

# Synthesis of hybrid colloidal particles: From snowman-like to raspberry-like morphologies

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## Abstract

Colloidal particles with a controlled morphology combining both organic and inorganic parts were synthesized through a seeded emulsion polymerization process. Silica seed particles (from 100 to 400 nm in diameter) were first surface-modified by the adsorption of an oxyethylene-based macromonomer. Then, emulsion polymerization of styrene was carried out in 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 to control the morphology of the final hybrid nanoparticles. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Hybrid; Colloids; Morphology; Emulsion polymerization

## 1. Introduction

In the last few decades, the interest for hybrid particles with complex shapes that combine organic and inorganic parts has increased considerably due to the potential benefits of these nanoobjects in multiple areas of materials science [1,2]. Indeed, controlling the morphology of colloidal particles is an absolute necessity if one intends to master their physico-chemical properties.

As a standard example, core-shell particles consisting of an inorganic core surrounded with an organic shell are currently produced and the range of materials available to get such morphologies is wide [3]. Raspberry-like morphologies have also been frequently reported [4–6]. Today, much attention is devoted to the elaboration of colloidal nanoparticles with tuneable shapes. Yin and Xia have first assembled monodispersed polymer beads by physical confinement in the cylindrical holes patterned in a thin film of photoresist [7]. Later, Manoharan et al.

have reported a method based on the drying of oil-in-water emulsion droplets containing spherical polystyrene colloids, resulting in the formation of colloidal clusters with 2, 3 and up to 15 colloids [8]. Following a similar strategy, Yi et al. have extended this process to other monophasic systems, either still polymeric (based on polymethylmethacrylate particles) or fully inorganic (hydrophobic silica clusters) [9]. In fact, the synthesis of hybrid colloidal assemblies has been first reported by Xia et al. with the successful formation of hetero-aggregates of spherical colloids using a principle almost identical to their previous work [10]. However, the association between both materials was only based on weak physical interactions, some attractive capillary forces having formed during solvent evaporation, what suggests that the mechanical and chemical resistance of these aggregates is rather limited. This point could be a major drawback for some critical applications as well as the size of the so-formed hybrid colloidal clusters—that was bigger than 1 μm in all the last works we have discussed about—and the amounts of produced particles that are quite limited.

Here, we focus on the synthesis of large amounts of submicron-sized hybrid nanoparticles, consisting of polystyrene nodules associated to one single silica particle, leading to

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controlled morphologies. They may offer potential interest in various fields like optics, electronics, etc. We present the results obtained while investigating a strategy based on the controlled surface nucleation and growth of polystyrene nodules at the surface of silica nanoparticles through a seeded emulsion polymerization process. This process allowed us recently to elaborate daisy-like, multipod-like and raspberry-like colloids [11,12]. The aim of this work is to first describe more precisely the key experimental parameters that allow us to obtain various hybrid colloidal structures with original morphologies. We also focus for the first time on the formation of hybrid colloidal particles consisting of one or two polystyrene nodules attached to a single silica nanoparticle.

## 2. Experimental procedure and data treatment

### 2.1. 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. The macromonomer, poly(ethylene glycol) 1000 monomethyl ether methacrylate (PEG methacrylate) was obtained from Polysciences, and the nonylphenol poly(oxyethylene) non-ionic surfactant (Synperonic NP30, Fluka) was used without further purification. Deionized water was obtained with a MilliQ system (Millipore), and ethanol was purchased from J.T. Baker. Transmission Electron Microscopy (TEM) experiments were performed with a JEOL 2000 FX microscope (accelerating voltage of 200 kV). Scanning electron microscopy (SEM) observations were performed with a JEOL JSM-840A scanning electron microscope operating at 10 kV. UV analyses were carried out with an UV/vis spectrophotometer (UNICAM UV 4).

