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Synthesis of Daisy-Shaped and Multipod-like Silica/Polystyrene Nanocomposites

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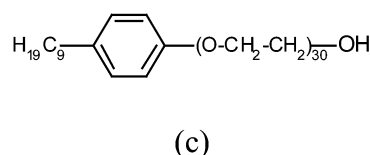
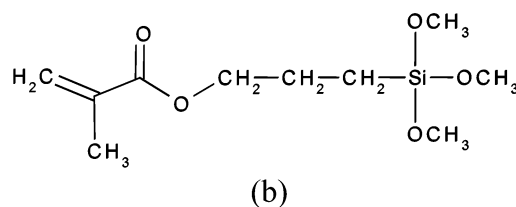
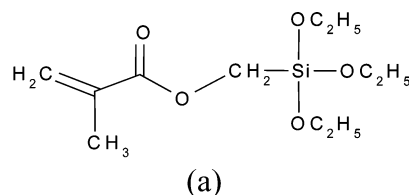
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ABSTRACT

The synthesis of composite particles with original morphologies resulting from the combination of an inorganic silica seed and polymer nodules is reported. To promote association between both components, the silica seeds are previously functionalized with an appropriate coupling agent carrying polymerizable groups. Following classical recipes, emulsion polymerization of styrene is achieved in the presence of these surface-modified particles and polystyrene is formed exclusively at the surface of the inorganic precursors. The density of the coupling agent, however, as well as the silica seed diameter have a strong influence on the particle morphology. In the case when this density is equal to 0.1 molecule nm⁻² (that is around 0.17×10^{-6} mol m⁻²) and the seed size is close to 170 nm, an interesting evolution of the morphology with the reaction time, from daisy-like toward multipod-like, is observed. Thus, the possibility to elaborate original building blocks with a defined shape and size is demonstrated.

Introduction. In recent years, considerable effort has been devoted to the design and controlled fabrication of nanomaterials with complex shapes. The interest in nanoscale materials stems from the fact that their optical, electrical, and chemical properties vary with their size, composition, and structural order. Therefore, effective strategies to build tailored nanomaterials reliably and predictably are required. Colloidal particles represent attractive building blocks, which enable one to elaborate ordered and hierarchical materials. For instance, aggregates of spherical colloids with well-controlled sizes, shapes, and structures have been fabricated by template-assisted self-assembly¹ and in an oil-in-water emulsion.² Core-shell colloidal particles and composite nanomaterials with different interesting morphologies have also formed the subject of numerous investigations, which have been largely spurred by the applicability of such materials in the areas of coatings, catalysis, and diagnostics.^{3–8} As an example, raspberry-like silica/poly(methyl methacrylate) and silica/polystyrene nanocomposites have been recently obtained through emulsion polymerization.^{9–10}



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Figure 1. Molecular structures of chemical components involved in the synthesis of the nanocomposites: (a) MMS, (b) MPS, (c) NP30 surfactant.

