Hybrid Dissymmetrical Colloidal Particles

Stéphane Reculusa,*,[†] Céline Poncet-Legrand,[†,‡,§] Adeline Perro,[†,‡] Etienne Duguet,[‡]
Elodie Bourgeat-Lami,[||] Christophe Mingotaud,[⊥] and Serge Ravaine[†]

Centre de Recherche Paul Pascal, CNRS, 115, avenue du Dr Schweitzer, 33600 Pessac, France, Institut de Chimie de la Matière Condensée de Bordeaux, CNRS, 87, avenue du Dr Schweitzer, 33608 Pessac Cedex, France, Laboratoire de Chimie et Procédés de Polymérisation, CNRS−CPE Lyon, Bâtiment 308 F, 43, boulevard du 11 novembre 1918, BP 2077, 69616 Villeurbanne Cedex, France, and Laboratoire des IMRCP, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse Cedex, France

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Colloidal particles with a controlled morphology combining both organic and inorganic parts were synthesized through a seeded emulsion polymerization process. Silica seed particles from 50 to 150 nm were first surface-modified by adsorption of an oxyethylene-based macromonomer or covalent grafting of a trialkoxysilane derivative. Then, emulsion polymerization of styrene was carried out in the presence of these particles, the formation of polystyrene nodules being highly favored at the silica surface in such conditions. While varying different experimental parameters, we have demonstrated that the ratio between the number of silica seeds and the number of growing nodules is a key parameter in controlling the morphology of the final hybrid nanoparticles. For instance, in the particular case when this ratio was close to 1, dumbbell-like or snowman-like particles were obtained. Further selective surface modification of their silica moiety was also tested successfully, indicating a potential application of these hybrid particles as original building blocks toward supraparticulate assemblies.

Introduction

In recent works, much attention has been devoted to the elaboration of colloidal clusters with tunable sizes and shapes. Indeed, controlling the morphology of colloidal particles is an absolute necessity if one intends to master their physicochemical properties. Many examples of colloidal particles with original morphologies formed in batch conditions have already been given in the literature but these almost exclusively deal with pure polymeric particles. This is well-illustrated by numerous works from Okubo and co-workers, which described the elaboration of rugby ball-like,[1] golf ball-like,[2] octopus-like,[3] or red blood corpuscle-like particles.[4] Such morphologies mainly result from phase separation phenomena occurring during seeded polymerization reactions, polymer seeds of poly-A being swollen by a different monomer B, and the resulting polymer poly-B being immiscible with poly-A. Thermodynamic parameters, like monomer−polymer swelling ratio or degree of cross-linking, as well as geometric ones (seed diameter) can explain the different morphologies obtained and in some conditions, one can observe some snowman-like particles (as demonstrated by Skjeltorp et al.,[5] Okubo et al.,[6] or Sheu et al.[7]). Although interesting from some mechanistic points of view, elaboration of such particles is rather limited for practical applications since the surface properties of poly-A and poly-B cannot be tuned specifically. In contrast, references dealing with the batch synthesis of colloids exhibiting an original morphology and associating two different inorganic constituents are very few. CdS−FePt heterodimers prepared by Gu and co-workers while heating FePt−CdS core−shell nanoparticles, taking advantage of surface dewetting when amorphous CdS was converted to its crystalline state and separated from FePt, are in fact the only example to our knowledge.[8] Had anyone succeeded in obtaining such particles, it would still be difficult to modify specifically the inorganic surface of each component.

From this statement, it seems that only a combination of organic and inorganic materials, whose surface chemistries might be different enough, could lead to hybrid colloids with tunable properties. Some intensive studies have already explored widely different ways to combine an organic part and an inorganic counterpart, like silica, titania, or alumina, and elaborate new hybrid materials. It is here necessary to make a distinction between bulk hybrid materials (monoliths, powders, and thin films, for instance) and particulate hybrids, such as organic−inorganic colloidal particles, which is our matter of interest. Recent reviews have discussed the potential

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* To whom correspondence should be addressed. E-mail reculusa@crpp-bordeaux.cnrs.fr.

[†] Centre de Recherche Paul Pascal.

[§] Present address: UMR Sciences pour l'Oenologie, 2 place Viala, 34060 Montpellier Cedex, France.

[‡] Institut de Chimie de la Matière Condensée de Bordeaux.

[||] Laboratoire de Chimie et Procédés de Polymérisation.

[⊥] Laboratoire des IMRCP, Université Paul Sabatier.