### 2.2. Methods

#### 2.2.1. Silica seeds synthesis

Silica particles were synthesized according to the well-known Stöber sol–gel process where temperature, among other parameters, allows the control of the final particle size [13–15]. 500 mL of absolute ethanol (J.T. Baker) and 35 mL of the aqueous solution of ammonia were introduced in a three-neck round flask of 1 L equipped with a refrigerating system. The mixture was stirred at 300 rpm to homogenize and heated at different temperatures. 15 mL of tetraethoxysilane were added quickly and the reaction occurred under permanent stirring at the chosen temperature (Fig. 1a).

For the specific case of particles larger than 250 nm, the synthesis was performed in two steps, following an approach inspired from the literature [16]. In a first stage, silica particles with a mean diameter of 150 nm ( $S_{150}$ ) were generated as described previously, at room temperature. In a second step, the above suspension was used as a seed for the growth of silica in order to get particles with a final diameter close to 400 nm. A 20 mL aliquot of the  $S_{150}$  suspension ( $[S_{150}] = 8 \text{ g/L}$ ) was introduced in a 500 mL three-neck round flask equipped

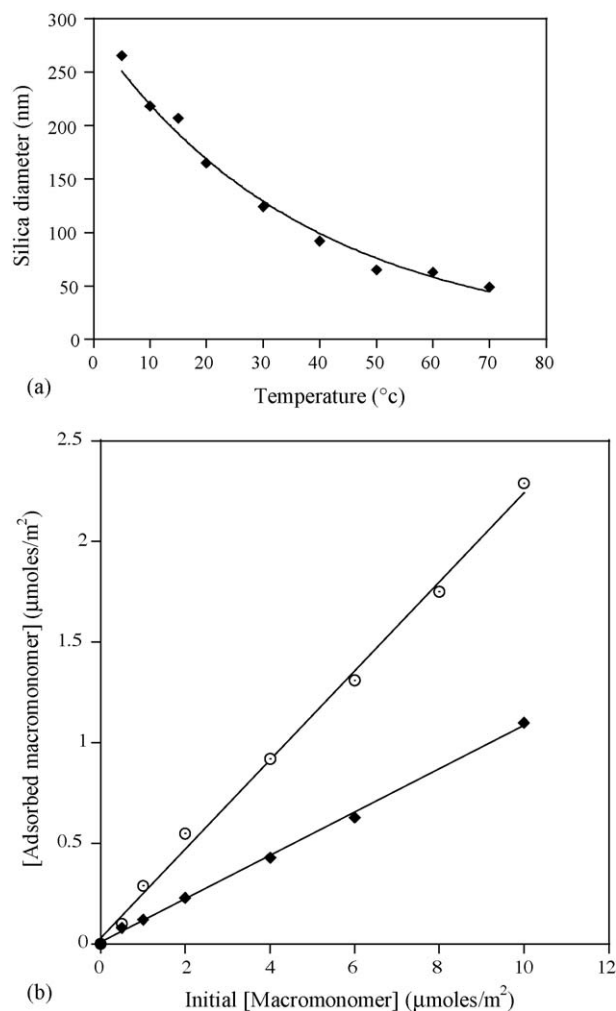


Fig. 1. (a) Evolution of the diameter of the silica particles as a function of the temperature. (b) Adsorption isotherms of macromonomer molecules onto 50 nm (full diamonds) and 400 nm (open circles) silica particles dispersed in water. ( $[S_{50}] = 1 \text{ g/L}$ ,  $[S_{400}] = 10 \text{ g/L}$ ;  $T = 25^\circ \text{C}$ ).

with a refrigerating system and containing 225 mL of absolute ethanol and 16 mL of the aqueous solution of ammonia. Then, a solution of 10 mL of TEOS diluted in 40 mL of absolute ethanol was introduced at the rate of 2 mL/h, at room temperature and under continuous stirring. In such conditions, the mixture was under the critical concentration of nuclei formation allowing the specific growth of silica seeds [17].

When the synthesis of silica particles was completed, the resulting suspension was dialyzed against water until neutral pH in order to remove the remaining reactants and replace ethanol with water. Silica suspensions were concentrated and their final concentration was determined by measuring the mass of a dried extract. Silica size was determined statistically by analyzing TEM pictures.

