Synthesis of Hybrid Core−Shell Nanoparticles by Emulsion (Co)polymerization of Styrene and γ-Methacryloxypropyltrimethoxysilane

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ABSTRACT: Core−shell nanoparticles with a polystyrene core and a hybrid copolymer shell were synthesized via emulsion polymerization of styrene and subsequent addition of γ-methacryloxypropyltrimethoxysilane (MPS) to produce the shell by copolymerization reaction of MPS with the residual amount of styrene. The influences of pH, the amount of MPS, and the addition mode of MPS on the particles size, morphology, and copolymer architecture in the shell were studied using dynamic light scattering (DLS), transmission electron microscopy (TEM), gas chromatography (GC), differential scanning calorimetry (DSC), solid-state NMR, and infrared (IR) spectroscopy.

Introduction

Nanoparticles are characterized by a high surface-to-volume ratio, allowing high reactivity at the nanosize or at the molecular level. The length scale effect involved make these particles really attractive in various fields of material science, such as optics, catalysis, microelectronics, coatings, biology, medicines, etc. In addition, organic−inorganic hybrid materials have recently raised interest in material science as they can exhibit an extremely high number of architectures and forms.[1−3] In particular, heterophase polymerization and colloidal chemistry make it possible to control the functionality of the particles surface and enable the synthesis of hybrid organic−inorganic colloids with designed morphologies at the nanoscale.[4] In a recent work, Tissot and Bourgeat-Lami[5−7] synthesized SiOH-functionalized polymer latexes using γ-methacryloxypropyltrimethoxysilane (MPS) as functional (co)monomer. The functionalized particles were used further to grow a silica shell by the sol−gel process.[7] They studied the influence of pH, the concentration of MPS, and the surfactant nature on the latex particles size, morphology, and surface properties. The authors found that the nature of the surfactant has a drastic influence on colloidal stability. They also found that the hydrolysis and condensation reactions of MPS depend on the concentration of MPS and on the pH of the suspension medium.

The simultaneous hydrolysis and condensation reactions of the alkoxysilyl groups make both the microstructure and morphology of the particles difficult to control. Actually, little research has been focused in this field, and only a few researchers have reported works on the polymeric system in question using semibatch processes,[8] pH control methods,[9] or miniemulsion polymerization techniques.[10−12] Most attention was paid to practical applications of the particles rather than to the analysis of the complexity of the reactions involved and of the resulting microstructure of the hybrid copolymers.[12,13]

The present paper deals with the preparation of core−shell nanoparticles with a polystyrene core and a hybrid copolymer shell and addresses the effects of operating conditions on the copolymer microstructure and particles morphology. Following our previous works, the shell is produced by emulsion copolymerization of styrene and MPS as illustrated in Figure 1. The effects of pH, the amount of MPS, and the addition mode of MPS on the latex stability, morphology, and copolymer architecture in the shell were studied in detail by doing further analyses such as transmission electron microscopy (TEM), dynamic light scattering (DLS), gas chromatography (GC), differential scanning calorimetry (DSC), solid-state NMR, and infrared spectroscopy (IR) in order to optimize the process of fabrication of the core−shell hybrid nanoparticles.

Experimental Section

Materials. Styrene (Aldrich) was distilled under vacuum before use. Potassium persulfate (KPS, Acros Organics) was used as initiator, and dodecyl thiol ($C_{12}H_{25}$-SH, Aldrich) was used as chain transfer agent. The surfactant was dimethylpropylammonium sulfonate (Ralufon, Aldrich) which was found in our previous work[6] to be an efficient stabilizer. γ-Methacryloxypropyltrimethoxysilane (MPS, Aldrich) was used as supplied. The water was desionized on mixed bed resins.

Preparation of the Hybrid Core−Shell Nanoparticles. The hybrid core−shell nanoparticles were prepared in two steps (Figure 1). Emulsion homopolymerization of styrene was first carried out at 70 °C up to ~70% conversion, using KPS

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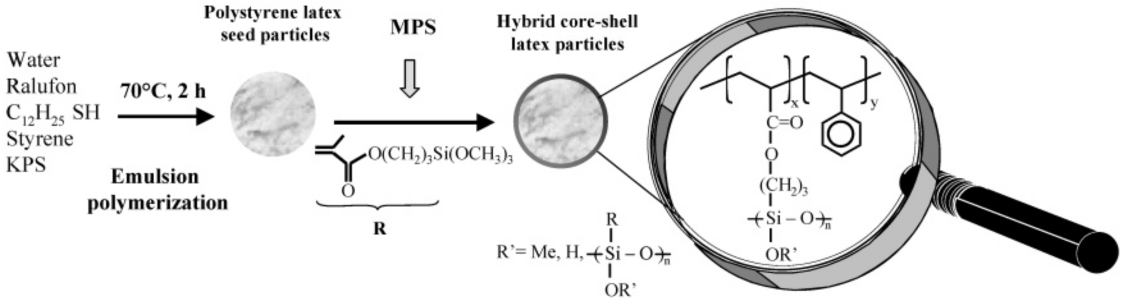

