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Hybrid Latex Particles Coated with Silica

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There exist in the literature a lot of works dealing with the coating reaction of colloidal particles with materials of different chemical composition. Since the pioneering works from Matijevic,[1−3] considerable efforts have been done on the synthesis of organic−inorganic colloidal particles with tailored morphologies.[4] Among the coating materials, silica is a very interesting candidate since it can be used in a lot of industrial domains ranging from paints and magnetic fluids to high-quality paper coatings. The procedures reported in the literature for the coating with silica generally involve surface modification of the core particles to increase chemical affinity with the shell[5] or the sequential adsorption of polyelectrolyte/SiO_2 multilayers through electrostatic attractions using the so-called layer-by-layer (LbL) deposition technique.[6,7] In the former procedure, a thin silica layer is first obtained by the controlled precipitation of silica from water using a sodium silicate stock solution and slowly decreasing the pH. Further silica growth is performed into ethanol/water mixtures using ammonia as catalyst and tetraethoxysilane as precursor.[5,8,9] The core can be subsequently removed by calcination or dissolution into acids or solvents to generate hollow microspheres.

In this communication, we report a new route for the synthesis of latex particles coated with a silica shell. Our strategy is divided in two steps as schematically represented in Figure 1. In a first step, MPS molecules are incorporated into polystyrene latex particles. Then a silica layer is formed on the hybrid particles surface by reaction of tetraethoxysilane in water, which are unusual conditions for the sol−gel reaction.

Hybrid latexes (diameter 139 nm as determined by dynamic light scattering and 12 wt % solid content) were synthesized in batch by adding 4 g of MPS to 10 g of styrene and introducing the mixture of monomers into 100 g of water containing 2 g of dodecyldimethylpropylammonium sulfonate surfactant and 0.1 g of potassium persulfate at 70 °C. The pH of the suspension was adjusted to 7 (to slow down MPS hydrolysis and condensation reactions) using a mixture of ammonium dihydrogenophosphate and disodium hydrogenophosphate. Stable latexes were obtained under these conditions whereas polymerizations performed in acidic medium gave rise to the formation of gels. Cleaning of the latex particles was performed by successive centrifugations/redispersions in water to remove free surfactant, nonreacted compounds and to eliminate the salt added. Complete conversion of the monomers into the copolymer was achieved as indicated by elemental analysis and gravimetric measurements. The structure of the copolymer was characterized by ^{13}C and ^{29}Si solid-state CP-MAS NMR spectroscopy.[10] The ^{13}C NMR spectrum of the cleaned latex particles, shown in Figure 2, supports the hybrid structure of the copolymer. The peak at 166.8 ppm in starting MPS, attributed to the carbonyl group of the methacrylate, is shifted to higher frequencies (175 ppm) while the signals at 137.4 ($\mathbf{C}H_2=$) and 124.7 ppm ($CH_3-\mathbf{C}H=$), assigned to the double bond, have disappeared, indicating that the MPS molecules have (co)polymerized. The structure of the copolymer is also supported by IR spectroscopy which shows absorption bands at 1600, 1494, and 1451 cm^{-1} characteristic of the aromatic ring of poly(styrene) and bands at 1722 and 1085 cm^{-1} corresponding to the C=O and Si−O−C bonds of the methacrylate side chains while the band at 1637 cm^{-1} assigned to the MPS double bond (C=C) has disappeared. All these results attest for the incorporation of MPS units in the copolymer chain by free radical polymerization. Concurrently, ^{29}Si NMR analysis gives evidence that no siloxane bonds have formed under our experimental conditions (Figure 3a). Only a sharp signal, corresponding to uncondensed trimethoxy silyl groups, can be identified at −42.7 ppm. So, all these results clearly indicate that free radical polymerization occurred faster than hydrolysis and condensation in our system and definitely support the copolymer structure shown in Figure 2.

Table 1. Measured and Predicted Values of Particles Size as a Function of the Amount of TEOS Added to the Organo-Mineral Latex Seed[a]

samples		18-0	18-1	18-2	18-3
TEOS (g)		0	3.1	5.6	10
diameters (nm)	predicted (DLS)[b]		160	174	194
	measured (DLS)	139	166	179	220
	predicted (TEM)[b]		155	169	188
	measured (TEM)	135	165	191	212

[a] The seeded growth reaction was performed on 10 g of the poly(styrene-*co*-MPS) latex suspension containing 1 g of the organo-mineral particles. [b] Determined using eq 1.