#### 2.2.2. Seeded emulsion polymerization process

Emulsion polymerization of styrene was performed in a thermostated reactor in the presence of the silica particles and the hydrophilic PEG methacrylate macromonomer. The macromonomer concentration was taken equal to  $1.55 \mu\text{moles}$

per m<sup>2</sup> of silica surface. The emulsion was stabilized by a non-ionic surfactant (NP30), at a concentration of 3 g/L chosen such as latex particles with a diameter close to 170 nm were obtained after 2 h of reaction. Then, the suspension was purged with nitrogen and heated at 70 °C before addition of sodium persulfate (0.5% by weight relative to monomer) to initiate the polymerization. Samples were taken from the batch at different times to study the kinetics of the reaction and its consequences on the particles morphology.

### 2.2.3. Adsorption isotherm determination

A known amount of the silica dispersion was mixed with a known volume of calibrated absorption solutions. The dispersion was stirred at 300 rpm during 3 h to reach the equilibrium. It was next centrifuged at 4600 rpm for 40 min, and the macromonomer concentration in the supernatant was determined by UV spectroscopy analysis at 208 nm. A calibration curve was used to determine the absorbent concentration in the supernatant solution.

## 3. Results and discussion

### 3.1. Preliminary studies

#### 3.1.1. Synthesis of silica particles

A few works [18,19] have been devoted to the synthesis of silica particles according to the Stöber procedure. The results show that three main parameters affect the particles size and distribution (temperature of the reaction, TEOS and ammonia concentration). In this work, we have focused on the first one. As shown in Fig. 1a), the diameter of the silica particles decreases exponentially when the temperature increases, according to the Arrhenius law. A similar result was previously observed [20,21] and can be attributed to the fact that an increase of the temperature facilitates the nucleation rate.

To overcome the intrinsic hydrophilic character of the silica particles and to favor the growth of polystyrene nodules on their surface, a coupling agent is needed. Previous works [11] have demonstrated that such a surface affinity may be tuned by the preliminary adsorption of macromonomer molecules based on ethylene oxide units. This macromonomer is mainly hydrophilic due to the presence of ethylene oxide groups ( $n \sim 23$ ), which are able to form hydrogen bonds with silanol functions present on the silica surface. It is indeed well-known that poly(ethylene oxide) strongly adsorbs onto silica nanospheres [22]. At one of its ends, this molecule also contains a methacrylate group that constitutes a polymerizable group for the later reaction of styrene. In order to determine the behavior of the macromonomer on the silica surface, adsorption isotherms were performed (Fig. 1b).

Whatever the diameter of the silica particles, the amount of adsorbed macromonomer molecules increases linearly with the initial concentration of coupling agent. The adsorbed amount represents roughly 12% and 24% of the initial amount added in the reactor, for the 50 and 400 nm silica particles, respectively. No plateau is observed in the range of concentration 0–10 μmol/m<sup>2</sup>, suggesting that the saturation of the surface of

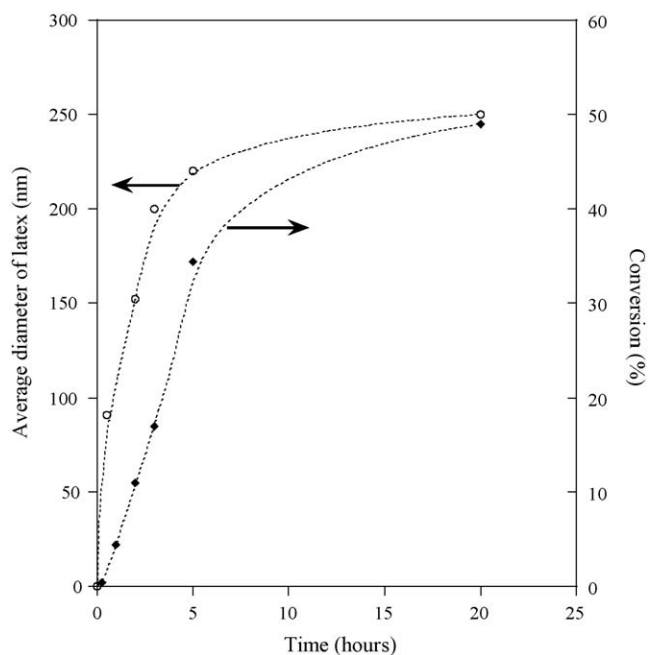


Fig. 2. Conversion versus time curves for emulsion polymerization of styrene performed at 70 °C in the absence of silica particles. [Styrene] = 10 g/L.

