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Highly Swollen Liquid Crystals as New Reactors for the Synthesis of Nanomaterials

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Synthesis and self-assembly of nanomaterials can be controlled by the properties of soft matter. On one hand, dedicated nanoreactors such as reverse microemulsions or miniemulsions can be designed. On the other hand, direct shape control can be provided by the topology of liquid crystals that confine the reacting medium within a specific geometry. In the first case, the preparation of micro- or miniemulsions generally requires energetic mechanical stirring. The second approach uses thermodynamically stable systems, but it remains usually limited to binary (water + surfactant) systems. We report the preparation of different families of materials in highly ordered quaternary mediums that exhibit a liquid crystal structure with a high cell parameter. They were prepared with the proper ratios of salted water, nonpolar solvent, surfactant, and cosurfactants that form spontaneously swollen hexagonal phases. These swollen liquid crystals can be prepared from all classes of surfactants (cationic, anionic, and nonionic). They contain a regular network of parallel cylinders, whose diameters can be swollen with a nonpolar solvent, that are regularly spaced in a continuous aqueous salt solution. We demonstrate in the present report that both aqueous and organic phases can be used as nanoreactors for the preparation of materials. This property is illustrated by various examples such as the synthesis of platinum nanorods prepared in the aqueous phase or zirconia needles or the photo- or γ-ray-induced polymerization of polydiacetylene in the organic phase. In all cases, materials can be easily extracted and their final shapes are directed by the structure-directing effect imposed by the liquid crystal.

Introduction

Objects at the nanometric scale exhibit specific properties, generally due to their limited size ranging between single molecule and bulk material, that can enhance quantum size effects. Their exceptional high surface over volume ratio provides also specific features in catalysis or molecule adsorption. Among the different chemical syntheses that could be developed, those requiring self-assembly at the molecular scale or between building nanoblocks appear to provide attractive synthesis pathways.[1−4] Among them, the dynamic properties of soft matter, as, for example, surfactant-based micellar systems, constitute an efficient driving force for the organization of solid phases. The successful production of polymers, hybrid materials, ceramics, with hierarchical structures, as well as of nanostructured materials based on surfactants and block copolymers self-assembly has been recently demonstrated.[5−8] Similar approaches using xanthates and related compounds[9] or addition of polymerizable functions (polymerizable surfactants: "surfmers")[10−12] were also successful. This demonstration has been especially illustrated by the tremendous amount of literature on the preparation of mesostructured oxides where assembling forces based on electrostatic or H-bonding interactions between surfactants

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and inorganic species achieved the control of the final framework of porous silica and related materials.[13−23] However, it appears that many developments, among them, some being called “bio-mimetic” or “bio-inspired”, may be expected in the design of hierarchically nanostructured materials or self-assembled superlattices, from the control of organic−inorganic, organic−organic, or inorganic−inorganic interface properties.[24−40] In parallel, even with no specific interaction, one may also use liquid crystals as molders; such a mechanism was defined as “true liquid crystal templating”. It implies the direct embedding of an inorganic network in the aqueous phase of a binary liquid crystal with the imprinting of the liquid crystal reverse structure on the final solid framework architecture.[41−50] This method is very interesting because one can theoretically design porous solid frameworks with morphology of any type of mesophase. Besides, liquid crystals were also used as reacting media, either to prevent aggregation of nanoparticles or to build superlattices of metal or polymers nanowire arrays.[51−63]

All reactions described above imply binary systems, namely, water plus some structuring agent. However, syntheses were also developed in ternary (water:oil:surfactant) systems. Most of these are based on water in oil reverse microemulsions where aqueous vesicles stabilized by surfactants molecules constitute spherical nanoreactors dispersed in a nonmiscible organic solvent.[64−70] The restricted size of these microemulsions allows the synthesis of rather monodisperse nanoparticles.[49,71−83]

Quaternary systems (water:oil:surfactant:cosurfactant) were also developed to form miniemulsions that exhibit no long-range order where stable nanodroplets of one phase, stabilized by the combined effect of a surfactant and a cosurfactant, are dispersed in a continuous non miscible phase.[84−89]

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These "oil in water" miniemulsions do not form spontaneously, but they require highly energetic stirring by ultrasonication, microfluidization, or high-pressure homogenization as well as the addition of an emulsion stabilizer in order to prevent Ostwald ripening.[85] Surfmers were also employed,[12,90] and many classes of materials, organic or inorganic, were successsfully synthesized through this process.[91−94]

Unlike miniemulsions, liquid crystals form spontaneously, a normal stirring usually contributes to the homogenization, when the components are mixed with the proper ratios, but they are mostly limited to (water:surfactant) binary systems with some possible addition of a small amount of swelling additives. We presented recently a new approach where quaternary systems containing a large amount of nonpolar solvent, usually used for miniemulsions, can lead to liquid crystals that are subsequently used as nanoreactors. We named these systems highly swollen liquid crystals (SLCs), and we demonstrated that macroscopic zirconia needles could be obtained by a slow crystal growth inside these SLCs.[95−97] We show in the present report (i) that this concept can be extended to all classes of surfactants, (ii) that different kinds of materials can be synthesized within, and (iii) that the structure of the SLC can direct the final morphology of the materials synthesized inside. The hexagonal structure of these SLCs was reported several years ago for compositions based on the anionic SDS surfactant, and it was demonstrated that they remain stable even after the addition of particles in the nonpolar cylinders.[62,98−101] However, they were never developed as actual nanoreactors, that is, as systems wherein chemical reactions are performed instead of the simple inclusion of objects prepared in another way.