In a second step, the trimethoxysilyl groups trapped into the organo-mineral seed latexes were reacted with tetraethyl orthosilicate (TEOS) in water under basic conditions to yield silica-coated latex particles. In a typical procedure, 10 g of the cleaned aqueous latex suspension (containing 1 g of MPS-functionalized seed particles) and 0.02 g of sodium hydrogenocarbonate (pH = 8.5) were introduced in a flask under magnetic stirring. Then, 10 g of TEOS was added dropwise at a rate of 0.2 mL/h, and samples were taken regularly to follow particles growth. Silica formation was clearly evidenced by ^{29}Si NMR (signals at −102 (Q^3) and −111 ppm (Q^4), Figure 3b) and IR spectroscopy (peaks at 1100 and 469 cm^{-1} characteristic of the Si−O−Si bonds) analyses. In addition, the transmission electron micrograph[12] reported in Figure 4a clearly shows that silica has grown radially outward from the seed latex particles giving silica-coated organo-mineral particles with a core−shell morphology. By increasing the concentration of the sol−gel precursor, it was possible to increase and to control the thickness of the inorganic shell. The diameters of the core and core−shell particles were determined by dynamic light scattering and from the TEM images taken at various stages of the seeded process (Table 1). Both DLS and TEM measurements indicate an increase in particles size with increasing the

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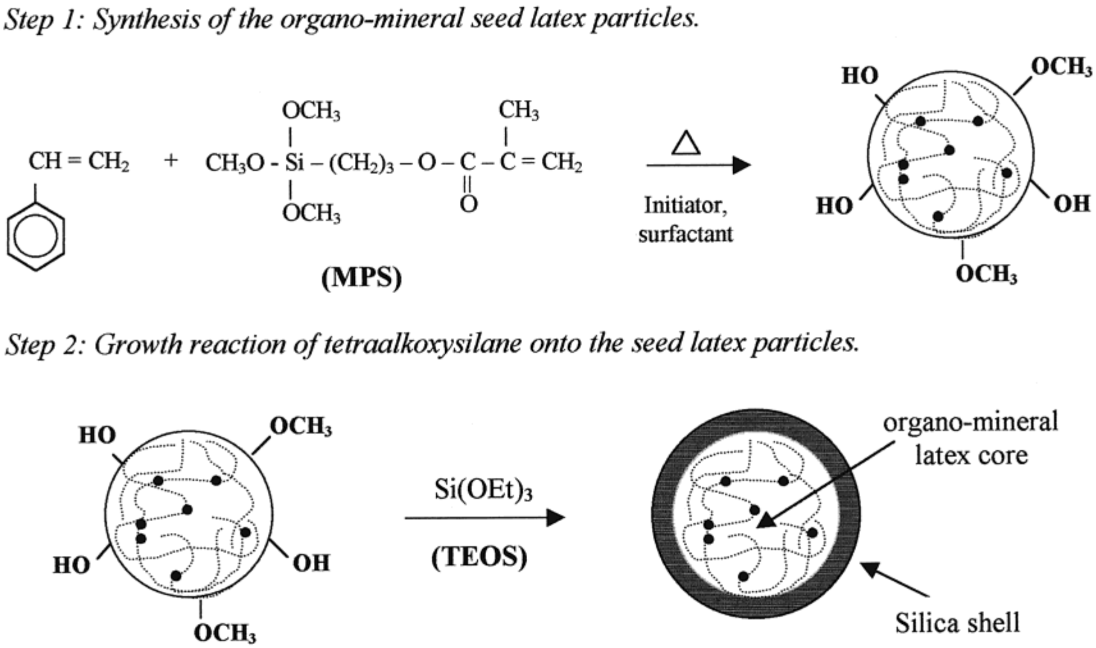

Figure 1. Schematic representation of the different steps involved in the coating reaction of organo-mineral latex particles with silica.

