Syntheses of Raspberrylike Silica/Polystyrene Materials

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Raspberrylike hybrid organic−inorganic materials consisting of spherical silica beads supporting smaller polystyrene particles were prepared through a heterophase polymerization process. In a first step, micrometer-sized silica particles were synthesized according to procedures inspired from the literature. In a second step, a poly(ethylene glycol) macromonomer was adsorbed on the surface of the silica beads. Finally, polymerization of styrene was achieved in water with a nonionic surfactant as an emulsifying agent and sodium persulfate as an initiator. Scanning and transmission electron microscopies show that the presence of the macromonomer on the surface of the silica particles is a determining parameter in order to get the raspberrylike morphology.

Introduction

In the past few years, a lot of work has been done in the field of colloidal particles made of materials of different compositions, as reported in recent reviews on the subject.[1−3] As an example, core−shell particles consisting, for instance, of an inorganic core surrounded with an organic shell are currently widely produced and the range of materials available to get such morphologies is large. Caruso et al.[4] recently described the synthesis of magnetic nanocomposites through a layer-by-layer deposition of magnetite nanoparticles on polystyrene microspheres. Using a similar approach, Gittins and Caruso[5] reported the coating of gold colloids with an organic shell consisting of polyelectrolytes. Apart from these techniques of deposition, surface chemistry reactions are also of interest.[6] As an example, Mornet et al.[7] used water-in-oil microemulsions to encapsulate maghemite into silica nanoparticles. Imhof[8] also described the formation of a titanium dioxide shell around

the surface of cationic polymer microspheres. In a similar approach, Tissot et al.[9,10] reported the coating reaction of polystyrene latex particles with a silica layer, using a silane coupling agent in order to compatibilize core and shell materials.

If core−shell particles are among the most popular hybrid particles synthesized, other morphologies are of interest. We report here the synthesis of hybrid silica−polystyrene raspberrylike particles. In recent works, such structures were obtained by self-assembly techniques. For example, Kulbaba et al.[11] described the assembly of positively charged polyferrocenylsilane microspheres with negatively charged silica particles involving electrostatic forces. Stronger attachments were used by Fleming et al.[12] to associate silica microspheres and polystyrene nanospheres either with chemical (amine−aldehyde) or biochemical (avidin−biotin) linkages. Nevertheless, in all these studies, the particle syntheses and their assembling are disconnected stages.

The main difference between our work and those previously described—where the particles are prepared separately and then assembled—is that the polymer particles are synthesized in situ onto the silica surface. In this field, silica is the most commonly used inorganic support due to two main reasons. First, synthesis of silica particles is quite easy to perform and well documented in the literature.[13,14] Second, the potential applications of silica-based systems are various: gas−liquid chromatography, paintings, catalyst supports, etc.

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Consequently, previous works involving silica-based systems have been already reported. Recently, raspberrylike silica/poly(methyl methacrylate) nanocomposites were obtained through emulsion polymerization.[15] Involving acid−base interactions between a silica sol and a basic monomer like 4-vinylpyridine is also a way to get such nanocomposites with silica particles encapsulated in the polymer.[16,17] Lascelles et al.[18] have also described the influence of synthesis parameters on the formation of silica/polypyrrole nanocomposites in dispersion polymerization, whereas Yoshinaga et al.[19] studied the adsorption and spontaneous polymerization of surface-active monomers on colloidal silica and alumina. Since silica is initially hydrophilic, its surface needs to be modified to allow anchoring and polymerization of hydrophobic monomers. This is usually achieved by the adsorption of a macromolecule[20] or by the chemical grafting of an appropriate alkoxylsilane.[21] While the former approach gave nanocomposite particles with a raspberrylike morphology, the latter procedures resulted in the formation of organic−inorganic nanoparticles with a core−shell structure.[22]

In the present work, we aim to report new results along these lines on the synthesis of raspberrylike silica/polystyrene particles in emulsion polymerization. Our technique includes three distinct stages. First, monodisperse silica particles with controlled diameters were obtained by experimental procedures inspired from those previously described by Stöber et al.[13] and Kang et al.[14]

The second stage is crucial and involves the adsorption of a macromonomer, i.e., a macromolecule with a polymerizable group, poly(ethylene glycol) monomethyl ether methacrylate, which is expected to react with the growing polystyryl radicals and thus promotes anchoring of the polymer chains on the silica surface.