the silica seeds does not occur. According to the results of a preliminary study [11], the following experiments were carried out with a concentration of the coupling agent of 1.55 μmol/m<sup>2</sup>, which allows the preferential growth of the polystyrene nodules on the surface of the mineral particles.

#### 3.1.2. Kinetics of polymerization

The evolution of the conversion rate as a function of time is depicted in Fig. 2. It shows that the mechanisms involved in the polymerization process can be divided in three distinct categories, an initiation phase in the earliest period of the reaction, a linear evolution, corresponding to the growth of the polymer nodules and a stabilization phase.

Preliminary studies have shown that the presence of silica particles does not introduce any variation of the kinetics of the polymerization [23]. This phenomenon is related to the introduction of a large amount of surfactant, which inhibits the potential stabilization of the growing polystyrene nodules by the silica particles.

This study allowed us to determine the quantity of latex particles that were formed during the reaction, which was found to be constant. Therefore, we are able to precisely adjust the value of the ratio between the number of silica seeds ( $N_S$ ) and the number of polystyrene nodules ( $N_P$ ), which is a key parameter to control the morphology of the resulting hybrid particles.

### 3.2. Observed morphologies

#### 3.2.1. $N_P/N_S = 1$

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 (Fig. 3a).

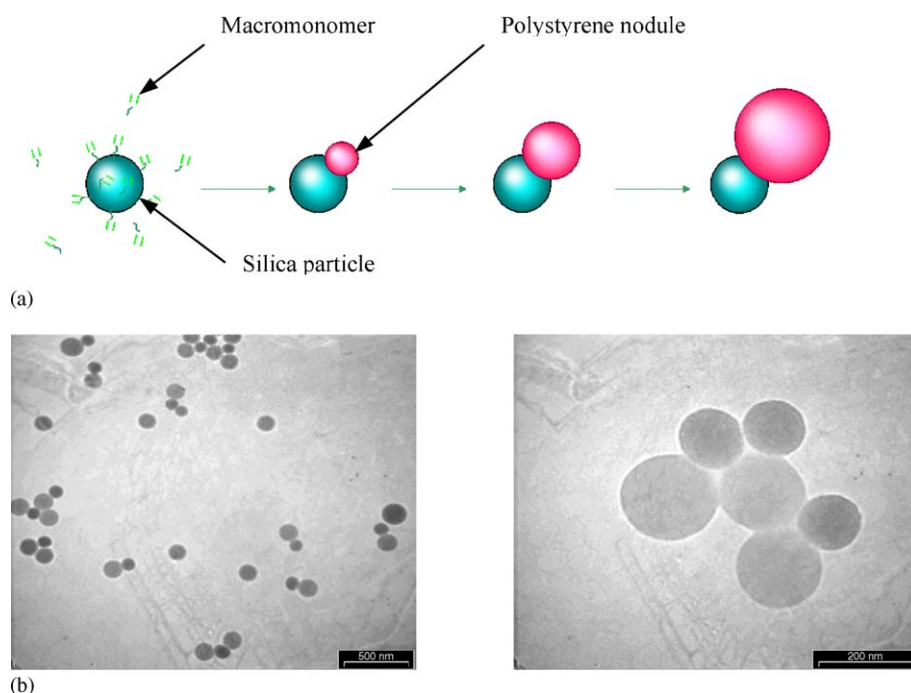


Fig. 3. (a) Schematic representation of the growth of the polystyrene nodule on the silica surface. (b) TEM pictures of hybrid nanocomposites when  $N_p/N_s = 1$ . Diameter of the silica seeds: 100 nm. Reaction time: 2 h. Scale bar: 500 nm (left); 200 nm (right).