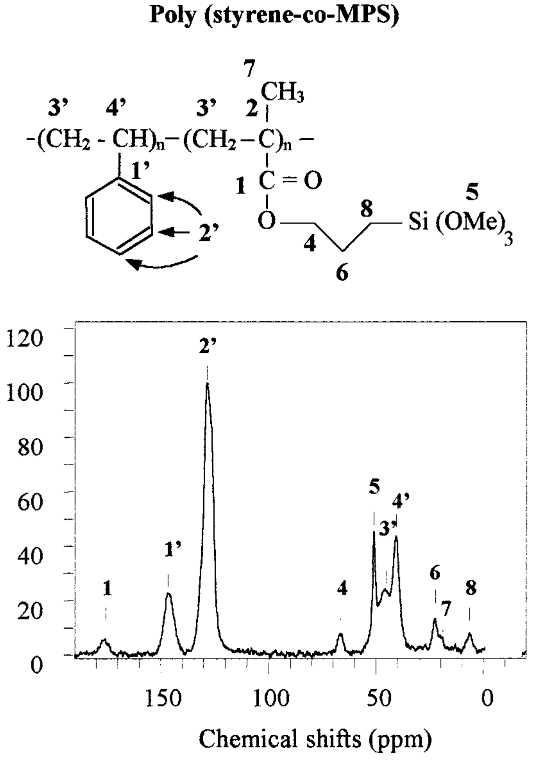

Figure 2. ^{13}C NMR spectrum of the organoalkoxysilane modified polystyrene latex particles.

TEOS concentration. A 40 nm thick silica layer could be deposited on the seed particles without loss of colloidal stability. Unfortunately, increasing further the TEOS concentration resulted in the apparition of a second phase corresponding to nonreacted TEOS molecules which accumulate in water. It seems therefore that hydrolysis and condensation reactions no longer take place when the core particles are transformed into silica spheres. Giving a constant particle number, the theoretical diameter of the core–shell particles can be calculated as a function of the amount of TEOS added

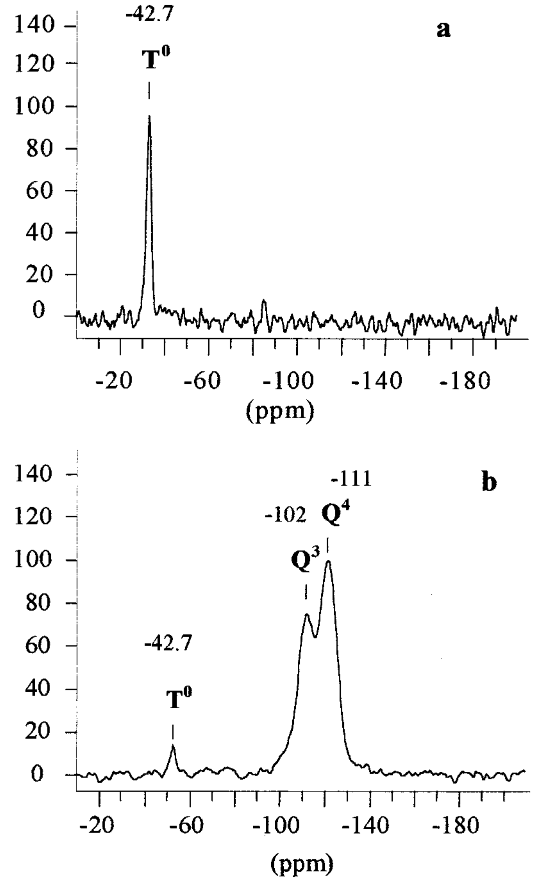

Figure 3. ^{29}Si NMR spectra of the organo-mineral seed latex particles: as synthesized (a) and coated with silica (b).

using eq 1[13] and compared to the experimental values.

$$D_{\text{core-shell}} = D_{\text{core}}\sqrt[3]{\frac{1.8x + 1.045}{1.8x}}$$

$$\text{with } x = \frac{\text{seed (g)}}{\text{silica (g)}} \text{ and silica (g)} = \frac{m_{\text{TEOS}} \times 61}{208} \quad (1)$$

