Controlled Nanoparticle Growth

Highly Stable Metal Hydrous Oxide Colloids by Inorganic Polycondensation in Suspension**

Corine Gérardin, Nicolas Sanson, Frédéric Bouyer, François Fajula, Jean-Luc Putaux, Mathieu Joanicot, and Thierry Chopin*

The interest in finely dispersed particles with controlled properties significantly increased in recent years not only for fundamental reasons but also due to the various applications of well-defined nanoparticles (e.g., in catalysis, magnetism, microelectronics, optics, and medicine). The properties of nanoparticles depend not only on their chemical composition but also on their size and morphology. Hence, much effort has focused on the development of new strategies for the synthesis of particles with controlled characteristics. Nevertheless, further improvements are still required, especially with regard to size control over a wide range, shape design, and long-term stability of colloidal suspensions in the presence of additives.

Here we report on the preparation of highly stable suspensions of metal hydrous oxides. The most commonly used method of generating metal hydroxide nanoparticles is through precipitation from homogeneous solutions by hydrolysis of metal cations.[1–3] The key parameters in the synthesis are the pH value, the temperature, the nature of the counterions, the reactant concentrations, the aging time, and also processing conditions, such as the feed rate of reactants. Growth control can be achieved by the use of strong complexing agents[4] or polyelectrolytes. Particle suspensions thus produced are electrostatically stabilized and are unstable at high ionic strength. Nanoreactor-based methods of preparation using surfactant or amphiphilic block copolymer assemblies allow dispersions of uniform particles to be directly prepared.[5–8] They were mainly developed for the preparation of metallic or semiconducting nanoparticles, and are based on the use of preformed micelles in an organic solvent. The water-in-oil microemulsion method[9–10] is also used to prepare nanoparticles in the inner aqueous phase of reverse micelles.[11]

Here we present a direct method for the preparation of sterically stabilized colloids of metal hydroxides in aqueous media, based on the use of double hydrophilic block copolymers (DHBCs). The DHBCs do not self-assemble in water; they behave as soluble polymers or polyelectrolytes. To ensure simultaneous control of particle growth and stabilization, DHBCs with an anionic metal-binding block and a neutral stabilizing block were used. The metal-complexing block acts as a growth inhibitor, while the neutral block promotes colloidal stabilization. A review on the synthesis and applications of DHBCs was recently published by Cölfen.[12] Such polymers proved to be convenient for controlled precipitation of inorganic powders[13–16] and the preparation of nanosized metal particles[17] in polar solvents. DHBCs were also used to control the morphology of organic crystals and for separating racemates into enantiomers.[18] The aim of our approach has been to elucidate the mechanisms of the formation of nanoparticles from aqueous inorganic precursors in the presence of hydrophilic block copolymers. Knowledge of the mechanisms that combine induced structuring of the polymers and inorganic polycondensation is necessary for designing size- and shape-controlled particles with long-term colloidal stability.

The strategy of nanoparticle formation is summarized in Figure 1, which schematically presents the different steps involved in the synthesis. First, hybrid precursors are prepared by mixing inorganic species and hydrophilic block copolymers. The aqueous inorganic precursors can be either solutions of salts of metal ions, such as Al^{3+}, La^{3+}, and Cu^{2+} or condensed entities, such as polycationic clusters, prepared by controlled partial prehydrolysis of metal ions M^{n+}. Polymetallic species such as Al_{13}^{7+} and Al_{30}^{18+} have been prepared[19] and used as precursors. By varying the degree of partial prehydrolysis of the metal ions ($h_1 = [OH^-]_{added}/[M]$), the size and the charge density of the inorganic precursor were tuned. When copolymers and inorganic precursors are mixed, complexation of the metal ions by the polyelectrolyte block occurs. As will be shown, complexation induces the formation

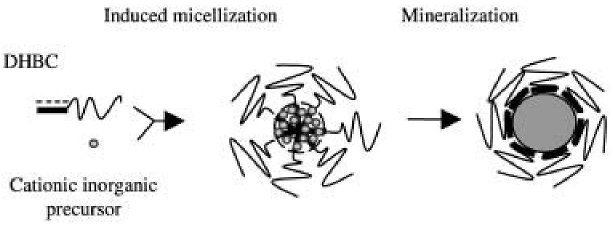

Figure 1. Schematic scenario of the different steps involved in nanoparticle formation.