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applications of such assemblies mainly characterized by their high surface/volume ratio and the potential new properties resulting from synergetic effects between the organic and the inorganic moieties.[9−11]

Among the different morphologies described in the literature, core−shell and raspberry-like particles are the most frequently quoted. To obtain core−shell particles, encapsulation of one material by another (maghemite by silica,[12] polystyrene by silica,[13] polystyrene by magnetite,[14] or silica by polystyrene[15,16]) is mandatory. Recently, we have also described the elaboration of submicrometer-sized composite particles with various morphologies, such as daisy-like, pentapod-like, and raspberry-like.[17,18] Here, we will focus on the formation of dissymmetrical colloidal particles, whose size is smaller than 1 μm, consisting of one polystyrene nodule attached to a single silica nanoparticle. These structures should be considered as dissymmetrical since they result from the modification of an initially symmetrical particle (here, the silica seed) whose some symmetry elements (like a center of symmetry) are modified by a chemical or physicochemical process that we call the dissymmetrization stage.

So far, the few works that described production of such particles involved strategies mainly based on surface modification at two-dimensional interfaces. Casagrande and Veyssié first reported the synthesis of amphiphilic microparticles,[19] called by de Gennes "*Janus*" particles,[20] while chemically modifying one hemisphere of glass beads partially immersed in a protective cellulose varnish layer. Later, Fujimoto et al. described the synthesis of "unsymmetrical microspheres" at the air−water interface of a Langmuir trough, taking advantage of regioselective surface modification onto the hemisphere in contact with the subphase.[21] Inspired by these results, our group has extended this strategy to other interfaces such as liquid−solid and gas−solid to prepared dissymmetrical silica particles with a much smaller size (around 100 nm).[22,23] More recently, Nagle and coworkers used filtration over a membrane covered with silica or latex nanospheres to deposit single gold colloids onto them.[24] Despite the strong potential interest that dissymmetrical particles may raise in various fields such as stabilization of complex fluids, electronic displays, biomimetic systems, or vectorization, as has already been discussed in a recent review by our group,[25] convenient techniques of production leading to significant amounts of particles have not yet been proposed, all the previous quoted works involving plane interfaces with limited working areas.

The purpose of this paper is to demonstrate that common batch reactions can attractively solve this issue. Indeed, in some well-chosen conditions, the controlled surface nucleation and growth of an organic polystyrene nodule at the surface of an inorganic silica particle allows obtainment of some dissymmetrical particles—with a much smaller size and a higher versatility than all the works reported previously—whose main characteristics are simultaneously (a) a well-defined morphology, (b) a controlled size until less than 100 nm, and (c) a hybrid character, since they result from the association of two different materials.

Materials and Methods

Materials. Tetraethoxysilane (TEOS, Fluka), (methacryloxymethyl)triethoxysilane (Gelest - ABCR), (aminopropyl)triethoxysilane (Aldrich), styrene (Sigma), divinylbenzene (Sigma), sodium persulfate (Aldrich), and ammonia (25% in water, SDS) were purchased in their reagent grade and used without further purification. The macromonomer, poly(ethylene glycol) monomethylether methacrylate (PEG 1100 methacrylate), was obtained from Polysciences and the surfactant (Synperonic NP30) from Fluka. Deionized water was obtained with a MilliQ system (Millipore) and ethanol was purchased from J.T. Baker.

Methods. *Synthesis of Silica Particles.* Five hundred milliliters of absolute ethanol and 37.5 mL of an aqueous solution of ammonia were introduced in a three-neck round flask of 1 L equipped with a reflux condenser. The mixture was stirred at 300 rpm to homogenize and was heated at different temperatures, depending on the desired final particle diameter (50 nm at 70 °C; 100 nm at 50 °C; 150 nm at 35 °C). After stabilization, 15 mL of TEOS was added quickly and reaction occurred at the chosen temperature with constant stirring. To graft polymerizable groups onto the silica surface, a given volume of (methacryloxymethyl)triethoxysilane (MMS) was added directly into the particle suspension. After the mixture was stirred for 10 h at ambient temperature, the reaction medium was heated to 80 °C for 2 h to promote covalent bonding. A similar procedure was carried out with (aminopropyl)triethoxysilane to graft amine groups at the silica surface of the hybrid particles. When the synthesis was completed, the main part of ethanol and ammonia was first removed through evaporation under reduced pressure. All the silica suspensions were then dialyzed against water until neutral pH to remove the remaining reactants and replace ethanol with water. If necessary, the silica suspensions were concentrated and their final concentration was determined by measuring the mass of a dried extract. Silica particle sizes were determined statistically while analyzing TEM pictures.