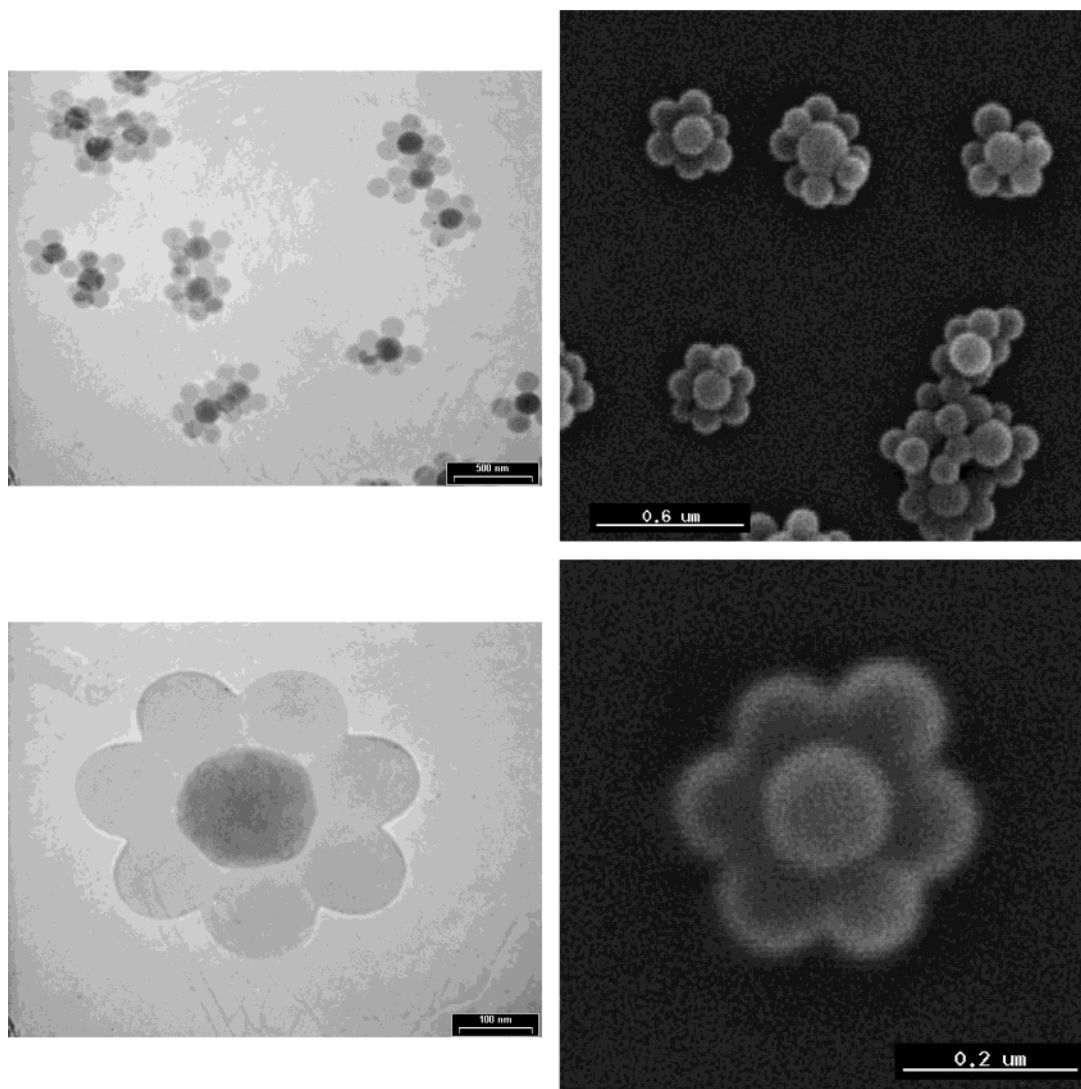


Figure 2. TEM (left) and SEM (right) pictures of daisy-shaped silica/polystyrene nanocomposites. Diameter of the MMS-grafted silica particles: 170 nm. Reaction time: 1 h. Density of coupling agent: 0.1 molecules nm^{-2} .

Here, we report a synthesis of daisy- and multipod-shaped silica/polystyrene nanoparticles. Our method involves the emulsion polymerization of styrene in the presence of a nonionic surfactant, an initiator, and silica beads prefunctionalized with a trialkoxysilane bearing a polymerizable group. Control of the shape is correlated with the density of the latter at the surface of the silica particles, the surfactant concentration, the size of the silica beads and the reaction time.

Experimental Section. Materials. Tetraethoxysilane (TEOS, Fluka), styrene (Sigma), sodium persulfate (Aldrich), and ammonia (25% in water, SDS) were purchased in their reagent grade and used without further purification. Methacryloxypropyltrimethoxysilane (MPS) and methacryloxymethyltriethoxysilane (MMS) were purchased from ABCR, and the surfactant (Remcopol 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.

Synthetic Procedures. First, 80 nm silica particles were synthesized according to the well-known Stöber procedure.¹²

100 mL of absolute ethanol and 7.5 mL 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 and heated to 60 °C. Then, 3 mL of TEOS were added into the solution and the reaction occurred during 24 h under permanent stirring. 170 nm silica particles were synthesized through a similar procedure at room temperature.

The functionalization of the silica beads was carried out by adding methacryloxypropyltrimethoxysilane (MPS) or methacryloxymethyltriethoxysilane (MMS) (Figure 1) directly into the nanoparticles dispersion. The amount of coupling agent was calculated such as their density at the nanoparticle surface was assumed to be nominally 0.1, 1, or 5 molecules nm^{-2} . After it was left to react overnight, the mixture was held at 80 °C for 1 h to promote covalent bonding of the organosilane to the surface of the silica nanoparticles.¹³ The silica suspensions were then purified through dialysis against water until neutral pH was reached and finally adjusted to 10 g L^{-1} .