Syntheses and Experimental Procedures

Preparation of Pure SLCs. The preparation of different samples of SLC was performed according to a general procedure starting with the dissolution of the surfactant into the aqueous phase and the addition of the organic swelling agent under mechanical stirring. An unstable white emulsion was obtained. The cosurfactant was added dropwise under energetic stirring with a vortex tube shaker until the whole solution gives a clear and rigid mesophase. The SLC samples displayed in this study were prepared according to the following procedures: Sample **1.A** was prepared with sodium dodecyl sulfate (SDS) (Acros) as follows: 0.8 g of SDS was dissolved at 35 °C for 3 h, in 2 mL of water containing 0.035 g of NaCl ([NaCl] = 0.3 M) and 0.2 mL of NaOH (N) (final pH = 11); 4.94 mL of cyclohexane was further added under stirring, and the final hexagonal SLC was obtained after the addition dropwise of 0.43 mL of 1-pentanol. Sample **1.B** was prepared with cetylpyridinium chloride (CTPCl) (Aldrich) as follows: 1.0 g of CTPCl was dissolved at 35 °C for 3 h, in 2 mL of water containing 0.04 g of Na_2SO_4 ($[Na_2SO_4] = 0.15$ M) and 0.22 mL of concentrated H_2SO_4 (final pH = −0.6); 5.0 mL of cyclohexane was further added under stirring, and the final hexagonal SLC was obtained after the dropwise addition of 0.354 mL of 1-pentanol. Sample **1.C** was prepared with cetyltrimethylammonium chloride (CTAC) (Aldrich) as follows: 1.0 g of CATC was dissolved at 35 °C for 3 h, in 2 mL of water containing 0.04 g of Na_2SO_4 ($[Na_2SO_4] = 0.15$ M) and 0.22 mL of concentrated H_2SO_4 (final pH = −0.6); 5.0 mL of cyclohexane was further added under stirring, and the final hexagonal SLC was obtained after the dropwise addition of 0.26 mL of 1-pentanol. Sample **1.D** was prepared with Tergitol 15-S-15 ($CH_3(CH_2)_{14}(OCH_2CH_2)_{15}OH$) (Union Carbide) as follows: 2.4 g of Tergitol 15-S-15 was dissolved at 35 °C for 3 h, in 2 mL of water containing 0.035 g of NaCl ([NaCl] = 0.3 M); 3.3 mL of cyclohexane was further added under stirring, and the final SLC was obtained after the dropwise addition of 0.3 mL of 1-pentanol.

Synthesis of Metal Particles. The metal nanoaggregates were prepared as follows: 5 mL of an aqueous solution of hexachloro platinic acid was prepared by dissolving 0.2 g of $H_2Pt^{(IV)}Cl_6$ in 5 mL of water. SDS (2.0 g) was added and stirred until full dissolution, then 5.8 g of cyclohexane was added under stirring. 1-Pentanol (0.8 g) was added dropwise under strong shaking by a vortex shaker until the pristine white emulsion gave a yellowless transparent rigid gel, placed in a "septum" sealed vial, was obtained. The hexagonal symmetry of this SLC was checked by small-angle X-ray diffraction (SAXD). For sample **2.A**, the vial was submitted to a high γ-irradiation dose of 96 kGy that destroyed the SLC. For sample **2.B**, the gel was left under CO bubbling for the following cycle: 25 min bubbling, 6 h of rest; this cycle was repeated three times. For sample **2.C**, the sample was first reduced by a continuous flow of CO for 25 min, then irradiated for 6.5 h with γ radiation (5 kGy h^{-1}, total amount of 32 kGy). The sample was left sealed for 2 days under CO atmosphere. Sample **2.D** was prepared in a lamellar SLC: 5 mL of an aqueous solution of hexachloroplatinic acid was prepared by dissolving 0.2 g of $H_2Pt^{(IV)}Cl_6$ in 5 mL of water. SDS (2.0 g) was added and stirred until full dissolution, then 5.8 g of cyclohexane was added under stirring. 1-Pentanol (0.9 g) was added dropwise under strong shaking by a vortex shaker until the pristine white emulsion gave a yellowless transparent rigid gel that was left in a "septum" sealed vial. The lamellar structure was confirmed by polarized optical microscopy. The gel was left under CO bubbling for 25 min of bubbling, 16 h of rest, another 25 min bubbling, and a last aging of 7 h. For sample **2.E**, palladium fibrils were obtained by reduction of Pd^{II} (0.015 M $Pd(NO_3)_2$) in the water phase (pH = 2) in the hexagonal phase by CO. In this case, some large palladium particles were also observed. For sample **2.F**, 1 g of SDS was dissolved in 2.5 mL of a solution of $H_2Pt^{(IV)}Cl_6$ (0.1 M) and $SnCl_4$ (0.01 M). Cyclohexane (3.5 mL) were further added, and 0.8 g of 1-pentanol was added dropwise under strong shaking by a vortex shaker until the pristine white emulsion gave a transparent rigid gel. The gel was placed in a sealed vial, and a bubbling with CO was applied for 25 min twice, with an aging step of 17 h between. The SLCs were further destabilized by the

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addition of 5 mL of ispropanol, and the particles were all recovered by centrifugation (5 min, 2000 rps) and further washing with 2-propanol.