Hybrid Particles Synthesis. Emulsion polymerization of styrene was performed in the presence of silica particles. In the case where bare silica particles are used, a preliminary step of adsorption of

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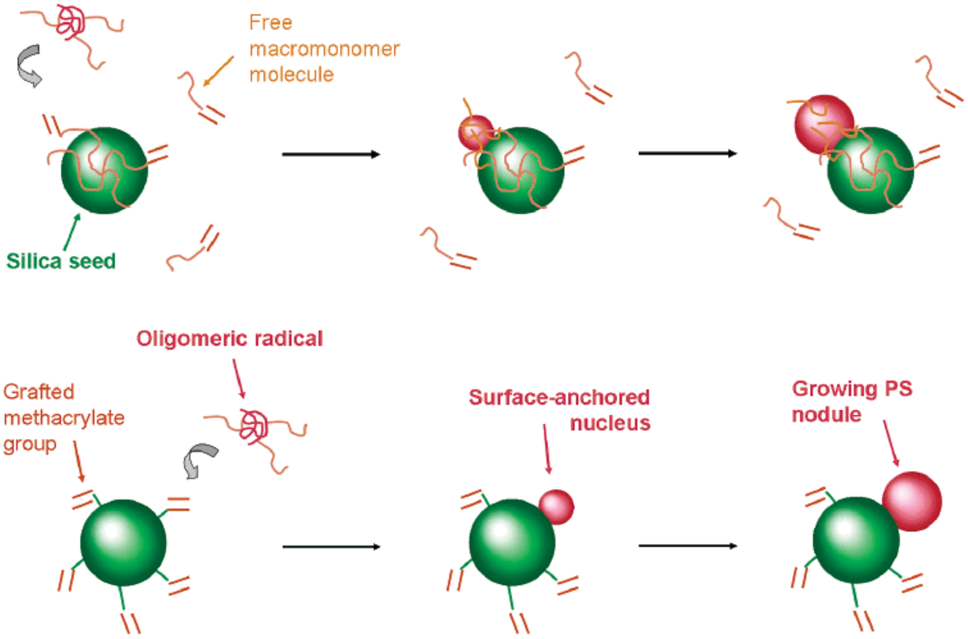
Scheme 1. Comparison of Both Synthetic Routes To Obtain Dissymmetrical Particles from Silica Particles: Physico-chemical Association with a Macromonomer (Top) and Covalent Grafting onto Functionalized Silica (Bottom)



hydrophilic poly(ethylene glycol) methacrylate macromonomer is necessary. To do so, a stock solution of the macromonomer was added to the silica suspension in deionized water. Adsorption was performed at 25 °C and allowed to equilibrate for at least 24 h. The chosen concentration was taken equal to 1.5 μmol of methacrylate groups/m^2 of inorganic surface. After this step was completed, the suspension was transferred into a thermostated reactor and the monomer was introduced. To stabilize the emulsion, a surfactant is usually added which can also tune the size of the latex particles. In our case, we used a nonylphenol poly(oxyethylenic) nonionic surfactant (Synperonic NP30) and its concentration (3 g·L^{-1} in all the cases) was chosen such that we had latexes with diameters around 300 nm at the end of the reaction. Then, the suspension was purged with nitrogen and heated to 70 °C before adding sodium persulfate as initiator (0.5 wt % relative to monomer) to start polymerization. Samples were taken from the batch at different times to study the kinetics of the reaction and its consequences on the particles morphology.

Transmission Electron Microscopy. TEM experiments were performed with a JEOL 2000 FX microscope (accelerating voltage of 200 kV). The samples were prepared as follows: silica particles and hybrid particles were dispersed in water and one drop of the dilute suspension was deposited on a copper grid coated with a carbon membrane.

Results and Discussion

To generate some dissymmetrical particles that associate one silica "seed" particle to a single polystyrene nodule, some requirements come to mind. First, it seems obvious that the theoretical ratio between the amounts of both types of particles should be as close as possible to 1. Second, the association of both materials should rely on some favorable interactions that the polystyrene nodules have to develop toward the inorganic silica surface. We have already demonstrated that this surface affinity could be achieved by the preliminary adsorption of macromonomer molecules based on ethylene oxide units or the covalent grafting of functional trialkoxysilanes.[17,18] Both systems are represented in Scheme 1.

In the first case, the copolymerization of monomer molecules with macromonomer units leads to partially hydrophilic oligomeric radical species that can adsorb very fast at the silica surface, then become a nodule, and evolve as a mature polymeric particle. In the second case, the surface grafting of methacrylate groups modifies the hydrophobicity of the silica surface, which promotes the fast polymerization of monomer molecules or oligomers directly onto the silica surface. All the silica seed particles used in this work were synthesized according to the well-known Stöber sol−gel process where temperature, among other parameters, allows controlling the final particle size.[26−28] Their surface modification was then carried out as described in the Experimental Section and the two synthetic routes have been compared.