Finally, synthesis of the polystyrene particles is achieved through an emulsion polymerization process of styrene by heating the system in the presence of a nonionic surfactant (Remcopal NP30) and an initiator (sodium persulfate). Once the reaction is completed, hybrid particles with a raspberrylike morphology are obtained.

In the past, Furusawa et al.[20] were among the first to report such morphologies through in situ polymerization of styrene at the surface of silica spheres. However, the system was quite different from ours since the adsorbed molecule was hydroxylpropylcellulose−which has no reactive properties in the polymerization process−and the surfactant, sodium dodecyl sulfate, was anionic.

Materials and Methods

Materials. Tetraethoxysilane (TEOS, Fluka), styrene (Sigma), sodium persulfate (Aldrich), and ammonia (25% in water, SDS) were purchased in their reagent grades and used without further purification. The macromonomer, poly(ethylene glycol) 1000 monomethyl ether methacrylate (PEG methacrylate) was obtained from Polysciences, and the surfactant (Remcopal NP30) was a gift from CECA S.A. (Paris). Deionized water was obtained with a MilliQ system (Millipore), and ethanol was purchased from J. T. Baker.

Methods. *Synthesis of 500 nm Silica Particles.* Absolute ethanol (100 mL) and 22 mL of the aqueous solution of ammonia were introduced in a three-neck round flask of 250 mL equipped with a refrigerating system. The mixture was stirred at 300 rpm to homogenize. A solution of 10 mL of TEOS diluted in 40 mL of absolute ethanol was prepared separately and introduced continuously at the rate of 7.8 mL·h^{-1}. Reaction occurred at room temperature under continuous stirring.

Synthesis of 1 μm Silica Particles. The synthesis was performed in two steps. In a first step, silica particles with a mean diameter of 450 nm were prepared as described previously. In a three-neck round flask of 250 mL equipped with a refrigerating system, 100 mL of absolute ethanol and 22 mL of an aqueous solution of ammonia were introduced and stirred at 300 rpm to homogenize. A solution of 10 mL of TEOS diluted in 60 mL of absolute ethanol was then introduced at the rate of 10.8 mL·h^{-1} under stirring. TEOS addition was completed after 6.5 h and the resulting silica suspension was denoted as S$_{450}$.

In a second stage, the above suspension was used as a seed for the growth of silica in order to get particles with a final diameter close to 1 μm. A 10 mL aliquot of the S$_{450}$ suspension, containing an estimated 1.3 10^{12} particles, was first centrifuged and rinsed with absolute ethanol. This operation was repeated twice and the particles were finally redispersed into 5 mL of absolute ethanol. These 5 mL were then introduced in a 250 mL three-neck round flask equipped with a refrigerating system and containing 100 mL of absolute ethanol and 22 mL of the aqueous solution of ammonia. Finally, a solution of 5.2 mL of TEOS diluted in 62 mL of absolute ethanol was added dropwise over 3 h under stirring at 300 rpm, which represents an addition rate of 22.4 mL·h^{-1}. Several withdrawals were made from the solution in order to evaluate the evolution of the particle diameter as a function of the volume of TEOS added. When the reaction was fully completed, particle size was determined to be around 1000 nm.

Silica Suspensions Treatment. All the silica suspensions were dialyzed against water until neutral pH in order to remove ammonia and replace ethanol with water. The suspensions were concentrated and their final concentration was determined by measuring the mass of a dried extract.

Silica Particle Size Measurements. Granulometry experiments were performed on a Malvern Mastersizer apparatus.

Hybrid Particle Synthesis. Emulsion polymerization of styrene was performed in the presence of the silica particles after adsorption of hydrophilic PEG methacrylate macromonomer. 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 macromonomer concentration was chosen such as to saturate the silica surface, which corresponds to the beginning of the adsorption plateau on the adsorption isotherms (not shown here). The concentrations used for both samples, calculated as a function of the whole surface area developed by the silica particles, are listed below.

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(21) Bourgeat-Lami, E.; Lang, *J. Colloid Interface Sci.* **1998**, *197*, 293−308.