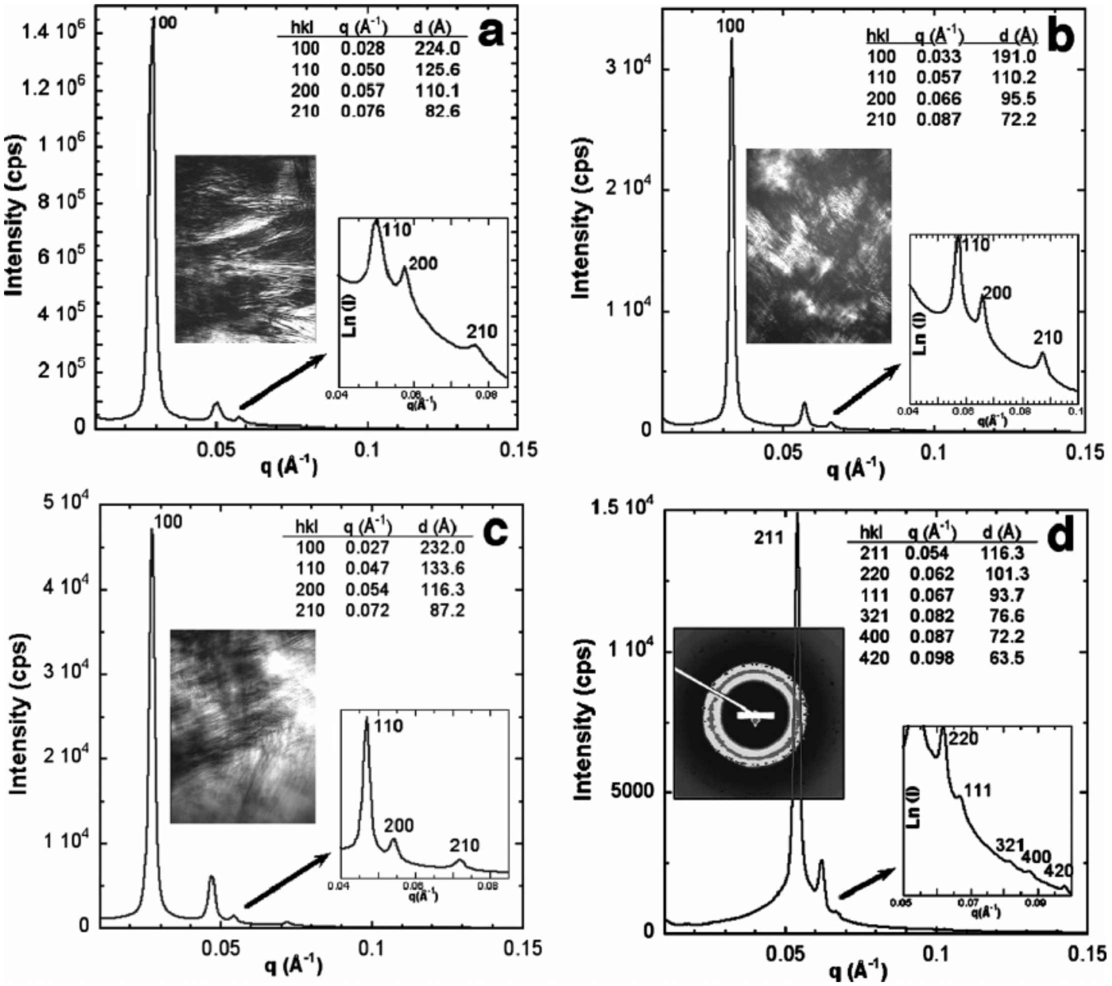
Synthesis of Zirconia. The synthesis of zirconia needles from zirconium sulfate colloids (ZSC), detailed in ref 97, can be summarized as follows: the colloidal suspension was prepared by adding dropwise 450 mL of an aqueous solution of zirconia oxychloride (1.5 mol L^{-1}) into 30 mL of a sulfuric acid solution (1.5 mol L^{-1}) heated at 80 °C, under magnetic stirring. One obtained a final (Zr^{4+}:H_2SO_4) molar ratio of 15:1, and aliquots of 15 mL of the colloidal suspension were put inside an acetyl-cellulose membrane tubing (12−14 000 MW) and then submitted to static dialysis for 24 h against 150 mL of deionized water. The concentration of the colloidal suspension was further increased by evaporation at 45 °C under dynamic vacuum up to reach a final zirconium concentration of 3.4 mol L^{-1}. To prepare the liquid crystal doped with ZSC, 1.0 g of CTPCl was dissolved in 2.0 mL of ZSC. Cyclohexane (5 mL) and 0.3 mL of 1-pentanol were further added in this solution and mixed vigorously with a vortex shaker, until the formation of a transparent gel formed by the hexagonal liquid crystal. The vessel was sealed and stocked at room temperature for several weeks. Macroscopic white needles appeared after 4 weeks of rest, which grew up to 2 cm in length as the rest time increased. The SLC was further destabilized by the addition of 10 mL of cyclohexane, and the particles were recovered by settling after washing with 20 mL of a mixture of 1-pentanol (1 mL) in cyclohexane (19 mL). This process was repeated three times. Crystals were further dried at room temperature for 72 h and octahydrated zirconium oxychloride was identified after this step. Calcination (120 °C/6 h, 200 and 600 °C/2 h) led to the formation of zirconia (sample **3.A**).

Synthesis of Polymers. The polymer samples were prepared as follows. For sample **4.A**, the solution was prepared by mixing 2 mL of an aqueous solution containing 0.0351 g of NaCl and 0.8 g of SDS with 5 mL of cyclohexane containing 0.19 g of 1,4-diphenylbutadiyne (Sigma Aldrich). The SLC was structured by the addition of 0.8 g of 1-pentanol under strong stirring. It was γ irradiated for 20 h, under nitrogen atmosphere (total amount of 90 kGy). The mesophase was further destabilized by the addition of 5 mL of ethanol and 5 mL of water. A phase separation occurs with the organic portion on the top containing the polymer. The polymer was recovered as a solid floating on water after full evaporation of the organic phase. Samples **4.B** and **4.C** were prepared according to the same process; sample **4.B** was prepared in pure cyclohexane, and sample **4.C** was prepared in the cyclohexane phase of the SLC. For sample **4.C**, the SLC was prepared as for sample **4.A**, but the organic phase was made of 3.8 g of cyclohexane, 0.38 g of 1,4-diphenylbutadiyne (Sigma Aldrich), and 0.193 g of benzone methyl ether (Fluka) used as a polymerization catalyst. The so-obtained SLC was left under UV irradiation (100 W, 365 nm) for 12 h. The polymer fibers were recovered according to the same process

Experimental. SAXD experiments were conducted at the D24 synchrotron beamline of the DCI ring at LURE (Orsay, France). A Ge(111) single-crystal curved monochromator provided a beam focused in the horizontal plane. The selected wavelength was 1.49 Å. The incident beam intensity was monitored by an ionization chamber, and its size (typically 0.4 × 1.5 mm^2) was determined by collimating slits upstream and downstream from the monochromator. To reduce absorption and parasitic scattering, the beam path was kept under vacuum, and slits were placed before the sample to suppress parasitic signal. The sample-to-detector distance was adjusted to 2.50 m in order to cover the required scattering vector range. The scattering patterns were recorded with a gas-filled, position-sensitive detector or an image plate. Samples were put in a 1-mm-thick Lindeman capillary. Because of the high intensity, the X-ray diffraction pattern was not corrected for any background scattering for the laboratory SAXD apparatus, which explains the lower resolution, compared with other patterns. The γ-irradiation source was a ^{60}Co γ facility of 7000 Curies with a dose rate of 5300 Gy h^{-1} at Orsay (1 Gy = 1 J kg^{-1}). Transmission electron microscopy (TEM) observations were performed with a JEOL JEM 100 CXII transmission electron microscope at accelerating voltage of 100 kV. The sample drops were deposited and dried on carbon-coated copper grids.