Silica−Polystyrene Association with Macromonomer Molecules. The emulsion polymerization of styrene was first carried out in the presence of silica particles of 50 nm at a concentration of 10 g·L^{-1} and a given amount of macromonomer (1 g·L^{-1}, i.e., around 1.5 μmol/m^2 of silica surface). The hybrid particles obtained under such conditions have been observed by transmission electron microscopy (TEM) and some representative pictures of the sample are provided in Figure 1. In such conditions, the affinity between the organic and the inorganic counterparts is confirmed since every polystyrene nodule (in light gray) is in contact with at least one silica particle (in darker gray). The statistical calculations of the respective numbers of polymer nodules and inorganic seeds lead to a ratio around 0.25. Since this statistical value is independent of the reaction time, one can consider that the number of polymer particles is constant with time all along the polymerization. In other words, one can count 4 silica particles per nodule at any time.

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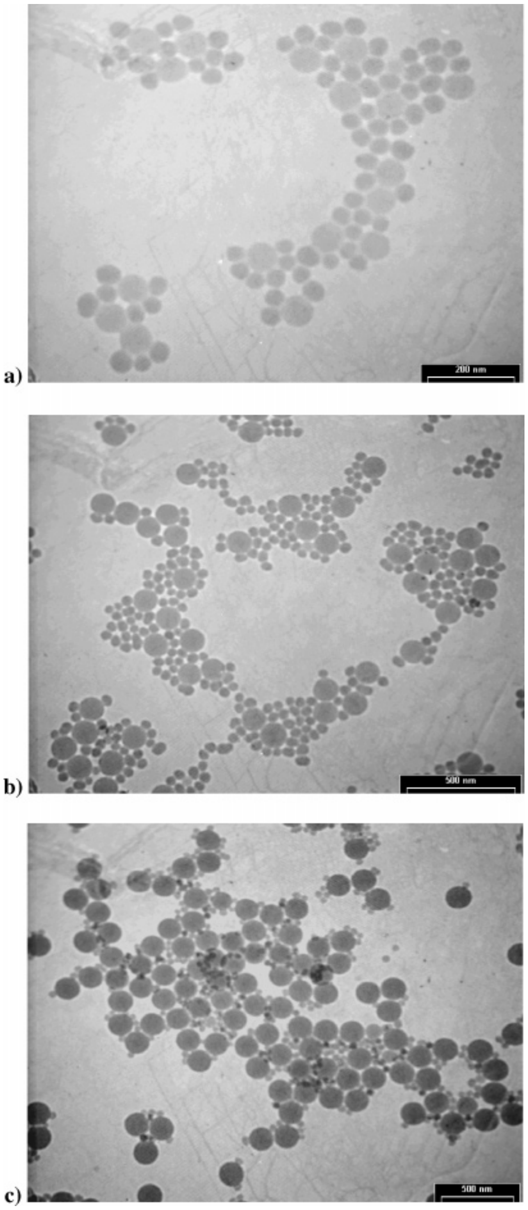


Figure 1. Morphological evolution of hybrid nanoparticles with time: (a) 20 min; (b) 45 min; (c) 120 min. [Silica: $d = 50$ nm, $C = 10$ g$\cdot$L^{-1}; macromonomer: $C = 1$ g$\cdot$L^{-1}].

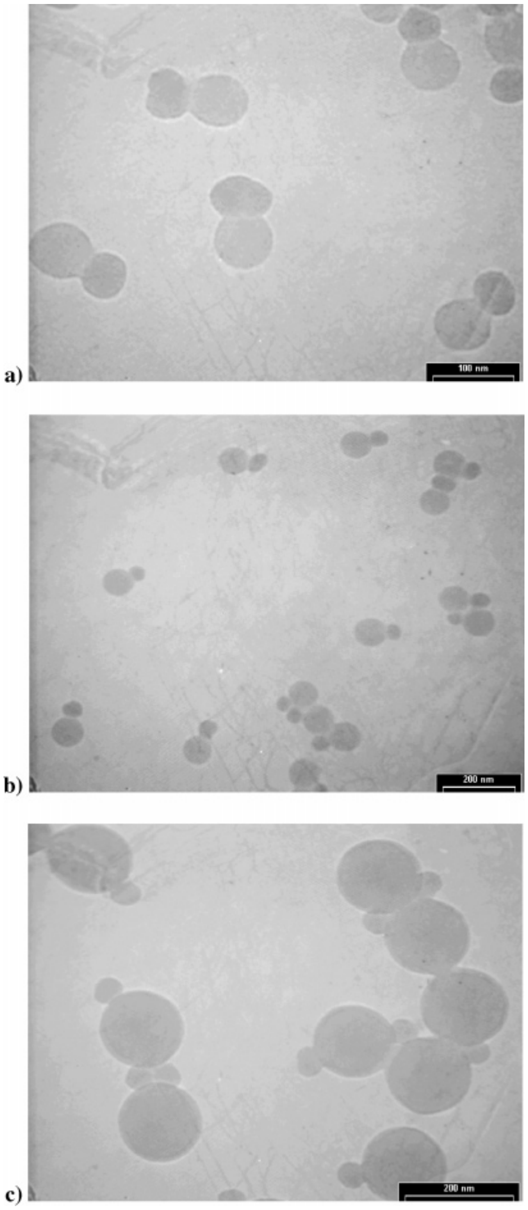


Figure 2. Morphological evolution of hybrid nanoparticles with time: (a) 20 min; (b) 45 min; (c) 120 min. [Silica: $d = 50$ nm, $C = 2.5$ g$\cdot$L^{-1}; macromonomer: $C = 0{,}25$ g$\cdot$L^{-1}].