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[*] Dr. C. Gérardin, N. Sanson, Dr. F. Bouyer, Dr. F. Fajula
Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique
UMR 5618 CNRS ENSCM
8, rue de L'Ecole Normale, 34296 Montpellier cedex 5 (France)
Fax: (+33) 4-6716-3465
E-mail: gerardin@cit.enscm.fr

Dr. J.-L. Putaux
Centre de Recherches sur les Macromolécules Végétales CNRS associated with the Joseph Fourier University of Grenoble (France)

Dr. M. Joanicot
CNRS Rhodia Complex Fluids Laboratory
Rhodia Inc.
Cranbury, NJ 08512 (USA)

Dr. T. Chopin
Rhodia Centre de Recherches d'Aubervilliers
93308 Aubervilliers (France)

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of well-defined nanoaggregates. The aggregates are then direct precursors for particle formation. In a final step, mineralization of the core of the aggregate can occur by completing hydrolysis and condensation in suspension.

The block copolymers used in this study were poly(acrylic acid)-*b*-polyhydroxyethylacrylate (PAA-*b*-PHEA) and poly(acrylic acid)-*b*-polyacrylamide (PAA-*b*-PAM). Only asymmetric copolymers in which the anchoring block is much smaller than the stabilizing block were examined. The pH value of the copolymer solution was adjusted to 5.5, which corresponds to a degree of dissociation of the acrylic acid groups of about 50%, and then the solution was added to solutions of metal ions. Metal complexation by acrylate groups leads to the spontaneous formation of large aggregates. The degree of metal complexation is expressed as the number of acrylate groups added per metal atom ($R = [\mathrm{AA}]/[\mathrm{M}]$). The hydrodynamic diameter, determined by dynamic light scattering (DLS), was 40 nm for aggregates formed from $\mathrm{Al_{13}}^{7+}$ ions and $\mathrm{PAA_{1900}}$-*b*-$\mathrm{PHEA_{8200}}$, as opposed to 11 nm for the corresponding copolymer in solution.

Small-angle neutron scattering (SANS) experiments were performed to characterize the nanostructure of the assemblies. Figure 2 shows the scattering curve of an aggregate from $\mathrm{Al_{13}}^{7+}$ ions and $\mathrm{PAA_{1900}}$-*b*-$\mathrm{PHEA_{8200}}$, together with the scattering curve of the same copolymer in water. The two curves represent scattering from suspensions at the same copolymer concentration, in the absence and in the presence of metal polycations. Since the $\mathrm{Al_{13}}$ clusters were prepared in $\mathrm{D_2O}$, the $\mathrm{Al_{12}(AlO_4)(OD)_{24}(D_2O)_{12}}^{7+}$ species have scattering-length densities that practically match the scattering-length density of $\mathrm{D_2O}$. Then, the scattered intensity of the cation/polymer mixture essentially arises from the polymer blocks. The scattering curve of the copolymer is characteristic of a polymer in a good solvent, whereas that of the cation/copolymer mixture reveals that supramolecular aggregates with a spherical core–corona structure were formed. At low values of q (the amplitude of the scattering vector), the observation of a much higher scattering intensity for the suspension with polycations compared to that of the polymer solution supports the formation of polymer aggregates. In the low-q regime, Guinier behavior allows the radii of gyration R_G of the copolymer and of the aggregate to be determined. The R_G value was 11 nm for micelles of $\mathrm{PAA_{1900}}$-*b*-$\mathrm{PHEA_{8200}}$ with $\mathrm{Al_{13}}^{7+}$ ions and 2.5 nm for the copolymer in solution. The high-q range of the scattering curve (Figure 2) characterizes the outer layer of the micelle; a power-law behavior of the intensity ($I(q) \propto q^{-3.9}$) indicates the presence of a diffuse corona consisting of polymer chains in a good solvent. The value of the power exponent is in good agreement with an excluded-volume model that accounts for self-avoidance and mutual avoidance of the chains in the corona. The sharp decrease in intensity ($I(q) \propto q^{-1.7}$) of the scattering curve of the aggregate in the intermediate q range ($0.025 < q < 0.045$ Å^{-1}) suggests that a dense core with a sharp interface is formed by the collapsed polyelectrolyte blocks. The scattering curve of the micelle was simulated (Figure 2) by using Pedersen's model,[20,21] which was developed for form factors of core–corona assemblies of block copolymers. The simulation gave a mean core diameter of the micelle of 12 nm. Figure 3 shows a cryo-TEM image of micelles formed from $\mathrm{Al_{13}}^{7+}$ ions and $\mathrm{PAA_{2800}}$-*b*-$\mathrm{PHEA_{11100}}$, embedded in a thin film of vitreous ice. Well-separated isotropic objects with a small size distribution around a mean diameter of 9 nm are observed; some larger and elongated aggregates can also be seen. The TEM image confirms the concentration of the inorganic ions in a dense central part of the aggregates, and the mean core diameter measured here is in agreement with the values obtained by simulation of the SANS curves. The micelles have a very small zeta potential (−3 mV), which is consistent with the neutral blocks forming the micelle corona. Suspensions were also investigated by ^{27}Al NMR spectroscopy in solution. The NMR signal at $\delta = 63$ ppm, characteristic of the tetrahedral site in $\mathrm{Al_{13}}$ clusters, disappeared on formation of micellar aggregates, and this is consistent with the formation of a dense insoluble core containing the Al species.