Results and Discussion

Stability of SLCs. Lyotropic hexagonal mesophases consist of infinite liquid cylinders organized on a hexagonal lattice with surfactants at the interface of the cylinders. The hexagonal phase defined as “direct” involves nonpolar tubes regularly spaced in a polar medium. Swelling of these hexagonal phases may occur through two different processes: one may either increase the distance between adjacent cylinders, the cylinders themselves remaining unchanged, or increase the radius of the cylinders without changing drastically the distance between them. The existence of the hexagonal SLCs was initially demonstrated by L. Ramos et al. in the phase diagram of quaternary mixtures combining the anionic surfactant SDS, an aqueous solution of inorganic salt (NaCl), cyclohexane as a hydrophobic swelling agent, and 1-pentanol as a cosurfactant.[98,100,101] They showed that the swelling provided by increasing the intercylinder space leads rapidly to a loss of the positional order of the tubes, therefore the hexagonal long-range order. On the contrary, the swelling of the cylinders themselves while keeping the intercylinder distance small, leads to a more stable hexagonal phase. However, in the latter case, stability is linked not only with the respective proportions of oil, water, and surfactant as well as the intrinsic geometry of surfactant molecules but also with the possibility to adjust the spontaneous radius of curvature of the surfactant monolayer that builds the cylinder walls to adapt to the increasing volume of organic solvent swelling the cylinders. This control is provided by the correct adjustment of the ionic force of the aqueous phase in order to partially screen the repulsion between charges on the surfactant heads. Hence, the correct adjustment between swelling solvent and salt in the aqueous phase is a prerequisite factor if one expects these lyotropic systems to display at room temperature a direct hexagonal phase constituted of a triangular array, in salted water, of infinite nonpolar cylinders swollen by nonpolar solvent and stabilized by a monolayer of the surfactant. This condition is very important if the added salt is also used as a reagent. The cosurfactant, e.g., 1-pentanol, is another factor that helps to stabilize the cylinder walls, but its amount depends slightly on the cylinder diameter. It has been demonstrated that the correct adjustment between cyclohexane and the ionic force of the aqueous solution by addition of a salt allowed the diameter of the nonpolar cylinders to be tuned over 1 order of magnitude (from 3 to 30 nm), while the distance between adjacent cylinders is kept small and nearly constant (about 3 nm).[98] If one assumes that these mesophases can be used as actual nanoreactors, one had to adjust their physicochemical properties as a function of the desired reaction instead



(a)

hkl	q (Å^{-1})	d (Å)
100	0.028	224.0
110	0.050	125.6
200	0.057	110.1
210	0.076	82.6

(b)

hkl	q (Å^{-1})	d (Å)
100	0.033	191.0
110	0.057	110.2
200	0.066	95.5
210	0.087	72.2

(c)

hkl	q (Å^{-1})	d (Å)
100	0.027	232.0
110	0.047	133.6
200	0.054	116.3
210	0.072	87.2

(d)

hkl	q (Å^{-1})	d (Å)
211	0.054	116.3
220	0.062	101.3
111	0.067	93.7
321	0.082	76.6
400	0.087	72.2
420	0.098	63.5

Figure 1. SAXD patterns of different examples of SLCs prepared with: (a) **1.A**, SDS as surfactant, cyclohexane as swelling agent, and 1-pentanol as cosurfactant at pH 11, (inset is polarized light microscopy); (b) **1.B**, with CTPCl as surfactant, at pH below 0; (c) **1.C**, with CTAC as surfactant; (d) **1.D**, with nonionic Tergitol 15-S-15 as surfactant (inset is image plate recording of the SAXD). Samples **1.A**, **1.B**, and **1.C** exhibit a hexagonal structure with four assignable peaks; **1.D** exhibits a well-defined cubic structure.

of the reverse. This implied that the nature of SLCs had to be extended over a broader range of compositions than those reported previously, that is, a hexagonal SLC prepared with the anionic SDS surfactant in neutral pH and with a limited domain of existence.[98] We show thereinafter that the concept of SLC is really generic and that it can be enlarged to various compositions including not only anionic but also cationic or nonionic surfactants.

Figure 1 displays the SAXD patterns of some examples whose nature of the surfactant, the inorganic salt, and/or the acidity were changed. Figure 1a displays the SAXD pattern of an SLC (sample **1.A**) prepared with SDS as surfactant, a basic (pH 11) aqueous solution of sodium chloride (0.3 M), cyclohexane as the nonpolar solvent swelling of the surfactant cylinders, and 1-pentanol as cosurfactant. Birefringence, a fingerprint of the anisotropic structure, is observed over the whole volume by polarized optical microscopy (inset). The system is highly ordered with four peaks being indexed in the hexagonal symmetry ($P6mm$, $a = 25.4$ nm). However, due to the nature of the surfactant head, the stability of this SLC is limited below pH = 1. This limit is overcome with cationic surfactants such as CTPCl (Figure 1b, sample **1.B**) or CTAC (sample **1.C**, Figure 1.c). At pH < 0, they both exhibit a $P6mm$ hexagonal symmetry with the cell parameter $a = 22.0$ and 26.7 nm, respectively. Finally, nonionic surfactants such as Tergitol 15-S-15 ($CH_3(CH_2)_{14}(OCH_2CH_2)_{15}OH$) can also structure a SLC (sample **1.D**) that exhibits in the present example a well-defined cubic structure ($Ia3d$, $a = 28.6$ nm) (Figure 1d). The nature of the components can be changed, too. Successful preparations were achieved with different swelling agents (cyclohexane, decane, 2,2,4-trimethyl pentane), with either pure or binary and ternary mixtures of different salts (NaF, NaCl, KCl, Na_2SO_4), and with various cosurfactants (1-pentanol, dimethyl-2 propanol-1, 1-decanol). These results demonstrate that the composition of SLCs can be adapted in order to fulfill the experimental conditions required to prepare new materials in the organic or in the aqueous phase.