The only noticeable evolution in the morphology of these hybrid particles is in fact the size of the polystyrene nodules, which increases with the reaction time, as it can be seen clearly on the pictures. Taking advantage of this result, the conditions of our experimental procedure have been modified to reach the targeted 1/1 ratio. The reaction was thus carried out with a silica concentration divided by 4 (2.5 g$\cdot$L^{-1}), while the macromonomer concentration was decreased so that the number of methacrylate functions remained constant with respect to the available inorganic surface (0.25 g$\cdot$L^{-1} i.e., 1.5 μmol$\cdot$m^{-2}). In these modified conditions, the morphology of the obtained nanoparticles is obviously different since each polystyrene nodule is on average bound to one silica particle, as shown in the Figure 2 TEM images. Depending on the reaction time and the size of the polymer nodule, one can observe the morphological evolution of the hybrid particles. After 20 min, both types of associated spheres have more or less the same size (around 50 nm) so that the resulting composites present a dumbbell-like morphology. Later on, the organic nodule becomes predominant in terms of volume fraction and the particle exhibits a snowman-like morphology.

Following the same principle, we tried to get hybrid nanoparticles starting from larger silica seeds. To do so, it is necessary to adjust the silica concentration so that the total number of silica particles remains constant, assuming that at the same time the number of polymer nodules formed during the emulsion polymerization process does not change. Having modified the silica concentration, it becomes also necessary to adjust the macromonomer concentration since the whole surface developed by the silica particles has also changed. For a given silica concentration, when the diameter of the silica particles is multiplied by a factor a, their total number is divided by a^3 whereas the total area is divided by a (the surface of each particle being increased by a factor a^2).

Table 1. Required Silica and Macromonomer Concentrations To Obtain Dissymmetrical Particles from Silica Seeds with Various Diameters

a	diameter d (nm)	a^3	C_{silica} ($\text{g}\cdot\text{L}^{-1}$)	a^2	$C_{\text{macromonomer}}$ ($\text{g}\cdot\text{L}^{-1}$)
1	50	1	2.5	1	0.25
1.3	65	2.197	5.5	1.69	0.42
1.6	80	4.096	10.0	2.56	0.64
2	100	8	20.0	4	1.0
3	150	27	67.5	9	2.25

As a consequence, the silica and macromonomer concentrations should both be adapted according to the silica particle diameter as summed up in Table 1. In such conditions, we obtained dissymmetrical nanoparticles whatever the reaction time. As an example, hybrid colloids obtained starting with 150 nm silica particles are presented in Figure 3. At low monomer conversion, the nodules are not yet well-formed and the sample looks more or less agglomerated, as shown in picture 3a. As time increases, the polystyrene particles become mature and spherical and their mean size, determined by statistical analysis of the TEM pictures, follows an evolution that is the same whatever the silica particle size.

For instance, as well-illustrated by picture 3c where the hybrid nanoparticles present a dumbbell-like morphology, the diameter of the polystyrene nodules is around 170 nm after 2 h of reaction, which is close to the diameter of the silica seed. These observations confirm that, in the very first stages of the polymerization, the reaction of styrene monomer dispersed in the water phase with PEG methacrylate molecules forms copolymers that readily adsorb at the silica surface. Later on, styrene molecules will diffuse from the monomer droplets through the continuous phase to react with the growing copolymer units, becoming nuclei that will further evolve as mature and individual latex particles. However, it is still difficult to consider whether the polymerization is initiated and the nodules nucleated in the continuous phase, such as in a classical emulsion polymerization process, or if these stages occurred at the silica−water interface.

Silica−Polystyrene Association with Functional Silane Derivatives. Apart from the macromonomer strategy, a series of experiments was also carried out with silica particles functionalized with silane derivatives bearing polymerizable groups. One of the most critical points here is to graft the most appropriate density of functional groups at the silica surface since this parameter is strongly determining its ability to capture the oligomeric polystyrene chains present in the continuous phase. Moreover, the higher the density of surface polymerizable groups, the higher the hydrophobic character of the silica surface and consequently the affinity of the growing hydrophobic polystyrene species for the silica seed particles. Different morphologies can thus be obtained depending on the number of double bonds present at the silica surface, as clearly demonstrated in our previous works.[18]