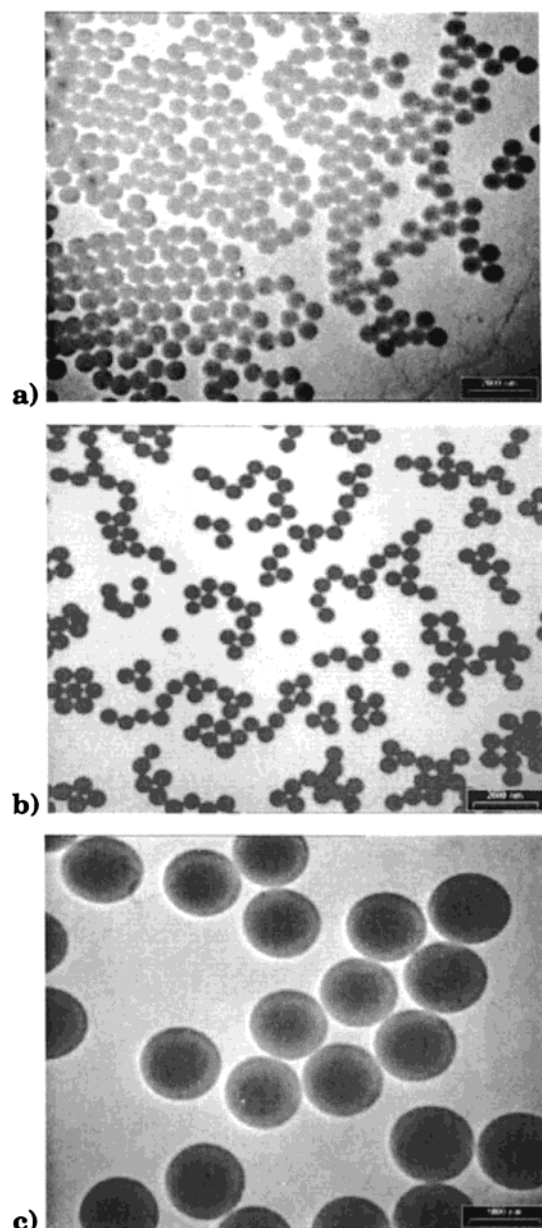(22) Sondi, I.; Fedynyshyn, T. H.; Sinta, R.; Matijevic, E. *Langmuir* **2000**, *16*, 9031−9034.

silica particle diameter (nm)	silica concn (g·L^{-1})	macromonomer concn (g·L^{-1})
500	10	0.1
1000	10	0.05

Figure 1. (a) Silica particles with a mean diameter around 500 nm. (b) Silica "seed" particles with a mean diameter around 450 nm. (c) Silica particles with a mean diameter around 1 μm resulting from a seed-mediated growth process. Scale bars: 2000, 2000, and 1000 nm, respectively.

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 and its concentration (3 g·L^{-1} in both cases) was chosen such that we got latexes around 200 nm. Then, the suspension was purged with nitrogen and heated to 70 °C before addition of the initiator (sodium persulfate, 0.5 wt % relative to styrene) to start polymerization. Samples were taken from the batch at different times to study the kinetics of the reaction and its consequences on the particle 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 nanohybrids were dispersed in water and one drop of the dilute suspension was deposited on a copper grid coated with a carbon membrane.

Scanning Electron Microscopy. SEM observations were performed with a Jeol JSM-840A scanning electron microscope

operating at 10 kV. The specimens were gold-coated prior to examination.

Results and Discussion

Silica Particles. In 1968, Stöber et al.[13] managed to obtain silica particles by ammonia-catalyzed hydrolysis of tetraethoxysilane (TEOS) in water−ethanol medium. Great interest was found in this procedure since well-defined particles with a spherical shape and a narrow size distribution were finally obtained. More recently, Kang et al.[14] have developed a procedure leading to around 400 nm diameter particles with controlled morphological properties. The Kang method consists of adding slowly a methanolic solution of TEOS in a mixture of methanol, water and ammonium hydroxide, whereas Stöber et al. mixed all the reagents together in ethanol as a solvent and varied the concentrations of the other constituents. To get silica particles with an approximate diameter of 500 nm and to control the particle size distribution, we have developed our own procedure consisting of a combination of both Stöber and Kang processes. In our method, a solution of TEOS in ethanol is added dropwise in a medium consisting of ethanol, water, and ammonia. Ethanol was used due to its low cost and low toxicity and its quick removal against water during dialysis. As shown in Figure 1, the silica particles obtained in this way are monodisperse and regular in shape.