The characteristics of the nanoassemblies formed with various multivalent ions (e.g., $\mathrm{Ca^{2+}}$, $\mathrm{Cu^{2+}}$, $\mathrm{Al^{3+}}$, $\mathrm{La^{3+}}$) and

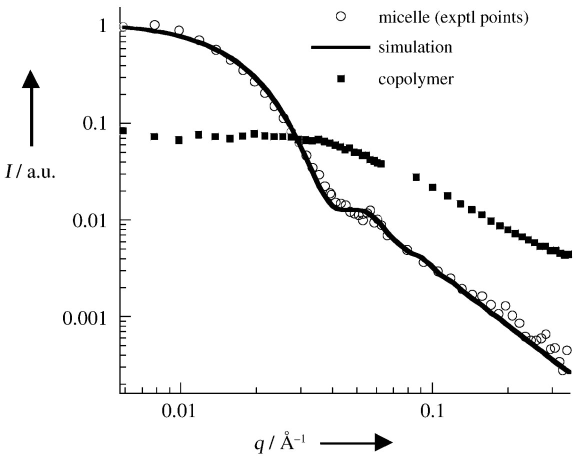

Figure 2. SANS curves of the nanoaggregate (○) obtained from the block copolymer $\mathrm{PAA_{1900}}$-*b*-$\mathrm{PHEA_{8200}}$ and $\mathrm{Al_{13}}^{7+}$ ions, and of the copolymer in water (■). The simulation (Pedersen's model) of the scattering curve of the nanoaggregate is shown as a full line.

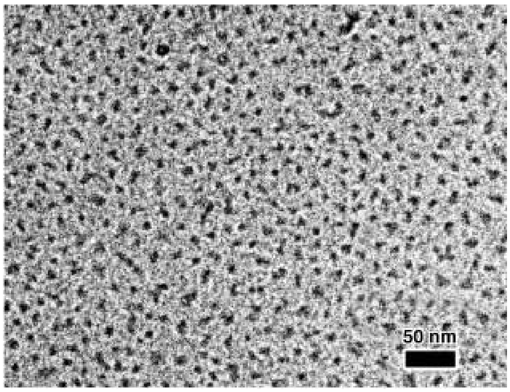

Figure 3. Cryo-TEM image of the micellar aggregates obtained from $\mathrm{Al_{13}}^{7+}$ ions and $\mathrm{PAA_{2800}}$-*b*-$\mathrm{PHEA_{11100}}$.

various asymmetric anionic–neutral block copolymers were similar. Their microstructures are similar to those of core–corona micelles of amphiphilic block copolymers such as polyoxyethylene-*b*-polyoxybutylene in water.[22] They can also be compared to microstructures formed from DHBCs and oppositely charged surfactants.[23] In the present case, the formation of core–corona structures is explained by the formation of an insoluble complex whose macroscopic precipitation is inhibited by the presence of neutral blocks. It is well known that in the presence of multivalent ions, oppositely charged polymers precipitate into compact structures, due to condensation of ions with the polyelectrolyte chains.[24] The neutral blocks sterically stabilize the water-incompatible phase. Induced amphiphilicity of DHBCs was reported for the formation of polyion complex (PIC) micelles from charged diblock copolymers with oppositely charged polymers or surfactants.[25–27] The formation of aggregates between DHBCs and metal ions was also reported by several authors.[28,29] The hybrid analogues of the PIC micelles described here exhibit a major difference in stability to PIC aggregates. In the case of polymer PIC micelles, complex formation is triggered essentially by electrostatic interactions and entropy gain for the released counterions of the polymers. With metal cations, the coordinative bond is an additional stability factor, and this could explain why inorganic/polymeric micelles are more stable than PIC micelles towards addition of salts.