To promote phase separation and hopefully obtain dissymmetrical particles, it is necessary to graft small amounts of polymerizable groups onto the silica surface. Various amounts of (methacryloxymethyl)triethoxysilane (MMS) were consequently added to the suspension of silica particles at the end of their synthesis, as described in the Experimental Section. After purification and dialysis, these surface-modified silica particles were used as seeds in an emulsion polymerization reaction as described in the previous part. Whereas polymer particles were forming and growing independently from the silica particles when no MMS had been added during the silica seeds syntheses, an added amount corresponding to 0.1 methacrylate group/nm^2 of silica surface was enough to obtain hybrid particles (i.e., 10^{17} functions$\cdot$m^{-2} or 0.167 μmol$\cdot$m^{-2}), whatever the size of the silica seed. Since the number of polymer nodules formed during the process was not influenced by the number of functional groups at the silica surface, dissymmetrical particles were again obtained successfully when the particular conditions leading to a 1/1 ratio between the silica seeds and the polymer nodules were fulfilled.

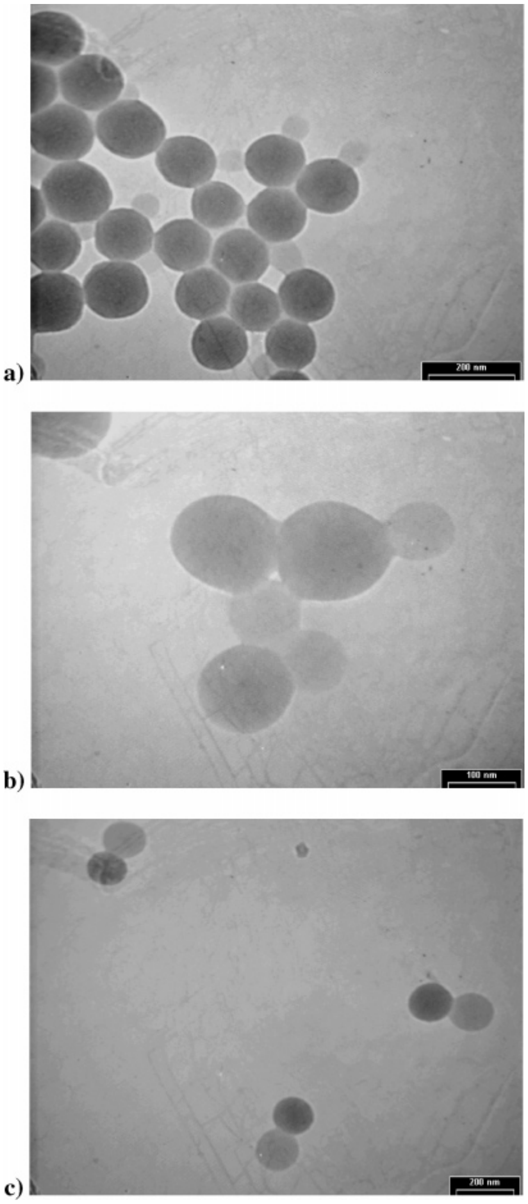


Figure 3. Morphological evolution of hybrid nanoparticles with time: (a) 30 min; (b) 60 min; (c) 120 min. [Silica: $d = 150$ nm, $C = 67.5$ g$\cdot$L^{-1}; macromonomer: $C = 2.25$ g$\cdot$L^{-1}].

Similar experiments were carried out with 80 nm silica particles functionalized with a larger amount of MMS (approximately 5 functions$\cdot$nm^{-2}, which is 50 times higher than that in the previous case). Under these conditions, more