During the seed-mediated process, a kinetic study was performed to see whether the control of the reaction was adequate enough. After the addition of half the total amount of TEOS, the current size of the particles was evaluated and was found to be 340 nm in diameter. Assuming complete conversion of TEOS into silica, one can determine at any time t of the growth process the volume of silica synthesized, $V_{SiO_2}(t)$, as a function of the total volume of TEOS added until that moment, $V_{TEOS}(t)$:

$$V_{SiO_2}(t) = \left(\frac{M_{SiO_2}}{M_{TEOS}}\right)\left(\frac{\rho_{TEOS}}{\rho_{SiO_2}}\right)V_{TEOS}(t) \approx 0.122\,V_{TEOS}(t) \tag{1}$$

where M_i, ρ_i, and V_i designate the molar mass, the density, and the volume of compound i, respectively.

The particle radius at a given time t, $r(t)$, can be then expressed as

$$r(t) = \left[\frac{3}{4\pi}v_p(t)\right]^{1/3} = \left[\frac{3}{4\pi}\left(v_p^0 + \frac{V_{SiO_2}(t)}{n_p}\right)\right]^{1/3}$$

And finally

$$r(t) = \left[\frac{3}{4\pi}\left(v_p(t=0) + \frac{0.122\,V_{TEOS}(t)}{n_p}\right)\right]^{1/3} \tag{2}$$

In this particular case, the initial volume of the particles, $v_p(t=0)$, equals 0. Even if we do not know the final number of particles n_p, we can estimate their final size $r(t_{end})$:

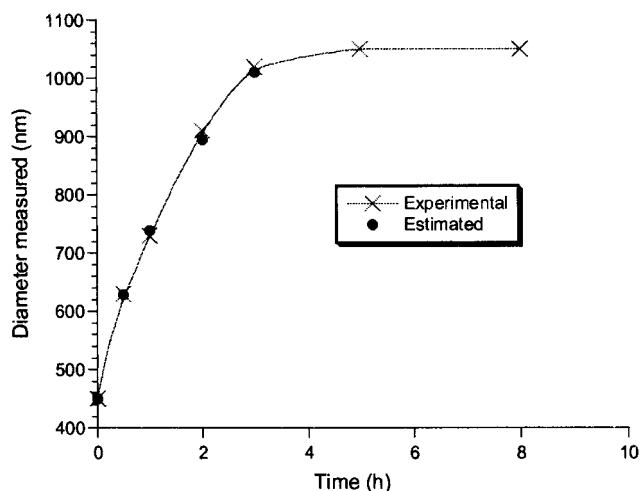$$\frac{r(t)}{r(t_{end})} = \left(\frac{V_{TEOS}(t)}{V_{TEOS}(t_{end})}\right)^{1/3} \tag{3}$$

Figure 2. Experimental (granulometry results) and predicted values of the silica particle diameter as a function of time during the growth process of the S$_{450}$ silica seed suspension.

Given for instance $t = t_{end}/2$, and assuming a constant rate of addition, it follows that

$$\frac{V_{TEOS}(t = t_{end}/2)}{V_{TEOS}(t_{end})} = \frac{1}{2} \quad \text{and} \quad r(t_{end}) = \sqrt[3]{2}r(t_{end}/2)$$

Knowing the particle radius at half the addition time $[r(t_{end}/2) = 340/2 = 170 \text{ nm}]$, we can determine the final particle size. The value thus calculated for the diameter (i.e., 430 nm) is in good agreement with the experimental one (450 nm). This confirms the assumption of very fast silica formation under our experimental conditions. As an alternative, it is also possible from eq 3 to determine the volume of TEOS needed to achieve a given silica particle size.

In the following, the above model was used to predict the evolution of the silica particle diameter as a function of time during the growth process of the S$_{450}$ silica seed suspension. The theoretical diameters determined from eq 2 are plotted versus time and are again in perfect agreement with the experimental values, as can be seen in Figure 2.

Hybrid Latex Particles. The morphology of the nanohybrids obtained under the experimental conditions reported previously is shown in Figure 3, whereas the mechanism that can be involved in the control of the morphology is schematically represented in Figure 4.