The hybrid nanoaggregates were used as precursors for nanoparticle formation. Particle growth and morphology control were investigated. Core mineralization was induced by hydroxylation of the metal cations. In this step, the hydrolysis ratio $h_2 = [OH^-]/[M^{n+}]$ was generally chosen to be equal to $n - h_1$. In the absence of copolymer, metal hydroxides obtained by hydroxylation are flocculated precipitates formed by the aggregation of particles. In the presence of copolymers, completion of metal hydrolysis in the aggregates leads to stable suspensions or settling precipitates, depending on two parameters: the prehydrolysis ratio $h_1 = [OH^-]/[M]$ and the degree of complexation R. The quantities R and h_1 are convenient means of controlling particle growth and stability. The mean particle size increases with increasing h_1 or decreasing R, as illustrated in Figure 4 for La^{3+}/PAA_{1000}-*b*-PAM_{10000} as a precursor for lanthanum-hydroxide-based nanoparticles. Figure 4 shows the hydrodynamic diameters of the particles and the corresponding micellar La^{3+}/PAA_{1000}-*b*-PAM_{10000} precursors as a function of the acrylate-to-metal ratio R. Three domains can be distinguished. Below a copolymer ratio R_1, flocculation occurs, and no stable colloids form. In addition, there is a minimum copolymer amount R_2 ($R_2 > R_1$) above which the hybrid precursor acts as a closed compartment for mineralization. Above R_2, particle sizes are similar to those of the corresponding precursor. In Figure 4, R_1 is 0.5 and R_2 about 2. Between R_1 and R_2, hydrodynamic diameters vary between 25 and 100 nm, and mineralization proceeds by enlargement of the core. Figure 5 shows TEM images of the particles for two values of R. For $R = R_1 = 0.5$, elongated particles about 80 nm long are obtained (Figure 5a). Electron diffraction studies revealed that cristalline lanthanum trihydroxide particles were formed. For $R = 3$, spherical particles with a mean diameter of about 8 nm are obtained (Figure 5b). For $R > R_2$, mineralization proceeds within the confined environment of the micellar precursors, and the particles retain the size and shape of the precursors.

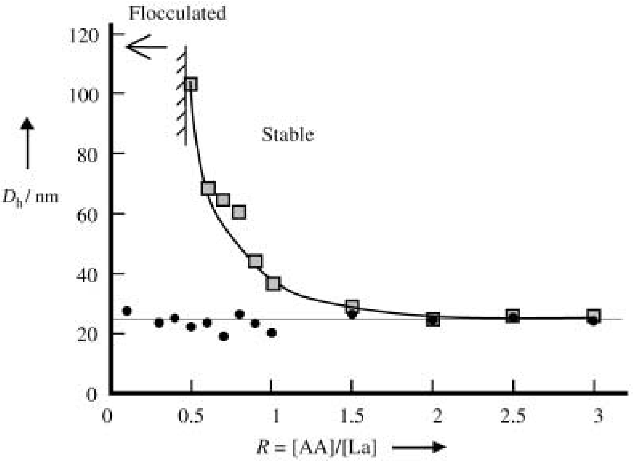

Figure 4. Hydrodynamic diameters as a function of the degree of complexation $R = [AA]/[M]$ of the particles (■) and of the corresponding La^{3+}/PAA_{1000}-*b*-PAM_{10000} precursors (●).