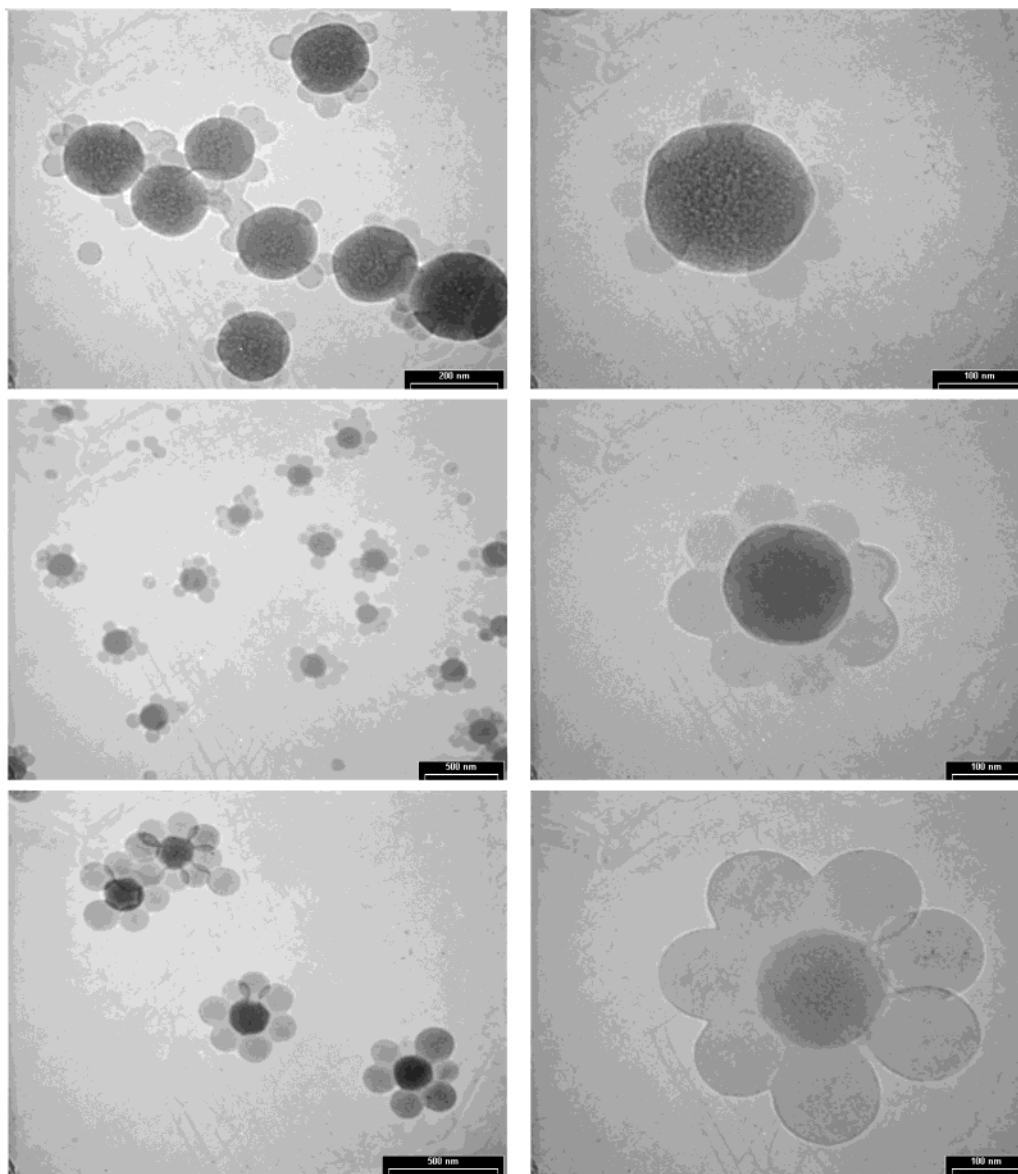


Figure 3. TEM pictures of daisy-shaped silica/polystyrene nanocomposites. Diameter of the MMS-grafted silica particles: 170 nm. Reaction time: 15 min (top); 30 min (middle); 1 h (bottom). Density of coupling agent: 0.1 molecules nm^{-2} .