The hybrid particles obtained when the ratio between the amounts of both types of particles is close to 1 have been observed by transmission electron microscopy (TEM). Some representative pictures of the samples are provided in Fig. 3b. As it can be expected, each polystyrene nodule is in average bound to one silica particle, leading to the formation of a large majority of hybrid structures with a snowman-like morphology.

### 3.2.2. $N_p/N_s = 2$

To verify if the ratio between the silica seeds and the growing polystyrene nodules is a key parameter to control the morphol-

ogy of the nanocomposites, the polymerization reaction was carried out with a ratio  $N_p/N_s$  close to 2. As shown in Fig. 4a), hybrid structures resulting from the growth of two latex particles on one silica seed are mainly obtained.

A closer look at these nanocomposites allows one to note that the angle between the two polystyrene nodules grown on the mineral sphere can take three different values. Indeed, statistical analysis reveal that it is equal to  $60^\circ$ ,  $90^\circ$  or  $120^\circ$  for ca. 25%, 50% and 25% of the hybrid particles, respectively (Fig. 4b). Further experiments are needed to explain both the geometric dispositions of the polymer nodules on the mineral

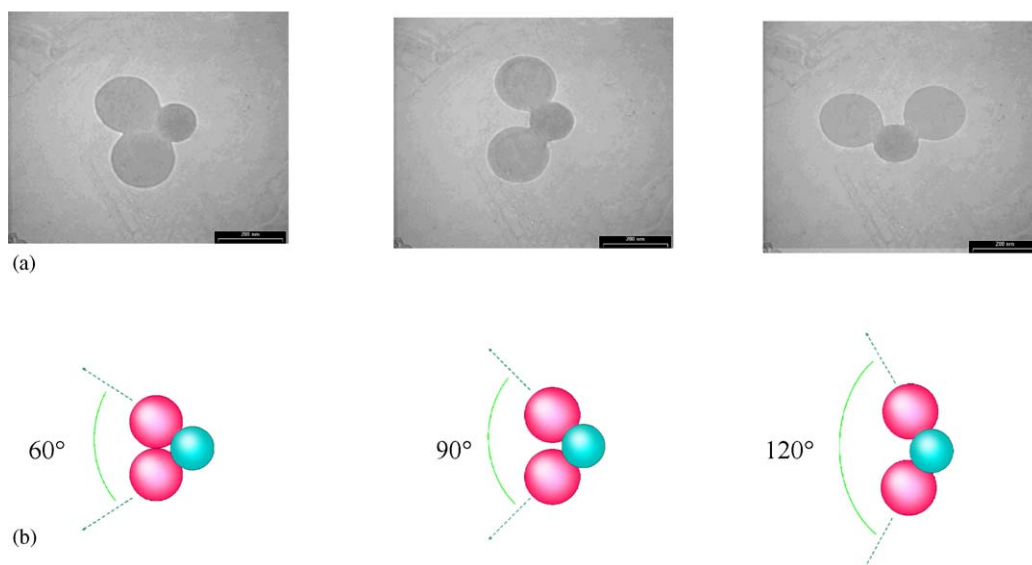


Fig. 4. (a) TEM pictures of hybrid nanocomposites when  $N_p/N_s = 2$ . Diameter of the silica seeds: 100 nm. Reaction time: 2 h. Scale bars: 200 nm. (b) Schematic representation of the three observed configurations resulting of the growth of two polymer nodules on one silica particle.