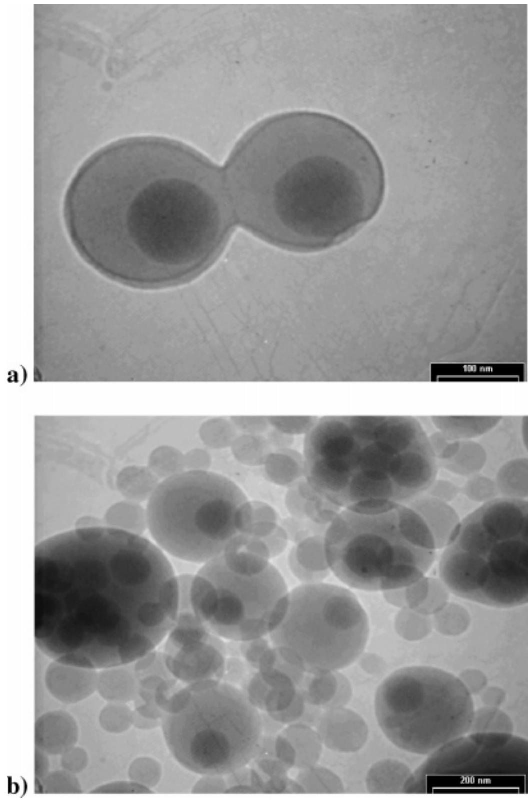
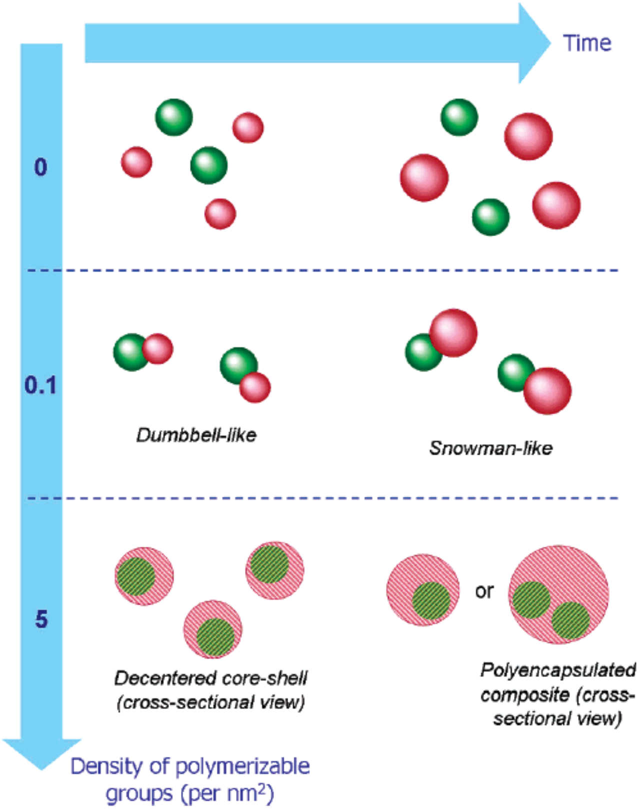


Figure 4. Hybrid particles obtained from functionalized silica particles (d = 80 nm; C = 10 g·L^{-1} and C_{MMS} = 5 functions·nm^{-2}) after (a) 30 min and (b) 1 h of reaction.

polymer chains are grafted onto the silica surface in the early stages of polymerization, which enhances the affinity between the growing polymer and the silica surface. As shown in Figure 4, the resulting hybrid morphology is noticeably different from the dumbbell- or snowman-like one obtained with low-functionalized silica particles of the same size. In fact, even at low conversion, i.e., after 30 min of reaction, one can already observe one or several silica particles encapsulated by polystyrene, forming some decentered core−shell particles. When the reaction time increases, the polymer part of the hybrid nanocomposites predominates in terms of volume fraction, as shown in Figure 4b, but the core−shell morphology still remains, along with free polystyrene nodules and composite particles containing several silica seeds. The different morphologies that have been encountered depending on the reaction time and the surface density of functional groups are represented in Scheme 2.

Selective Surface Modification of Dissymmetrical Particles. As mentioned in our Introduction, dissymmetrical particles can be used for several applications. Among the most promising, let us consider the case of the stabilization of emulsions. It is indeed well-known that dispersions of oil-in-water (or the opposite) are thermodynamically unstable structures that can however be stabilized using either a surfactant or colloidal particles. In the latter case, the resulting material is known as a Pickering emulsion.[29] Such an emulsion based on amphiphilic particles whose structure is similar to a surfactant molecule—that is, a structure associating a hydrophilic "head" and a hydrophobic "tail"—could

Scheme 2. Morphological Evolution of the Composites Formed Starting from Silica Particles with Various Densities of Methacrylate Groups at Their Surface



present new interesting properties and/or an enhanced stability. This could be achieved using dissymmetrical particles consisting of one hydrophilic sphere attached to a hydrophobic one. For that purpose, it might be necessary or at least useful to modify the surface properties or characteristics of both counterparts. On one hand, the resistance to some solvents of our hybrid particles could be improved cross-linking the polymer nodules. On the other hand, the surface chemistry of the inorganic moiety, which is easily tunable, could be modified in order to obtain a more or less hydrophilic character.

Along these lines, we have carried out some complementary experiments using a mixture of styrene and divinylbenzene as a cross-linker in the experimental setup (instead of styrene alone) to synthesize some dissymmetrical particles with cross-linked polymer nodules. TEM pictures of samples with various amounts of divinylbenzene (1−10% w/w) are very similar to those shown previously, as illustrated in Figure 5. One should note that the results do not depend on the association mode between the silica and the polymer. The resistance of polystyrene to solvents such as tetrahydrofurane (THF) was also tested by immersion (THF 80% v/v in water, 12 h) and the result was successful.