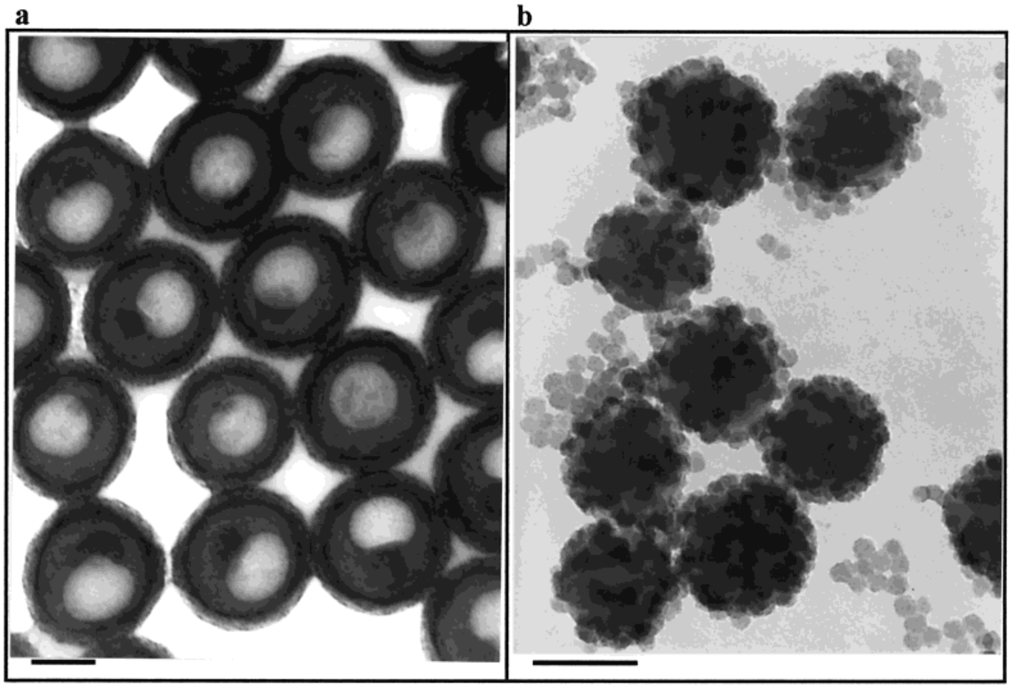

Figure 4. Transmission electron micrographs of silica-coated latex particles using (a) MPS functionalized polystyrene latex particles (sample 18-3) and (b) bare polystyrene latex particles as the seed. Scale bar: 100 nm.

The results reported in Table 1 show a good agreement between predicted and measured particles size except for large TEOS concentrations.

When nonmodified polystyrene latex particles were used as the seed, under otherwise identical experimental conditions, silica precipitation also occurs but as small silica beads deposited on the polymer particles as well as free silica particles (Figure 4b). It is then clear that the formation of a smooth and regular silica layer on the seed particles is highly dependent on the nature of the latex core. It is presumed that the success of the seeded growth process in our system is due to the unique hybrid structure of the copolymer. Although further work should be done to clarify the mechanism of the coating reaction, a reasonable assumption is that the hybrid latex particles act as a microreactor for the sol−gel process. Indeed, due to its hydrophobic character, TEOS can easily enter the polymer particles and chemically react with the methoxy or hydroxyl groups trapped inside them. The alcohol produced by the hydrolysis and condensation reactions may also help increase the solubility of TEOS into the particles. Polycondensation would be thus promoted by a high local TEOS concentration and by the silane coupling agent introduced into the hybrid latex core.

As a part of this work, the organic−inorganic core could be removed by calcination (600 °C in air), a method commonly used to create porosity in templated inorganic materials. The hollow structure of the resulting nanoporous colloid was confirmed by TEM and BET measurements. One important advantage of our system is that it is potentially applicable to a large range of core latexes which dimensions can be easily controlled by the nature of the surfactant or the amount of monomer. By varying the dimension of the core and shell materials, it is possible to synthesize porous nanostructures with adjustable properties. In addition, the aqueous route obviously offer interesting opportunities in many industrial applications (water-borne coating, paper and paint industries, etc.).

Supporting Information Available: Chemical composition of the organo-mineral seed latex particles; ^{13}C solid-state NMR spectra with attributions of MPS, polystyrene, and poly(styrene-*co*-MPS); FTIR spectra of the starting and silica-coated organo-mineral latex particles; measured vs predicted values of particles size of the silica-coated organo mineral latex particles; and FTIR spectrum and TEM micrograph of the hollow silica beads obtained after thermal degradation of the hybrid latex core. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(10) NMR measurements were performed on a Bruker DSX-300 spectrometer operating at 59.63 MHz (^{29}Si) and 75.49 MHz (^{13}C) by use of cross-polarization from proton (contact time 5 ms, recycle delay 1 s, spinning rate 10 kHz).
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(12) TEM experiments were performed with a Philips CM20 electron microscope using copper grids coated with Formvar/carbon films.[4]
(13) The density of the silica layer is assumed equal to 1.8 g/cm^3, and that of the core polymer is presumed to be close to the density of polystyrene (i.e., 1.045 g/cm^3).

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