Next, emulsion polymerization of styrene (100 g L^{-1}) was carried out within the silica suspension using a nonylphenol poly(oxyethylene) nonionic surfactant (NP30, 3 g L^{-1}) (Figure 1). The surfactant concentration was fixed in order to promote the growth of 170 nm latex particles within 2 h. The mixture was purged with nitrogen and heated to 70°C before addition of sodium persulfate (0.5 wt % relative to monomer) to initiate the reaction.⁹

Characterization. TEM experiments were performed with a JEOL 2000 FX microscope (accelerating voltage of 200 kV). The samples were prepared as follows: silica particles and nanocomposites were dispersed in water and one drop of the dilute suspension was deposited on a copper grid coated with a carbon membrane. 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. The nanohybrid morphology was characterized by transmission and scanning electron microscopies (TEM and SEM). Figure 2 shows that daisy-shaped particles are obtained after 1 h of reaction with 170 nm silica seeds. Each silica sphere is surrounded by polystyrene nodules with a diameter close to $135 \pm 10 \text{ nm}$, which seem to be strongly attached to the silica surface. No heterogeneous formation of free latexes can be observed. The reaction between free molecules of styrene and the methacrylate groups grafted onto the silica surface form copolymers during the first steps of the polymerization, further evolving as nuclei which grow with time to finally form polymer particles (see Figure 3). As a covalent bond is formed between the polymer nodules and the mineral seeds, no desorption of the organic petals can occur. The nucleation of polymer particles in solution followed by size-selected aggregation onto the silica seeds is not observed. The

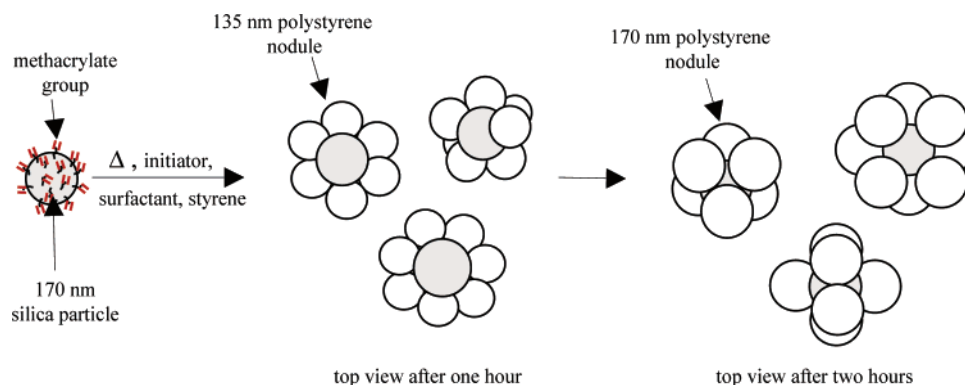


Figure 4. Schematic representation of the formation of the daisy- and multipod-like nanocomposites taking into account that the polymer nodules do not grow exactly at the same rate and that the silica colloids are not perfectly monodisperse in size.