The diameter of the cylinders of the SLC can also be adapted by varying the amount of swelling solvent. Figure 2 displays the evolution of the d spacing (d_{10}) for mesophases prepared with SDS and NaCl as a function of ρ (cyclohexane: water vol. ratio) varying from 0.2 to 4. The d spacing varies linearly from 6 to 35 nm with an increase in the cyclohexane volume. It is worth noticing that the amount of salt in the aqueous phase must be concomitantly adapted according to the empirical relationship

$$[NaCl] = 0.156\rho - 0.104 \quad (1)$$

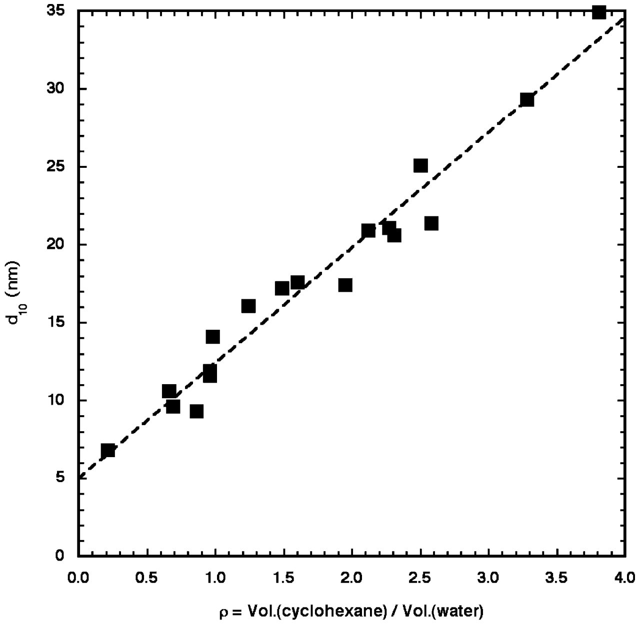


Figure 2. Evolution of the *d* spacing for pure SLCs prepared with SDS and different volumic ratio of cyclohexane over water.

When ionic precursors will be used in the aqeuous phase, they will play the function of the stabilizing salt, but their concentration will depend also on the previous relation, which can be a drawback for certain syntheses.

Preparation of Metal Nanorods and Nanoslabs. Among the different nanomaterials, those exhibiting a high shape factor (nanorods, nanowires, lamellae, etc.) are very attractive because of their anisotropic electrical, optical, magnetic, and mechanical properties, along with their potential applications in nanodevices.[26,62] Many approaches have been used for their synthesis, including controlled growth,[39,102] self-assembly,[103] laser ablation,[104] and thermal processing,[105−110] but many of these syntheses were performed within the structure of a porous hard matrix (mesoporous silica, carbon, or peptide nanotubes) or by the reverse print of the matrix structure.[40,111−113] For example, platinum nanowires synthesized in mesoporous silica FSM-16 exhibited unique properties in CO chemisorption, water−gas shift reaction, and magnetism due to their morphology provided by the mesoporous channels of FSM-16.[114,115] However, the recovery of the metal structure requires usually an additional step of dissolution of the solid matrix in a corrosive medium. Self-assembly of nanoparticles can be achieved also with the help of confinement inside soft matrixes such as liquid crystals, but there is no straightforward relationship between the geometry of the liquid crystal and the final morphology of the particles synthesized inside.[57,62] For example, syntheses by Ding et al. of palladium nanoparticles in an inverted hexagonal mesophase led to isotropic particles and preparation by Lee et al. of silver particles in a hexagonal phase made with nonionic Triton ×100 gave again polydisperse and mostly isotropic particles, even if some rods could be observed.[52,59]

In our study, metal nanostructures were synthesized inside the aqueous phase of a SLC (SDS:1-pentanol:cyclohexane:water). It must be noticed first that, when the reaction proceeds in bulk water, a polydiperse distribution of nanoparticles is obtained. Polarized light micrographs and SAXD confirm the anisotropic structure of a mesophase that verifies the *P*6*mm* hexagonal structure both before and after doping the aqueous medium with hexachloroplatinic acid ($H_2Pt^{(IV)}Cl_6$) in concentrations ranging from 0.05 to 0.2 mol L^{-1}. The hexachloroplatinic acid was not only used as a reagent but also as a SLC stabilizer in place of sodium chloride. The comparison between platinum particles synthesized in this SLC using various reduction methods is displayed in Figure 3. When a high irradiation dose of γ rays was applied (92 kGy with a SLC containing a 0.1 M aqueous solution of platinic acid) (sample **2.A**), a complete amorphization of the liquid crystal was observed. In that case, the mesophase could not prevent a diffusion-controlled aggregation of particles. They aggregated according to an isotropic fractal-like growth mechanism (Figure 3a). When the reduction of the platinic acid into platinum was obtained by a slower chemical reduction (bubbling of 1 atm carbon monoxide) of Pt^{IV} (0.1−0.2 M) (sample **2.B**), the color of the phase gradually changed from yellow to dark purple and the liquid crystal became less viscous as the reaction proceeded. Rodlike aggregates made of monodisperse well-crystallized Pt nanoparticles (diameter of 2.5 nm) were obtained (parts b and c of Figure 3) and X-ray photoelectron spectroscopy (XPS) analysis confirmed the total reduction of platinum but reveal some traces of remaining surfactants that could help to stick the nanoparticles together in the aggregate. These aggregates remained stable upon extraction and washing. Hence, the confinement provided by the SLC led the particles to aggregate with a preferential orientation instead of the 3D isotropic fractal growth observed in the destroyed SLC. It is worth noticing that the progressive disappearance of the platinic acid, along with the progressive acidification of the solution due to the reduction of platinum, decreased the stability of the SLC in the final steps of the reaction (SAXD shows an effective loss of crystallinity of the mesophase at the end of the reaction). Finally, we observed that a further

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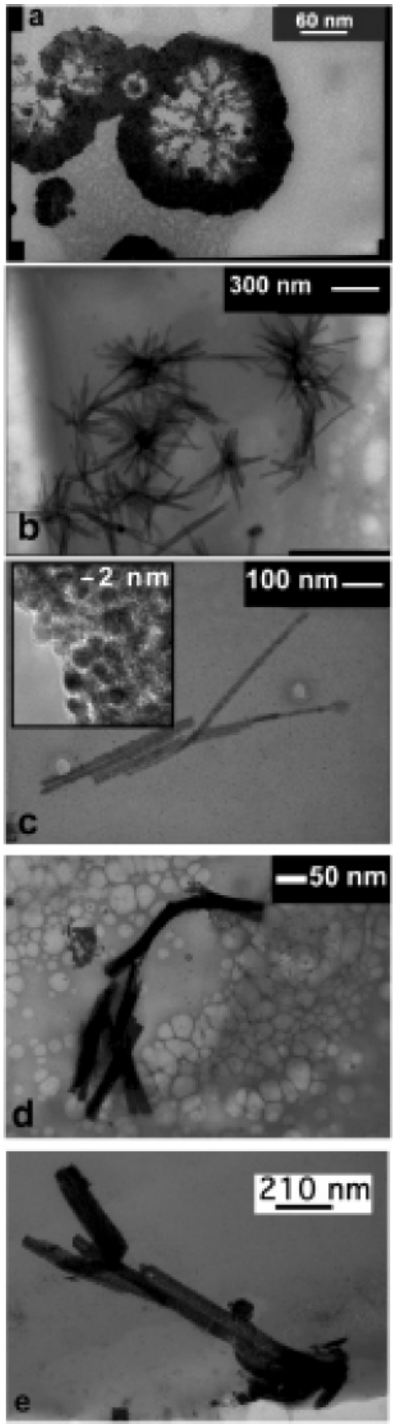