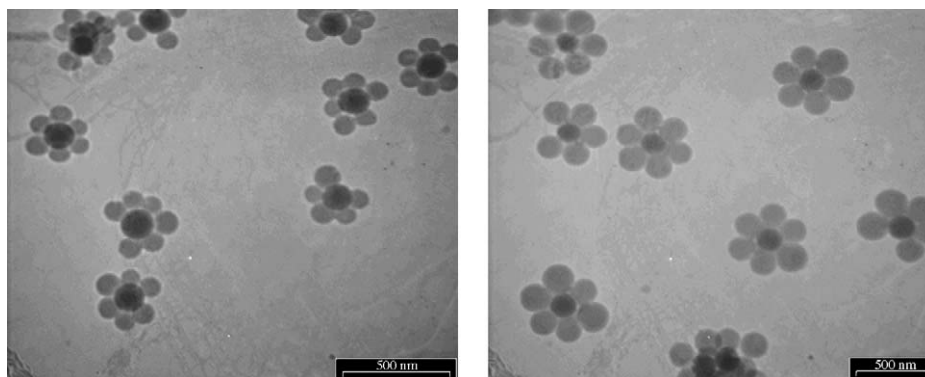


Fig. 5. TEM pictures of daisy-shaped nanocomposites obtained when  $N_P/N_S = 6$ . Diameter of the silica seeds: 200 nm. Reaction time: 30 min (left) and 1 h (right). Scale bars: 500 nm.

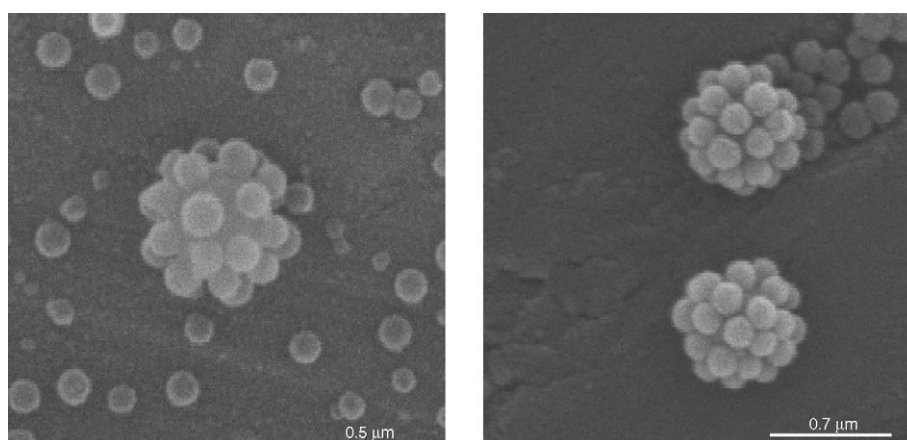


Fig. 6. TEM pictures of raspberry-like hybrid particles obtained when  $N_P \gg N_S$ . Diameter of the silica seeds: 325 nm (left); 450 nm (right). Reaction time: 2 h. Scale bar: 500 nm (left); 700 nm (right).

seeds and the statistical distribution between the three observed configurations.

### 3.2.3. $N_P/N_S = 6$

Fig. 5 shows that daisy-shaped particles are obtained after one hour of reaction. Each silica sphere is surrounded by six polystyrene nodules. A closer look at the TEM pictures shows that the polystyrene petals are located in the equatorial plane of the silica spheres. At the early stages of the reaction (Fig. 5a), they are not in contact. As they grow with time, they get in touch with their neighbors and completely surround the mineral seeds (Fig. 5 (left)). Such a preferential coplanar growth of the latex particles should result from a decrease of the surface energy of the system.

### 3.2.4. $N_P \gg N_S$

When the number of silica seeds is much smaller than the number of polymer nodules, raspberry-like particles are obtained (Fig. 6). Indeed, polystyrene nodules cover the entire silica surface, whatever the size of the mineral seed. They are mainly six-fold coordinated with their neighbors, while some of them are five-fold coordinated, in agreement with the fact that a perfect hexagonal lattice known in flat geometry is not able to fit

a curved topology. Additional experiments, not presented here, showed that the raspberry morphology was obtained in the very early stages of the reaction. This result underlines once more the determining role of the adsorbed macromonomer molecules, which strongly favors the polymerization process on the silica surface.

## 4. Conclusion

In summary, we have demonstrated the highly controlled synthesis of polystyrene/silica nanocomposites with various original morphologies through an emulsion polymerization process. The morphology of the hybrid particles can be tuned by adjusting the ratio between the number of the silica seeds and the number of the polystyrene nodules. 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 these original colloidal materials in two or three dimensions is the subject of intensive current and future studies in our group.