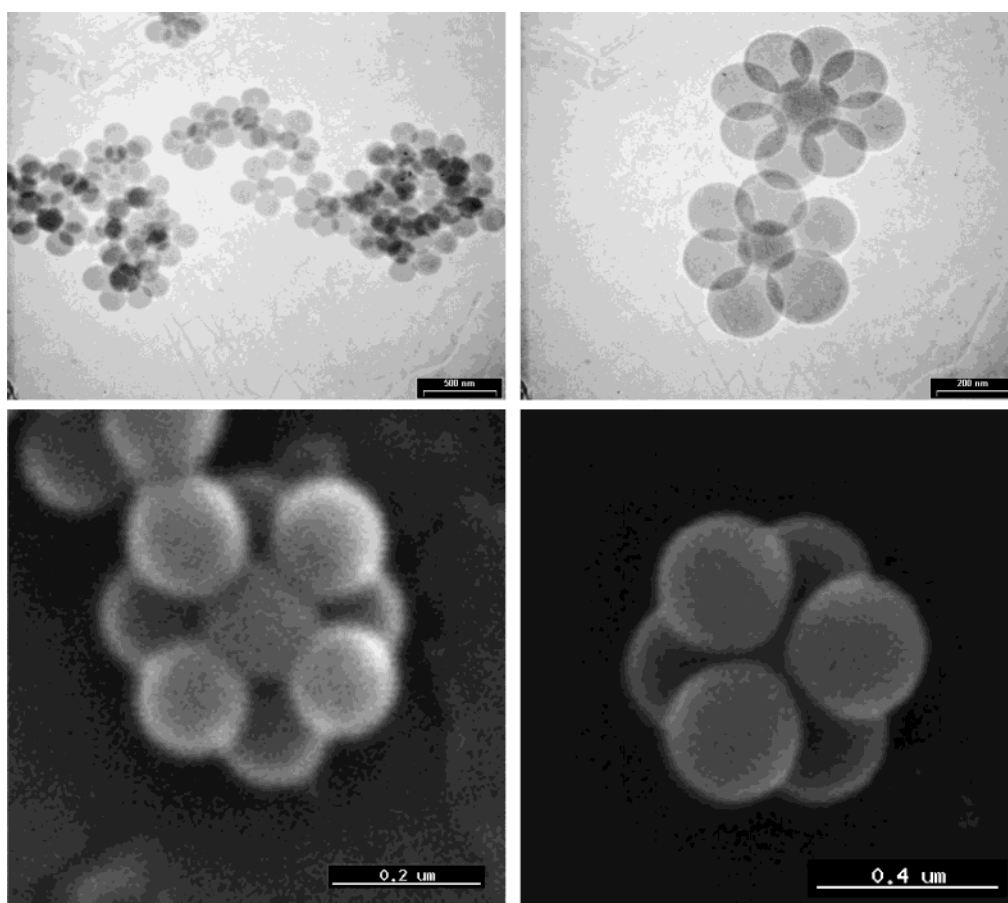


Figure 5. TEM (top) and SEM (bottom) pictures of silica/polystyrene hexapods and octopods. Diameter of the MMS-grafted silica particles: 170 nm. Reaction time: 2 h. Density of coupling agent: $0.1 \text{ molecules nm}^{-2}$.

spherical morphology of the polymer nodules results from a minimization of the surface energy. Some aggregated nanocomposites can be observed in Figures 2 and 3. This aggregation occurs during the drying of the sample for the microscopy experiments. A closer look at the TEM and SEM pictures shows that when the daisy-shaped nanoparticles have up to eight polystyrene petals, these are for the most part located in the same plane. When the number of nodules is larger than this value, at least one of them is located above (or below) the other ones.

The preferential coplanar growth of the latex particles should result from a decrease of the surface energy of the system. The schematic representation of the process involved in the synthesis of the daisy-shaped nanocomposites (see Figure 4) allows one to better understand the formation of this morphology. In fact, six 135 nm polystyrene nodules are needed to exactly surround a 170 nm silica sphere, taking into account a contact angle of $120 \pm 5^\circ$ resulting from the affinity of the polystyrene nuclei for the functionalized silica surface.

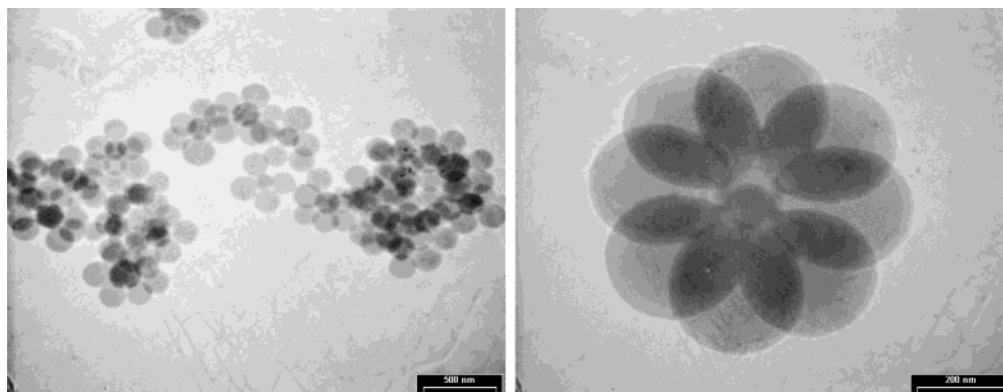


Figure 6. TEM pictures of silica/polystyrene hexapods and octopods. Diameter of the MMS-grafted silica particles: 170 nm. Reaction time: 14 h. Density of coupling agent: $0.1 \text{ molecules nm}^{-2}$.