For a better understanding of the above picture, we should first of all remember some properties of the molecular species involved and represented in Figure 5. The macromonomer (Figure 5a) is mainly hydrophilic due to the presence of ethylene oxide groups ($n \sim 23$), which are able to form hydrogen bonds with the silanol functions (-SiOH) present on the silica surface. It is indeed well-known that poly(ethylene oxide) strongly adsorbs onto silica.[23] At one of its ends, this molecule also contains a methacrylate group that constitutes a monomer unit for the later polymerization of styrene.

The nonionic surfactant (Figure 5b) also contains several ethylene oxide groups, which compose the hydrophilic part of the molecule while the hydrophobic character is brought by a rather short aliphatic chain.

Given the complex nature of our reaction medium—remember that apart from the silica dialysis, we get raspberrylike particles in a one-pot synthesis—it is quite difficult to explain the observed phenomenon with accuracy. However, we can briefly describe our system as a self-stabilized copolymerization between the PEG macromonomer and styrene.

During the early steps of the polymerization, free molecules of monomer and PEG methacrylate react to form copolymers. These copolymers will continue to grow until they reach a critical size and become nuclei. Due to the presence of ethylene oxide groups in the structure of the macromonomer, and also because of the presence of the surfactant, these nuclei can become steady and evolve as mature polymer particles.[24] This scenario also holds for the macromonomer adsorbed on the silica surface. In that case, the growing copolymers are expected to strongly attach on silica via the anchored PEG derivative. Free PEG molecules are also initially present in the suspension medium but it can be anticipated that the particles or at least the copolymers they form with styrene will also have a strong tendency to adsorb on silica.

Figure 6 provides evidence of the strong attachment of the polystyrene particles on the silica surface by comparing the TEM image of a raw sample with that of a suspension of the nanohybrid latex particles centrifuged and washed with water. Therefore, not only does the macromonomer promote interaction of the polymer chains with the silica surface but also it allows the formation of polymer particles that can self-assemble on the previously adsorbed copolymers. Then, a classical process of diffusion of the monomer occurs, starting from the monomer droplets stabilized by the surfactant toward the growing polystyrene spheres. Finally, when the polymerization is fully completed, polystyrene nodules of around 200 nm in diameter are obtained on the surface of the silica core.

Additional experiments, not presented here, showed that the raspberry morphology was obtained in the very early stages of the reaction while free polystyrene spheres were continuously produced in the later stages. This result suggests a strong affinity of the polymer for the silica surface at the beginning of the reaction and underlines the determining role of the adsorbed macromonomer molecules in the self-assembly process. In other words, the polymerization process is highly favored on the silica surface.

To confirm that the presence of the macromonomer is essential to control the morphology of the particles, the polymerization was performed as described previously but without the PEG methacrylate derivative. The TEM results, illustrated in Figure 7, clearly indicate that the raspberry morphology was obtained only when the macromonomer was present.

It is worthwhile to notice here that very small amounts of the PEG compound were sufficient to provide the observed morphological control. Moreover,