Post-functionalization of the silica surface of our dissymmetrical particles was also tested to see whether it was possible or not to graft new chemical groups onto the inorganic part of these original colloidal particles. To do so, (aminopropyl)triethoxysilane was added in a slightly basic water−ethanol (30:70 v/v) suspension of the hybrid colloids. After some dialysis and purification, the particles were mixed

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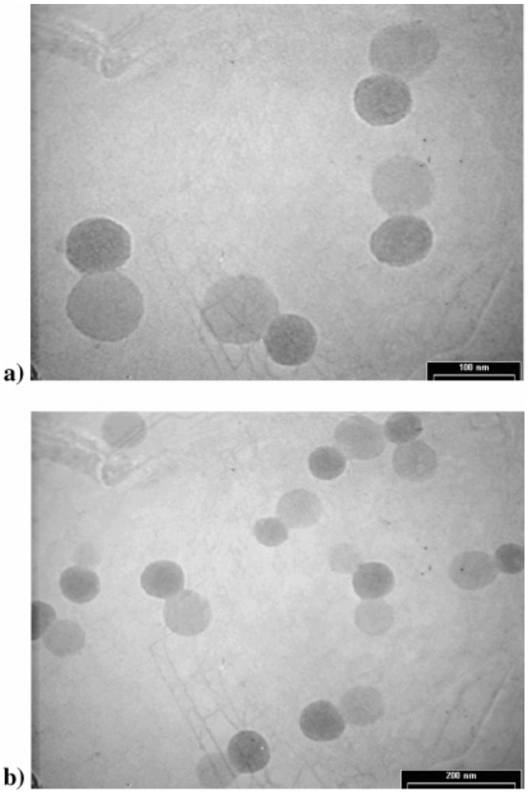

Figure 5. Dissymmetrical particles obtained from functionalized silica particles ($d = 65$ nm; $C = 5$ g$\cdot$L^{-1} and $C_{\mathrm{MMS}} = 0.1$ function$\cdot$nm^{-2}) after 1 h of reaction. The polymer nodules were cross-linked with 5% of divinylbenzene.

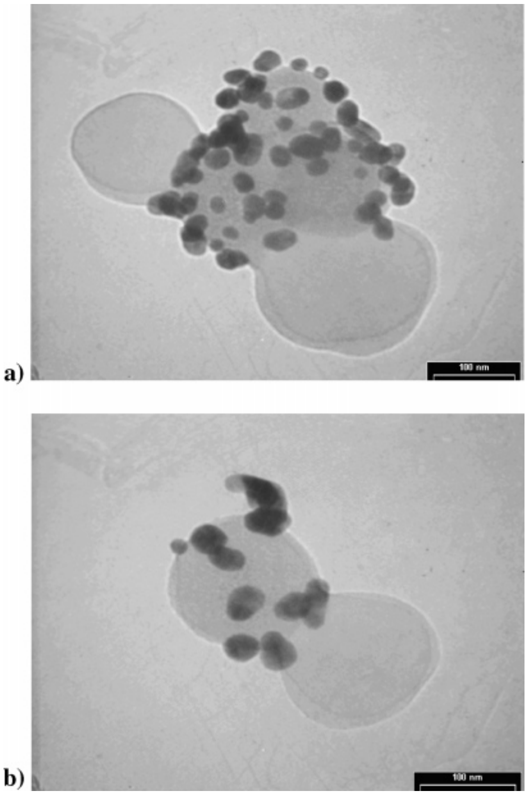

Figure 6. Dissymmetrical particles whose silica surface is selectively decorated by gold colloids.

together with an aqueous suspension of colloidal gold particles prepared according to the method of Grabar et al.[30] As expected, due to the well-known affinity of gold atoms for amine groups[31] and as illustrated in Figure 6, gold colloids do adsorb specifically onto the mineral silica surface, providing evidence of the functionalization treatment. This fact was observed whatever the association mode between silica and polystyrene (macromonomer or functional silane derivative), which indicates that the silica surface still remains accessible for chemical modification after the polymerization process. Such a result illustrates the efficiency of surface modification that can surely be extended to other functional groups (such as methyl, propyl, or octyl groups) that are able to tune the hydrophobic character of the silica surface.

Conclusion

With the final aim of obtaining hybrid functional nanoparticles, we have presented the elaboration of silica–polystyrene colloidal particles with a dissymmetrical morphology. Through an emulsion polymerization process of styrene in the presence of a hydrophilic macromonomer and silica seed particles, we were able to generate dissymmetrical structures associating each silica sphere to a single nodule, when the number of silica spheres was close to the number of nodules synthesized in situ. This parameter was found to be the most determining in controlling the hybrid morphology whereas the reaction time, which masters the diameter of the polymer nodule, allowed us to tune precisely the morphology and size of the composites. Similar results were obtained with silica particles functionalized with low amounts of methacrylate groups. Additional attempts have also been carried out successfully to synthesize hybrid particles with a cross-linked polymer part or a functionalized silica surface. Our further studies will now focus on the use of such original building blocks that could be helpful in generating new colloidal assemblies or acting as particulate surfactants.

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