Figure 3. TEM images of platinum nanoparticles prepared from hexachloroplatinic acid in a hexagonal SLC (a) **2.A**, by high γ-ray irradiation (96 kGy); (b and c) **2.B**, by CO reduction, leading to rodlike aggregation of the Pt pristine nanoparticles (inset of c, the high-resolution TEM confirms the preparation of Pt single crystals); (d and e) **2.C**, by CO reduction followed by a lower γ-ray irradiation of 32 kGy, giving a larger aggregation in sticklike particles (part e is a microtome slice).

reduction by γ-ray irradiation with a lower irradiation dose (10−20 kGy) increased the coalescence of these particles (sample **2.C**). The aggregates kept their sticklike shape, but single nanoparticles could not be clearly discriminated by TEM anymore due to the increased thickness of the aggregates (Figure 3d). However, they still exist as proven by the observation of a sliced particle with ultramicrotome (Figure 3e). The alternative process (initially relatively low γ irradiation followed by CO bubbling) gave the same result.

The structuring effect of the SLC geometry on the metal nanoaggregates morphology was unambiguously confirmed by similar syntheses performed with an SLC designed with a lamellar structure formed by the addition of a slight excess of 1-pentanol to the previously used hexagonal SLC (sample **2.D**). In this case, slabs of platinum made of aggregated nanoparticles are obtained, which also remain stable after extraction (Figure 3a.). This process was also extended to different metals, and syntheses performed with palladium (Figure 3b) (**2.E**, SDS/Pd, [Pd] 0.015M) or tin-doped platinum (Figure 3c) (**2.F**, SDS/H_2PtCl_6/$SnCl_4$, [Pt] = 0.1 M, [Sn] = 0.01 M) demonstrate from their morphology variations that the nature of the metal precursor can also alter the final morphology of the aggregate, depending on the initial size of the pristine nanoparticles and the competitive mechanisms between metal framework growth and particle aggregation.

It appears from these results that the type of reduction is not so important as far as one adopts a rather “gentle” process. Hence, the shape of the platinum framework itself is not affected by the SLC (we did not obtain a continuous Pt porous framework as it could have been expected), but the latter directs the way Pt nanoparticles synthesized in the SLC aggregate. The area of particle aggregation is the triangular space between three organic cylinders. This region defines a less-confined region than the direct intercylinder space itself, which is expected to drain the particles formed by the reduction of the hexachloroplatinic acid, leading to their aggregation along a direction parallel to the cylinder main axis. This mechanism can be compared with other methods previously reported such as, for example, the preparation of ZnS nanowires obtained by the directional aggregation and oriented growth of nanoparticles trapped in reverse micelles or short ZnS nanorods prepared in binary direct liquid crystals.[60,77] The strong adhesion between nanoparticles, even after several centrifugations and washings, can be assigned both to a remaining fraction of surfactant that still glues the particles together, and also protects them, but interfacial forces could also induce attractive interactions as was described previously.[61,116]

Preparation of Zirconia Needles. A detailed study of this preparation was reported elsewhere.[97] To summarize it, the slow crystallogenesis of the colloidal solution leads to the formation of macroscopic needles (**3.A**) with a high shape factor (at least 100) that keep their shape after thermal treatment (see Figure 5a). A closer observation shows that these needles are actually made of aggregated fibers aligned along the main axis and that this stacking creates interfiber voids whose average diameter can be visually estimated to 20 nm (parts b and c of Figure 5).

Preparation of Polymer Micro- and Nanowires. Another example of the versatility of these systems for the preparation of structured materials is provided by the preparation of polymers. Several polymer nanotubes and nanowires of conducting polypyrrole, poly(3,4-ethylenedioxythiophene), or polyaniline have been synthesized by electropolymeriza-

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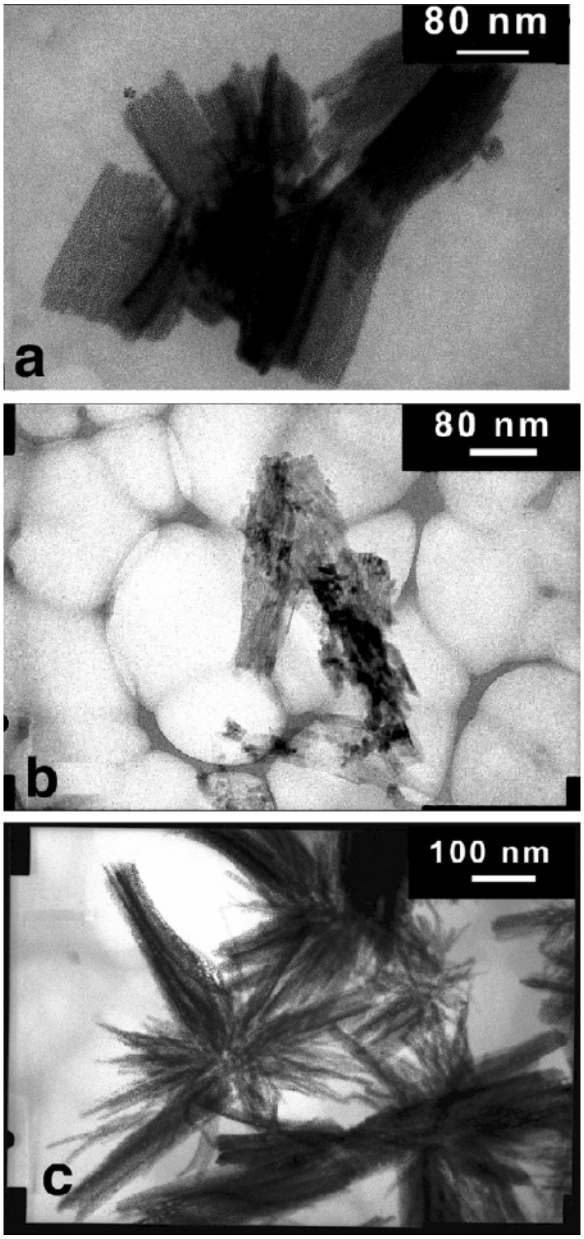