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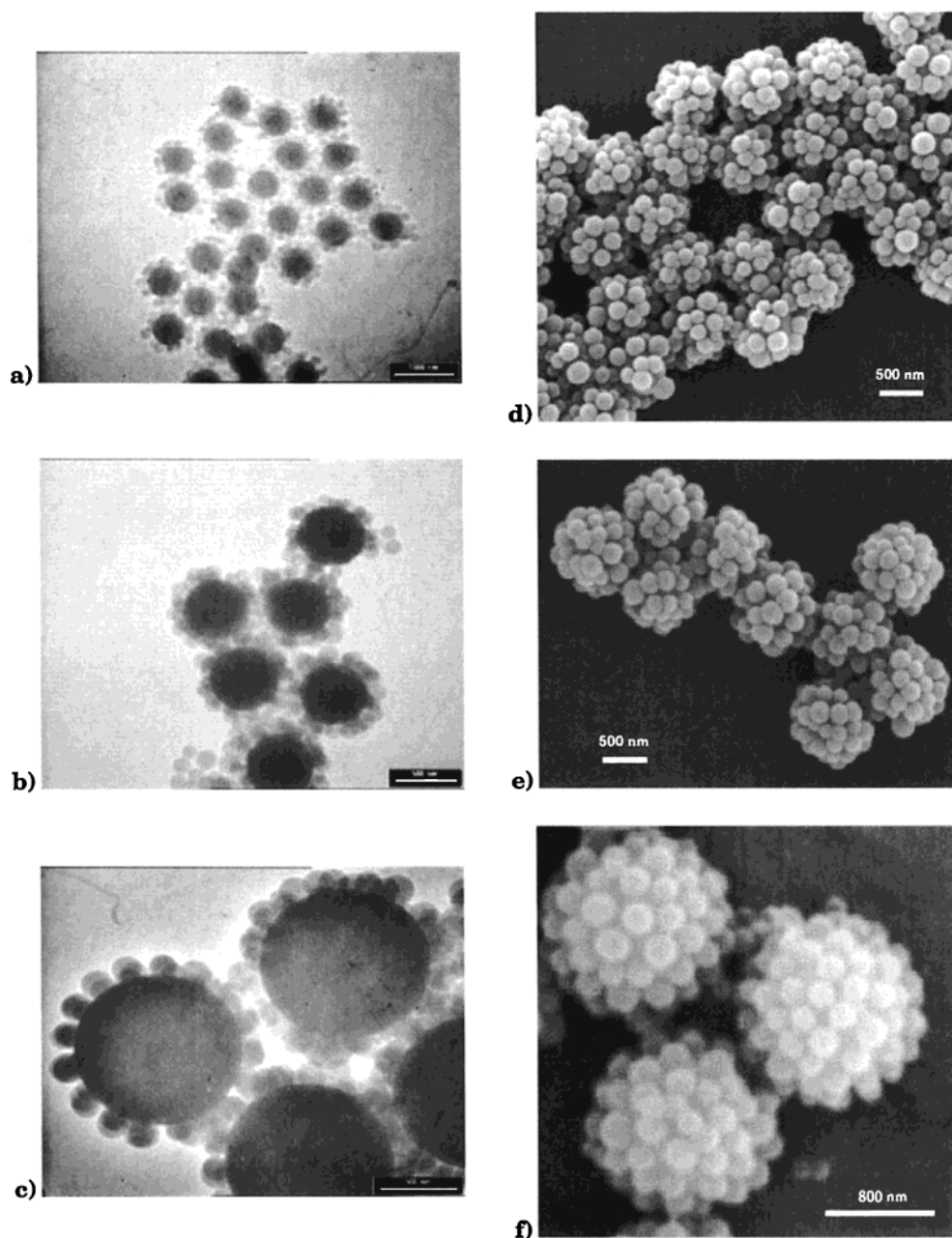(24) Ottewill, R. H.; Satgurunathan, R. *Colloid Polym. Sci.* **1995**, *273*, 379−386.

Figure 3. (a, b) TEM images of raspberrylike hybrids based on 500 nm silica particles. Scale bars: 1000 and 500 nm, respectively. (c) TEM image of raspberrylike hybrids based on 1 μm silica particles. Scale bar: 500 nm. (d–f) SEM images corresponding to samples a–c, respectively.
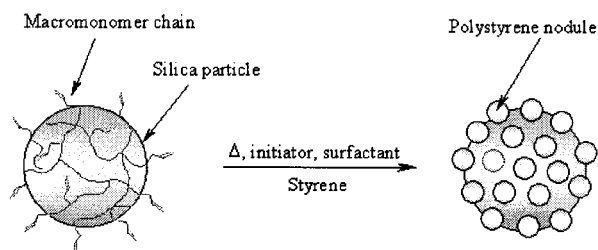

Figure 4. Schematic representation of the process involved in the synthesis of the raspberrylike silica/polystyrene nanohybrids.

the presence of the macromonomer also influenced the size of the final polystyrene nodules, which are bigger and more polydisperse when the surfactant is used alone. This last result suggests that a cooperative stabilization mechanism may operate between the sur-
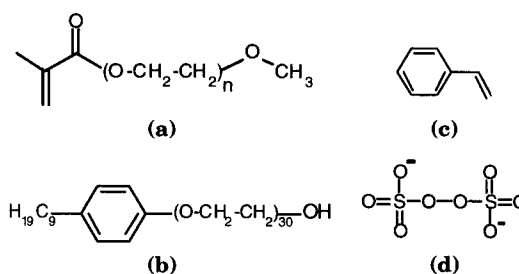