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## References

- [1] C. Sanchez, G.J. de, A.A. Soler-Illia, F. Ribot, T. Lalot, C.R. Mayer, V. Cabuil, *Chem. Mater.* 13 (2001) 3061–3083.
- [2] E. Bourgeat-Lami, *Dendrimers, Assemblies and Nanocomposites*, in: R., Arshady, A., Guyot (Eds.), Citus Book Editions, London, 2002, 149–194.
- [3] F. Corcos, E. Bourgeat-Lami, C. Novat, J. Lang, *Colloid Polym. Sci.* 277 (1999) 1142–1151.
- [4] C. Barthet, A.J. Hickey, D.B. Cairns, S.P. Armes, *Adv. Mater.* 11 (1999) 408–410.
- [5] M.S. Fleming, T.K. Mandal, D.R. Walt, *Chem. Mater.* 13 (2001) 2210–2216.
- [6] K. Kulbaba, R. Resenes, A. Cheng, A. Bartole, A. Safa-Senat, N. Coombs, H.D.H. Stöver, J.E. Greedan, G.A. Ozin, I. Manners, *Adv. Mater.* 13 (2001) 732–736.
- [7] Y. Yin, Y. Xia, *Adv. Mater.* 13 (2001) 267–271.
- [8] V.N. Manoharan, M.T. Elsesser, D.J. Pine, *Science* 301 (2003) 483–487.
- [9] G.R. Yi, V.N. Manoharan, E. Michel, M.T. Elsesser, S.M. Yang, D.J. Pine, *Adv. Mater.* 16 (2004) 1204–1207.
- [10] Y. Xia, Y. Yin, Y. Lu, J. MacLellan, *Adv. Funct. Mater.* 13 (2003) 907–918.
- [11] S. Reculosa, C. Poncet-Legrand, S. Ravaine, C. Mingotaud, E. Duguet, E. Bourgeat-Lami, *Chem. Mater.* 14 (2002) 2354–2359.
- [12] S. Reculosa, C. Mingotaud, E. Bourgeat-Lami, E. Duguet, S. Ravaine, *Nano Lett.* 4 (2004) 1677–1682.
- [13] W. Stöver, A. Fink, E. Bohn, *J. Colloid Interface Sci.* 26 (1968) 62–69.
- [14] C.G. Tan, B.D. Bowen, N. Epstein, *J. Colloid Interface Sci.* 118 (1987) 290–293.
- [15] R. Lindberg, G. Sundholm, B. Pettersen, J. Sjöblom, S.E. Friberg, *Colloids Surf. A* 549 (1997) 123–124.
- [16] S. Kang, S.I. Hong, C.R. Choe, M. Park, S. Rim, J. Kim, *Polymer* 42 (2001) 879–887.
- [17] S.L. Chen, P. Dong, G.-H. Yang, J.-J. Yang, *J. Colloid Interface Sci.* 180 (1996) 237–241.
- [18] M. Szekeres, J. Tóth, I. DeKány, *Langmuir* 18 (2002) 2678–2685.
- [19] R. Lindberg, G. Sundholm, B. Pettersen, J. Sjöblom, S.E. Friberg, *Colloids Surf. A* 123–124 (1997) 549–560.
- [20] C.G. Tan, B.D. Bowen, N. Epstein, *J. Colloid Interface Sci.* 118 (1987) 290–293.
- [21] S.K. Park, K.D. Kim, H.T. Kim, *Colloids Surf. A* 197 (2002) 7–17.
- [22] F. Corcos, E. Bourgeat-Lami, C. Novat, J. Lang, *Colloid Polym. Sci.* 277 (1999) 1142–1151.
- [23] E. Duguet, S. Reculosa, A. Perro, C. Poncet-Legrand, S. Ravaine, E. Bourgeat-Lami, C. Mingotaud, *Mater. Res. Soc. Symp. Proc.* 847 (2005) (EE1.1.1-10).