Figure 4. TEM images of (a) **2.D**, bi-dimensional Pt nanoaggregates prepared from hexachloroplatinic acid by CO reduction in a lamellar SLC; (b) **2.E**, rodlike Pd nanoaggregates prepared in a hexagonal SLC; (c) **2.F**, Pt/Sn nanoaggregates prepared in a hexagonal SLC.

tion within the structure of a nanoporous alumina matrix.[117] This approach can be compared with syntheses in oil in water miniemulsions.[85,86,94] The difference between SLCs and miniemulsions is the shape of the organic swollen vesicle: they are spherical in miniemulsions and cylindrical in SLCs. An additional feature of the hexagonal and cubic SLC is their optical transparency that allows photopolymerization processes to be used. We give thereinafter an example taken from the well-known family of polydiacetylene (PDA) polymers that are mostly developed for their electrical conductivity properties. To this purpose, diphenyl-1,4 butadiyne-1,3 (5−10 wt %) was dissolved in the cyclohexane fraction before its addition to the mixture forming an SLC, and two types of reactions were tested. In both cases, SAXD confirmed that the hexagonal symmetry was maintained after polymerization (Figure 6). First, the SLC phase was submitted to γ-ray radiolysis to induce polymerization. Nanowire arrays with orange color were obtained after irradiation with only a few kGy. The polymer (**4.A**) was extracted by destabilization of the mesophase upon addition of an excess

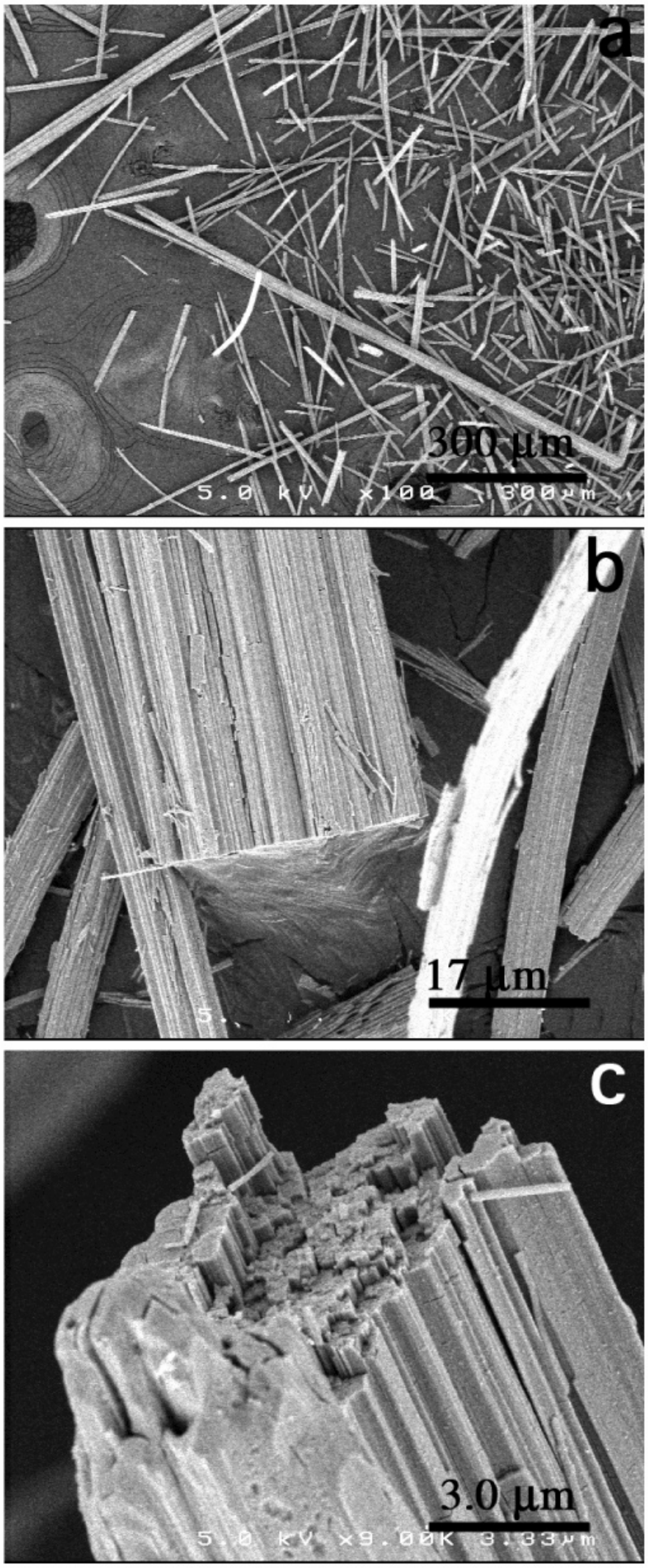

Figure 5. SEM images of zirconia needles (**3.A**) obtained after extraction and thermal treatment at 600 °C.