Figure 5. Molecular structures of the chemical components involved in the synthesis of the hybrid particles: (a) macromonomer, (b) surfactant, (c) monomer, (d) initiator.

factant and the macromonomer. Such a cooperative effect can also take place during the polymer assembly process. However, further experiments are needed to support the latter assumptions.
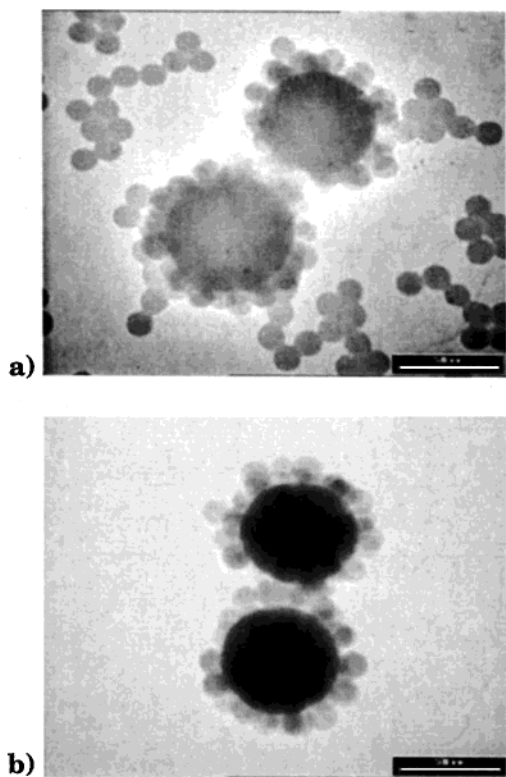
Figure 6. TEM images of the hybrid particles (a) before and (b) after (bottom) removal of free polystyrene particles (diameter of silica particles 500 nm). Scale bars: 500 nm.

Figure 7. TEM images showing the morphologies obtained (a) with and (b) without macromonomer (diameter of silica particles 500 nm). Scale bars: 1000 and 500 nm, respectively.

Conclusion

We managed to synthesize raspberrylike silica−polystyrene nanohybrids through emulsion polymerization. Well-defined silica spheres were first prepared via a base-catalyzed sol−gel process. Then the adsorption of a PEG methacrylate derivative was achieved on the silica surface to provide double bonds for reaction with the monomer. Finally, emulsion polymerization of styrene was performed with the help of a surfactant and with sodium persulfate as an initiator. Evidence is given that the final morphology of the nanohybrids is strongly dependent on the presence of the adsorbed macromonomer. The macromonomer derivative not only enables the production of rasp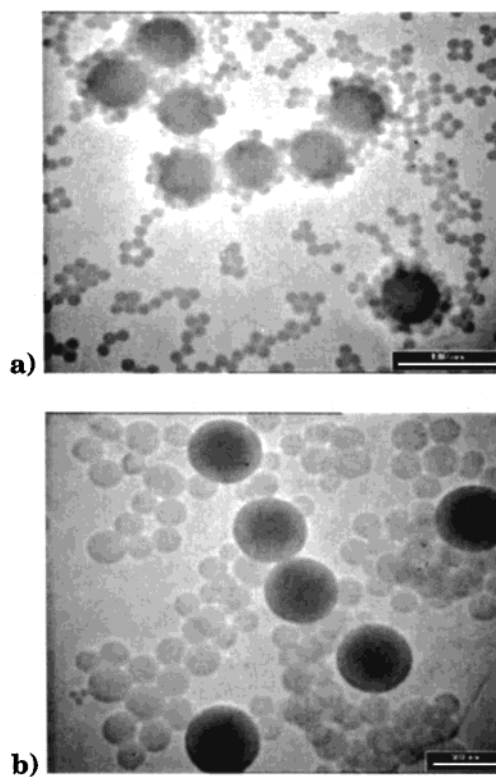berrylike silica−polystyrene materials but also ensures strong attachment of the polystyrene particles on the silica surface.

Further experiments are currently in progress in order to study the phenomenon at several scales with silica particles of various sizes. Influence of parameters such as the nature of the surfactant, the length of the macromonomer, and the various concentrations of the involved compounds is being discussed.

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