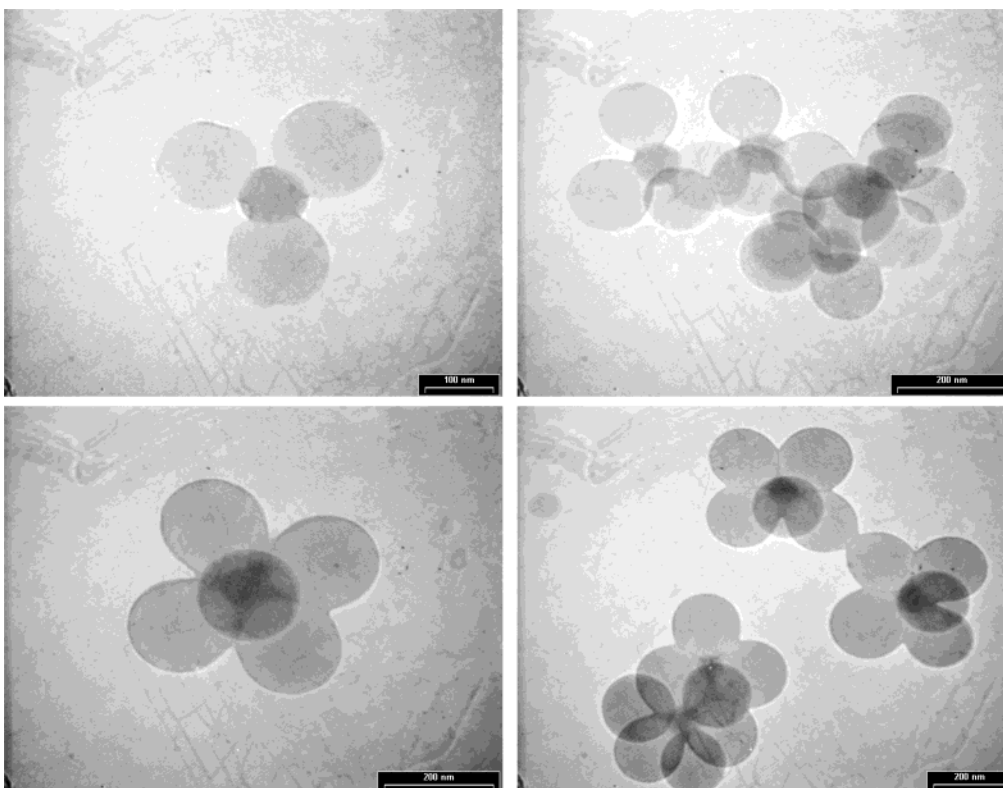


Figure 7. TEM pictures of silica/polystyrene nanocomposites. Diameter of the MPS-grafted silica particles: 80 nm. Reaction time: 1 h (top); 2 h (bottom). Density of coupling agent: $0.1 \text{ molecules nm}^{-2}$.

A slight and typical polydispersity of the silica precursors (ca. 10%) can partially explain the 5-, 7-, and 8-petal daisies shown in Figures 2 and 3. Moreover, the growth rate of the polystyrene nodules is not perfectly uniform with time. One can grow a little bit faster than others, forcing one or more petals to grow further out of the preferential plane because of steric reasons.

This displacement of the growth of some polystyrene nodules due to a steric hindrance involves an interesting evolution of the morphology of the nanocomposites with reaction time. As shown in Figure 5, hexapods or octopods constituted by a silica core and six or eight polystyrene nodules can be mainly observed after 2 h. Other morphol-

ogies (such as pentapods, heptapods, etc.) are also present in a small amount (25–30%). During the second hour of reaction, the barycenters of the polymer nodules move toward one moiety of the silica particle. They form equilateral triangles or squares (for hexapods and octopods, respectively), which shows the homogeneous size of the latices (i.e., 200 nm). These can then grow homogeneously without changing the global morphology of the nanocomposites anymore, as shown in Figure 6.

