribution obtained by Tri-laser Microtrac S3500 Laser Light Diffraction of the silica, nanocomposite and polymer micro-objects.
Figure 6. Fast magic angle spinning 2D heterocorrelated NMR spectra, with Lee-Goldburg homonuclear decoupling, of the nanocomposite objects. a) 2D $^1$H-$^{29}$Si NMR spectrum, indicating the strong magnetic communication of polystyrene hydrogens (CH/CH$_2$ at 1.4 ppm and phenyl at 7.1 ppm) with silicon-29 of silanols ($Q^3$ at -102.2 ppm) lining the mesochannel walls of the MCM-41 matrix. The orange area highlights the phenyl hydrogens communicating intimately with $Q^3$ silicons. The through-space correlation at the hybrid interface is operative when nuclei sit at less than 1 nm (cross-polarization time of 5 ms). b) 2D $^1$H-$^{13}$C NMR spectrum of the nanocomposite highlighting, selectively, the formation of polystyrene (CH/CH$_2$ at 40.9/46.6 ppm, phenyl-CH at 128.0 ppm and phenyl-C at 146.2 ppm) and the absence of monomer. The red dashed line indicates the strongly correlated $^{13}$C-$^1$H-$^{29}$Si spin system, involving aromatic groups of polystyrene and MCM-41 silanols.
Figure 7. TEM images of nanocomposite: a) taken with an incidence parallel to the direction of the silica mesopores and b) taken with an incidence perpendicular to the direction of the silica mesopores.
Figure 8. SEM microscopy of single micrometric gyroidal and tubular shaped objects made of polystyrene. Scale bars correspond to 2 µm.
Figure 9. Optical (left) and fluorescence (right) micrographs of the polystyrene micro-tubes (2.5 micron cross-section) after diffusion of yeast DNA (Saccharomyces cerevisiae DNA) at different diffusion times: a) after 1 hour diffusion and b-d) after 24 hours diffusion. Suspensions of the micro-objects have been obtained using water/ethanol mixtures (8.5:1.5 v/v). An aqueous suspension of yeast DNA previously marked with a fluorescent probe (propidium iodide) was added to the previous suspension and subjected to mild sonication at 0°C. The diffusion process was followed at different times. No diffusion is shown in the gyroidal and toroidal particles.
Figure 10. Manipulation of a tubular polystyrene micro-object as shown by SEM microscopy. a) The tubular polymeric micro-object before the electron-beam irradiation to the point indicated by the cross. b) The micro-object after bending by the targeted irradiation. This mechanical effect is obtained by the contraction of the porous polymeric texture as a response to the localized external stimulus. Scale bars correspond to 1 µm.

Figure 11. a) Small Angle X-ray Scattering of the polymer objects. b) Gel Permeation Chromatography (WATERS equipped with styragel columns with a molecular-weight range from 5000 to 4000000) of polystyrene whose the micro-objects are made, performed in tetrahydrofurane solution showing a number-average molecular mass $M_n$ of 48618, a weight-average molecular mass $M_w$ of 99161 and a polydispersity index $D=M_w/M_n$ of 2.04.
Figure 12. $^{13}$C solution NMR spectrum (Bruker Avance 500) recorded at 125.5 MHz and 20°C of polystyrene dissolved in CDCl$_3$ (5% by weight) with TMS as reference (right). Enlargement of the aromatic region of the $^{13}$C solution NMR spectrum (left). The polymer shows a concentration of $mm$ triads of 0.14, $mr$ of 0.19 and $rr$ of 0.67. A recycle delay 10s was applied.
Figure 13. Characterization of nanocomposite and polymer micro-objects of polymethylmethacrylate. a) $^{13}$C fast-MAS (15 KHz) CP NMR spectrum of polymethylmethacrylate nanocomposite. The absence of monomer residues is apparent. b) 2D ($^1$H-$^{29}$Si) HETCOR NMR spectrum with homonuclear Lee-Goldburg decoupling of polymethylmethacrylate nanocomposite. The spectrum can provide a direct demonstration of spatial proximity among the polymer protons and the silica surface. c) Differential scanning calorimetry of the porous polymeric micro-objects, where an exotherm transition precedes the glass transition during the first run: this phenomenon, similar to what obtained for polystyrene, is due to the excess surface energy $\Delta H = 6 \text{ J g}^{-1}$. During the second run the glass transition of the polymethylmethacrylate is apparent at 110°C. Calorimetric trace of MCM-41/polymer nanocomposite: the flat trace, evidenced in the circle, indicates the absence of the glass transition in the confined system.
**Solid State NMR Measurements.** The solid–state NMR spectra were run at 75.5 MHz for $^{13}$C and at 59.6 MHz for $^{29}$Si, on a Bruker Avance 300 instrument operating at a static field of 7.04 T equipped with 4 mm double resonance MAS probe. The samples were spun at a spinning speed of 15 kHz, and Ramped-Amplitude Cross-Polarization (RAMP-CP) transfer of magnetization was applied. The 90° pulse for proton was 2.9 µs (86 kHz). $^{13}$C Single Pulse Excitation (SPE) experiments were run using a recycle delay of 10 s and 100 s and Cross Polarization (CP) MAS experiments were performed using a recycle delay of 10 s and a contact time of 2.5 ms.

Phase-Modulated Lee-Goldburg (PMLG) heteronuclear $^1$H-$^{29}$Si and $^1$H-$^{13}$C correlation (HETCOR) experiment coupled with fast magic angle spinning (MAS) allows the registration of 2D spectra with high resolution both in the proton and silicon dimension. Narrow proton resonances, with line widths in the order of 1-2 ppm, are obtained with homonuclear decoupling during $t_1$; this resolution permits a sufficiently accurate determination of the proton species present in the system, as described elsewhere. Phase-Modulated Lee-Goldburg (PMLG) $^1$H-$^{29}$Si and $^1$H-$^{13}$C HETCOR spectra were run with LG period of 18.9 µs. The efficient transfer of magnetization to the carbon nuclei was performed applying RAMP-CP sequence. Quadrature detection in $t_1$ was achieved by time proportional phase increments method. Carbon signals were acquired during $t_2$ under proton decoupling applying two pulse phase modulation scheme (TPPM). Before each heteronuclear experiment samples are outgassed overnight and inserted in the ZrO$_2$ rotors in a dry box under nitrogen atmosphere.

**References**