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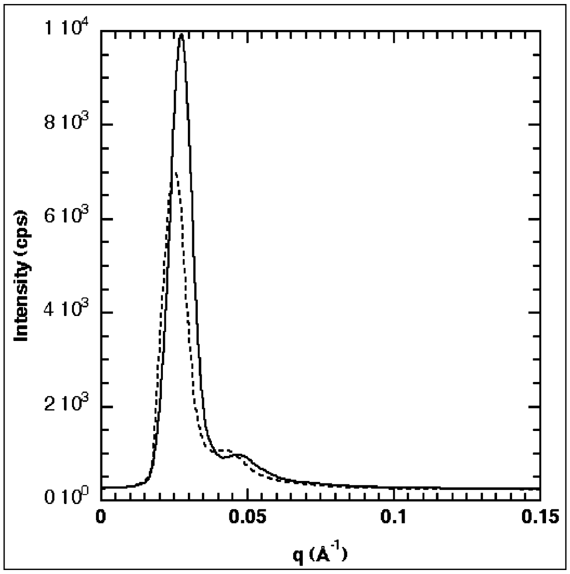

Figure 6. SAXD pattern of a SLC made with SDS and a salted solution of NaCl [0.3 M] without (dashed line) and with (solid line) PDA (10 wt %) diluted in the nonpolar phase (cyclohexane) (recorded on a laboratory SAXS apparatus).

of cyclohexane and recovered by solvent evaporation. This yielded a network of polymer nanowires (Figure 7a). A more conventional process consists of UV-induced polymerization of PDA in the presence of a free-radical initiator (benzone methyl ether). Following this process, syntheses were first performed in bulk cyclohexane, and we obtained spherical particles as expected from a bulk reaction (**4.B**) (Figure 7.b). When performed in the SLC (with a large excess of initiator), destabilization of the SLC in an excess of cyclohexane and recovery by solvent evaporation, one obtained large wires (**4.C**) (diameter of 0.5−1.0 μm) obtained by the crystallization of initial polymer fibers during the solvent evaporation (Figure 3.c). This latter example demonstrates also that the confinement of reagents, this time in the inner volume of the organic cylinders, provides an additional structuring effect that directs the final shape of the polymer particles.

Conclusion

The preparation of nanoscale devices by chemical processes may take advantage of the structuring properties of soft matter to engine particles or structures with a controlled geometry. Compared with the domains of syntheses that use confinement properties of binary mesophases (water−surfactant), the reactions performed in the SLCs, which are quaternary mesophases (water−organic solvent−surfactant−cosurfactant), allowed us to open a new domain of nanoreactors where metals, oxides, and organics can be synthesized. One may also expect that hybrid systems where organic fibers are synthesized by using UV-induced polymerization in the organic cylinders, prior to the reduction of metal nanorods or to the formation of an oxide framework in the aqueous phase, will be prepared soon. The SLCs provide a new approach for the synthesis of nanomaterials or nanostructured materials. They are highly flexible by the possibilities of composition (nature of the surfactant, salt, reagent precursor, pH, swelling agent), and they can be applied in the three main fields of materials science (metals, oxides, and polymers). Moreover, we demonstrated that these systems are by far much more stable than what could be expected from such complex mesophases, since they stand addition of various reagents as well as reacting processes within and still keep their long-range order. The numerous parameters that we are allowed to vary in the SLC preparation, as well as for the reacting system itself, suggest that this approach constitutes a promising new general concept to add to the field of self-assembled systems including liquid

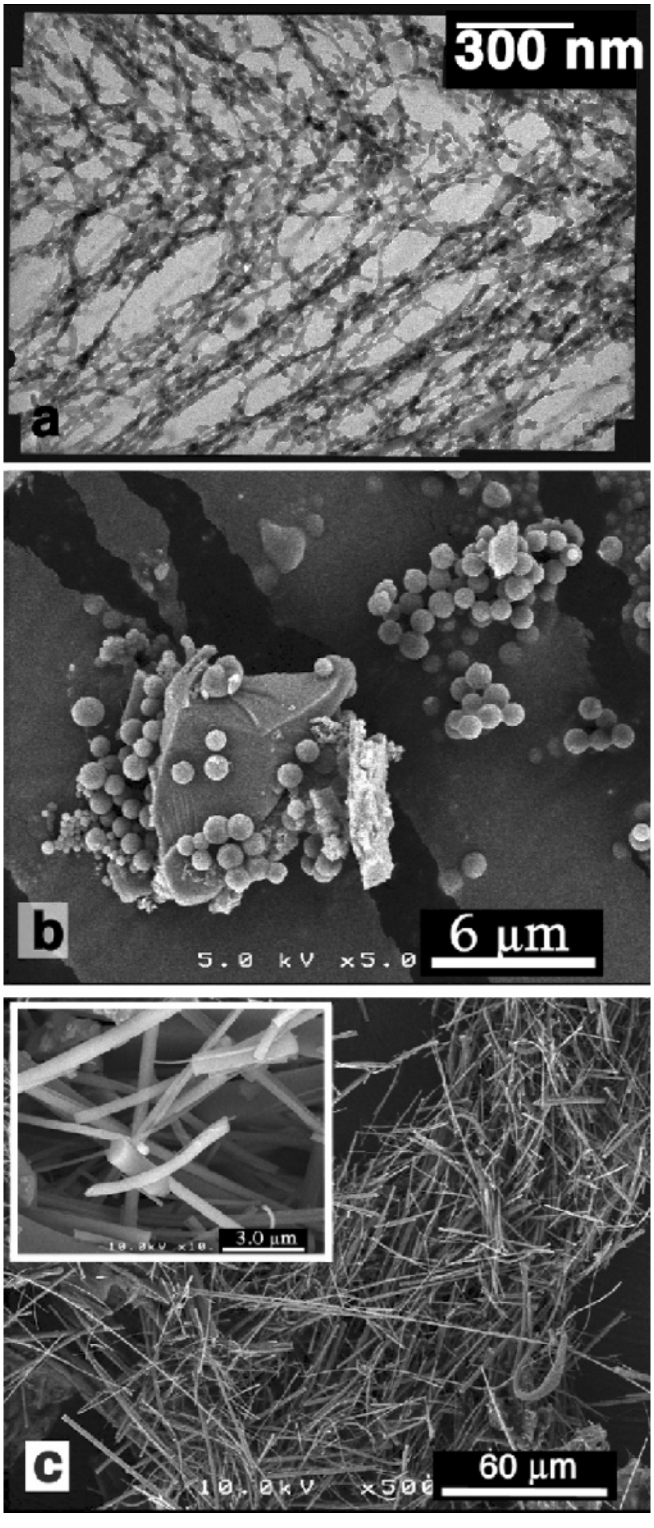

Figure 7. (a) TEM image of a PDA polymer prepared in SLC by γ irradiation (**4.A**); (b and c) SEM images of PDA prepared by UV irradiation in (b) bulk cyclohexane (**4.B**) and in (c) a SLC (**4.C**).

crystals, reverse microemulsions, and miniemulsions for the preparation of nanomaterials and mesoporous matrixes.

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