To verify if the ratio of the sizes of the silica seeds and the growing polystyrene nodules is a key parameter to control the morphology of the nanocomposites, the polymerization reaction was carried out starting with 80 nm silica particles

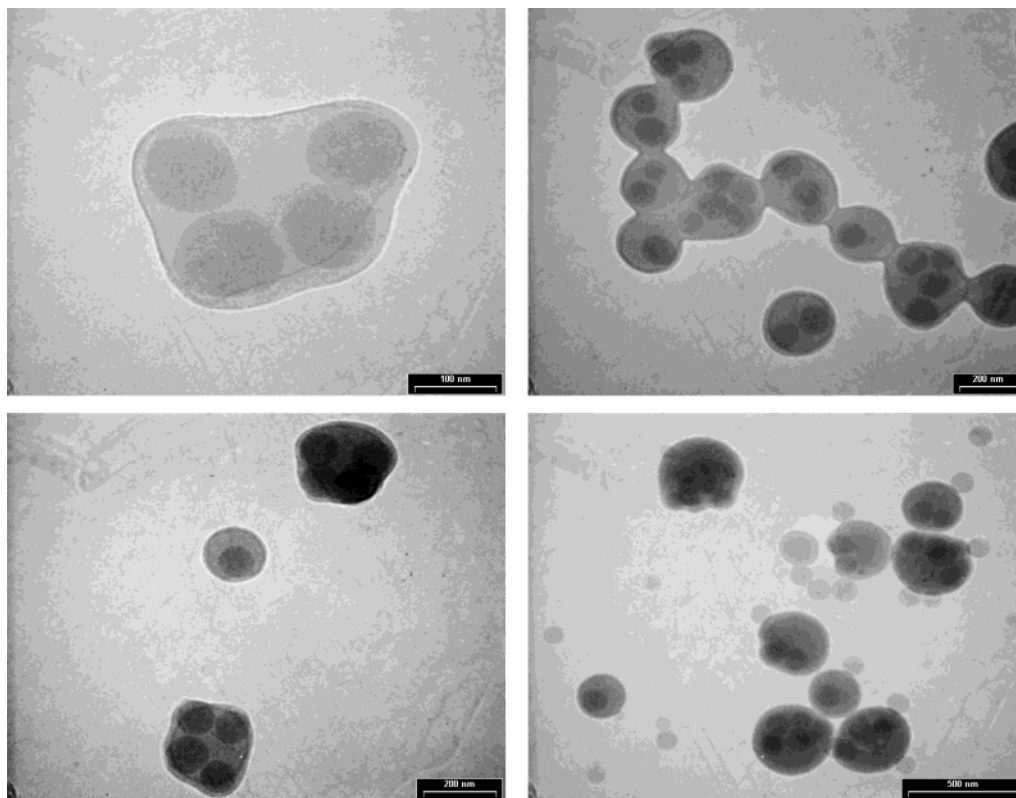


Figure 8. TEM pictures of silica/polystyrene nanocomposites. Diameter of the silica particles: 80 nm. Reaction time: 30 min (left); 1 h (right). Density of coupling agent: 1 MPS nm⁻² (top); 5 MMS nm⁻² (bottom).

grafted with MPS under similar experimental conditions. According to the previous discussion, multipods (mainly pentapods) with a small mineral core are formed after 2 h (see Figure 7). Once more, polymer nodules grow with time specifically at the surface of the mineral seeds.

The presence of the polymerizable groups at the surface of the silica particles is essential to get the daisy- and multipod-shaped nanocomposites, as similar polymerization carried out in absence of any of these derivatives involves only formation of polystyrene particles in the bulk. Moreover, the density of methacrylate groups at the silica surface strongly influences the final morphology of the nanohybrid materials. Indeed, polyencapsulation of the silica particles in a polystyrene matrix occurs when the reaction has been performed with 1 or 5 methacrylate functions per nm² at the surface of the silica beads (see Figure 8). This result can be explained by an increase of the affinity of the styrene molecules for the highly functionalized silica surface, which involves the formation of a polymer shell around the mineral particles.¹¹

Conclusion. In summary, we have demonstrated the highly controlled synthesis of daisy- and multipod-shaped polystyrene/silica nanocomposites through an emulsion polymerization. The morphology of the nanohybrid materials can be tuned by adjusting the density of polymerizable groups at the surface of the silica particles and the reaction time. The ability to form a statistically significant number of homogeneous nanomaterials makes this approach suitable for other studies aimed to use these structures as building blocks for more complex supraparticular assemblies. The incorporation

of reactive groups at the surface of the polymer nodules in order to allow the control of the ordering of the daisy- or multipod-shaped materials in two and three dimensions is the subject of intensive current and future studies.

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