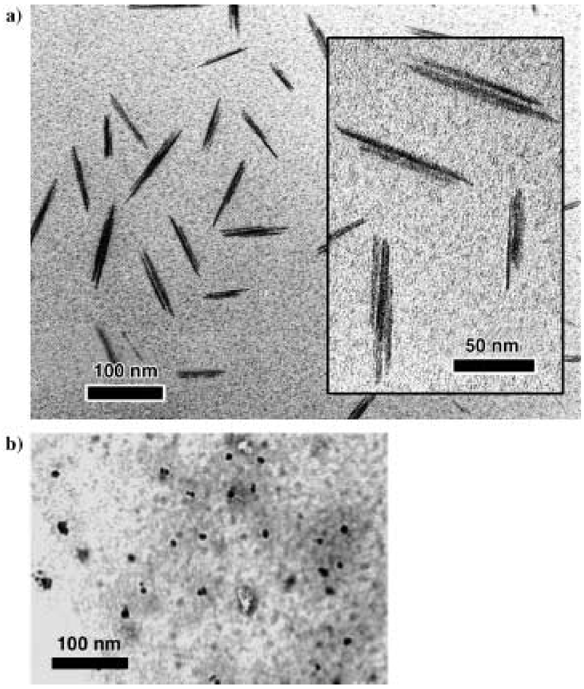

Figure 5. TEM images of the particles obtained from hydrolysis ($h_2 = 3$) of the mixtures La^{3+}/PAA_{1000}-*b*-PAM_{10000} for $R = 0.5$ (a) and $R = 3$ (b).

In the case of dispersed aluminum hydroxide particles prepared from Al_{13} clusters and PAA_{1900}-*b*-$PHEA_{8200}$, a similar dependence of size on R is observed. The average hydrodynamic diameter of the particles varies from 45 to 155 nm when R decreases from 1 to 0.6. Figure 6 shows TEM images of particles obtained for $R = R_1 = 0.6$ and $R = R_2 = 1$. Particles of aluminum hydroxide of varying size were

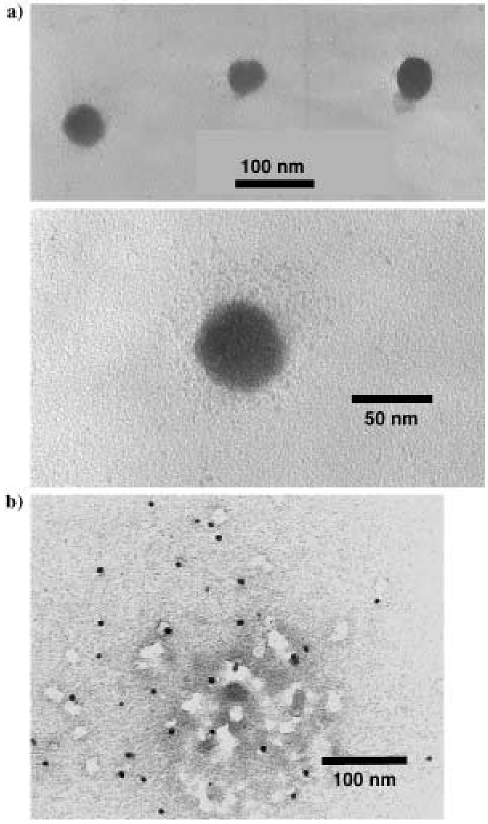

Figure 6. TEM images of the particles obtained by hydrolysis ($h_2 = 0.54$) of the mixtures Al_{13}^{7+}/PAA$_{1900}$-*b*-PHEA$_{8200}$ for $R = 0.6$ (a) and $R = 1$ (b).

obtained for intermediate values of R ($0.6 \leq R < 1$; Figure 6a), whereas for high *R* values ($R \geq 1$), metal hydrolysis and condensation reactions proceed within the restricted volume of the micellar core, and the particles remain small (8 nm) and spherical, as shown in Figure 6b.

In the case of copper-based precursors, stable polymer-protected platelets of copper hydroxide could be synthesized at low degrees of complexation, whereas high degrees of complexation led to spherical shapes. Moreover, by varying the prehydrolysis ratio h_1, it was also possible to change the shape. In all cases, the presence of the polymeric corona attached to the inorganic particle surface was checked by different techniques: SANS, TEM combined with DLS, IR spectroscopy, and electrophoresis.

The concept of a nanoreactor with a closed reservoir of metal ions can be used to explain the mechanisms of formation of the particles from the micelles only under conditions where a high degree of metal complexation ($R \geq R_2$) occurs. For intermediate degrees of complexation ($R < R_2$), the polyelectrolyte blocks act as surface-active agents during mineralization, while the neutral blocks provide the necessary steric stabilization of the particle. The complexation rate [AA]/[M] defines the degree of poisoning of inorganic polycondensation reactions. Therefore, it governs the total surface area of the particle suspension and controls the mean particle size. The particle size can also be tailored by varying the metal prehydrolysis ratio and the polymer block lengths, as will be detailed in a forthcoming paper. Finally, depending on the nature of the metal and the synthetic parameters, the preparation method can lead to different morphologies: spherical, elongated, or platelike particles.

A great advantage of the present method is that the colloids thus prepared are stable for months. The neutral polymer segments constitute an effective barrier against particle aggregation. In addition, suspension stability is neither affected by changes in pH value (at least in the range 5–11) nor by increases in electrolyte concentration. Both micelle and particle suspensions remained stable for ionic strengths up to 2.8 M. We also showed that the present block copolymers are better stabilizers than the corresponding homopolymers or random copolymers.

In summary, a method for the direct preparation of highly stable colloids of metal hydrous oxides was developed; hydrolysis and condensation of metal cations can be performed in suspension in the presence of double-hydrophilic block copolymers. Anionic–neutral copolymers simultaneously ensure control of growth and stabilization of the particles. Above a critical degree of complexation, particle size and shape correspond to those of the primary aggregates, whereas below that level, the particle size can be tuned by means of the degree of metal complexation. The present process directly produces sterically stabilized particles of metal hydroxides or metal basic salts with long-term stability. Since this preparation route was tested with Al^{3+}, La^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, and Ca^{2+} precursors, it can reasonably be speculated that it is applicable to many other metal ions. The direct precursors of the particles are micelle-like aggregates formed by inhibited precipitation of the insoluble ion/polyelectrolyte complex. For the first time, the core–corona microstructure of the assemblies has been extensively characterized. The hybrid micelles represent new supramolecular precursors for inorganic polycondensation reactions and should serve as model systems for reactions in confined environments. Since this preparation method is highly versatile and robust, it should open new opportunities for the preparation of nanomaterials and also for elucidating the mechanisms involved in soft aqueous chemistry of materials. Finally, the present suspensions may also be excellent candidates for fundamental studies of the phase behavior and dynamics of suspensions of stabilized plate-shaped or rodlike nanoparticles.

Experimental Section

$La(NO_3)_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were used as inorganic precursors. Pure solutions of Al_{13}^{7+} clusters were prepared by controlled prehydrolysis of an aqueous solution of $Al(NO_3)_3 \cdot 9H_2O$ (0.1 M) with a solution of sodium hydroxide (0.3 M) at 90 °C. A prehydrolysis ratio $h_1 = [OH^-]/[M]$ of 2.46 was used. The solution was analyzed by ^{27}Al NMR spectroscopy to ensure that it only contained Al_{13} species.[19] Ultrapure deionized water (MilliQ, Millipore, France) was used for the preparation of all solutions. PAA-*b*-PAM and PAA-*b*-PHEA copolymers were synthesized by free-radical polymerization at Rhodia (Aubervilliers, France); the synthesis has been described elsewhere.[30] The pH value of the polymer solutions was then adjusted to 5.5 before mixing with solutions of inorganic precursors, so that the PAA block is partially neutralized before mixing with inorganic cations. The concentrations of the mother copolymer solutions were approximately 5 wt %.

The particle suspensions were prepared at room temperature. The copolymer solution was added to the solution of the inorganic precursor, and the mixture vigorously stirred for 10 min. Particle suspensions were obtained by the addition of sodium hydroxide solution (1M). Metal concentrations in the final suspensions varied between 5×10^{-3} and 10^{-1}M.

Light-scattering measurements were carried out with a Zetasizer 3000HS instrument (Malvern, U.K.) with a 10 mW laser operating at 633 nm. Hydrodynamic diameters were obtained from measured diffusion coefficients by using the Stokes–Einstein equation. Small-angle neutron-scattering experiments were carried out at Laboratoire Leon Brillouin (Saclay, France). A q range from 0.004 to 0.5 Å^{-1} was measured. Suspensions were prepared in D_2O to enhance the difference in scattering-length density between solvent and particles. The scattering data were corrected for background intensity.

Transmission electron microscopy (TEM) was performed on a Jeol 1200 EXII microscope operated at 80 kV. Cryo-TEM images were recorded on a Philips CM200 "Cryo" microscope operated at 80 kV. Dry specimens were prepared by depositing one droplet of the micelle or particle suspension onto glow-discharged carbon-coated copper grids. After 1 min the excess liquid was blotted with filter paper, and the remaining film allowed to dry. Cryo-TEM samples were prepared, as described elsewhere,[31] by quench-freezing a thin film of the micelle suspension into liquid ethane at −171 °C. The specimen was mounted onto a Gatan 626 cryo-holder and transferred into the microscope. The micelles were observed at low temperature (−180 °C) embedded in a thin layer of vitreous ice.

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