Figure 1. Schematic representation of the formation of the hybrid core−shell nanoparticles by semibatch emulsion polymerization.

as initiator, dodecyl thiol as transfer agent, and Ralufon as surfactant. Then, a given amount of MPS was added as a shot or semicontinuously at a fixed rate to the suspension medium, and the copolymerization of styrene and MPS was continued until the steady-state conversion was reached. The pH value of the suspension was fixed at 7 by adding equivalent quantities of ammonium dihydrogen phosphate and disodium hydrogen phosphate or at 8.5 by adding sodium hydrogen carbonate. A typical recipe was as follows: styrene, 90 g; KPS, 0.7 g; chain transfer agent, 5.4 g; surfactant, 0.8 g; buffer, 0.2 g; water, 210 g; MPS, 9 g. In the semibatch processes and unless stated otherwise, the MPS feed rate was a constant 4.5 g/h for every recipe, regardless of the experimental conditions.

For the purposes of comparison, latexes were synthesized under identical conditions in the absence of styrene. Typically, 9 g of MPS was introduced at once at 70 °C in a double-wall thermostated reactor containing 210 g of water, 0.8 g of surfactant, 0.7 g of KPS, and 0.2 g of buffer and allowed to react for 3 h under mechanical stirring. The suspension pH was adjusted at 7 or at 8.5 as described above.

Characterization. ^{29}Si solid-state NMR measurements were performed on a Bruker DSX-300 spectrometer operating at 59.6 MHz by use of cross-polarization from protons. The contact time was 5 ms, the recycle delay 1 s (sufficient for a full relaxation of protons), and the spinning rate 5 kHz. The ^{29}Si NMR spectra were simulated using the DM-FIT program for quantitative analysis. The overall and the individual monomer conversions and the rate of MPS hydrolysis were measured by gas chromatography (GC). Aliquots were withdrawn as a function of time and dissolved in appropriate amounts of THF which was used as an internal standard for GC calibration. From the ratios of the peak areas of styrene, MPS, and methyl alcohol (MeOH) to THF obtained by GC, the concentrations of residual monomers and MeOH could be obtained.

Infrared spectra were recorded using a Nicolet FTIR 460 spectrometer on powder-pressed KBr pellets. Polymer samples were prepared by putting the latex into an oven at 100 °C for half an hour and then drying under vacuum at 50 °C for 5 h in order to remove most of the water and the residual amount of monomer. FTIR spectra were obtained at room temperature in the transmission mode between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1}.

The glass transition temperature (T_g) of the synthesized hybrid materials was measured using differential scanning calorimetry (DSC). Appropriate amounts of samples (dried as mentioned previously) were sealed in aluminum sample pans and prepared by compression molding. DSC thermoscans of the hybrid materials were then conducted under a dry nitrogen atmosphere at a heating rate of 20 °C/min from −80 to 180 °C in two scans using a Setaram DSC 131 apparatus.

Transmission electron microscopy analysis (TEM) was performed with a Phillips CM10 electron microscope operating at 80 kV. In a typical experiment, the latex suspension was diluted, and one drop of the colloidal dispersion was put on a carbon film supported by a copper grid and allowed to dry before observation.

The diameter, D_p, of the latex particles was measured by dynamic light scattering (DLS) using a Malvern Autosizer Lo-C instrument with a detection angle of 90°. The particle number per unit volume of water was calculated by the following equation:

$$Np/L = \frac{M\frac{C}{\rho}}{\frac{\pi}{6}{D_p}^3 V} \times 10^{19} \tag{1}$$

where M (g) is the mass of total monomers, C (%) is the overall conversion determined by GC, ρ (g cm^{-3}) is the density of the polymer,[14] D_p (nm) is the latex particles diameter, and V (L) is the total volume of water.

The fractional reduction of the particle number (FRPN) was calculated as follows:

$$\text{FRPN (\%)} = \frac{N_{p,init} - N_{p,end}}{N_{p,init}} \times 100 \tag{2}$$

where $N_{p,init}$ is the particle number before adding MPS and $N_{p,end}$ is the particle number at the end of the copolymerization reaction. The FRNP parameter represents the balance between the rate of new particles formation, radical capture, and particle−particle agglomeration.

Results and Discussion

Synthesis of Core−Shell Particles and Scheme of the Related Reactions. As mentioned above, styrene is homopolymerized up to around 70% conversion in order to yield a latex core through conventional emulsion polymerization. In a second step, residual styrene is allowed to copolymerize with MPS—added as a shot or semicontinuously—in order to form the shell of the nanoparticles.

The thermodynamic criterion governing the core−shell structure of the latex is that the final morphology of the particles should minimize the Gibb's free energy of the system. From this thermodynamic criterion, it can be concluded that the smaller the interfacial tension of the shell material, the easier the formation of the core−shell structure.[15] In the system under consideration, the particles surface contains hydrophilic SiOH groups formed by hydrolysis of the alkoxysilyl moieties of the copolymer.[7] The presence of these SiOH groups is expected to significantly decrease the surface tension of the shell which process promotes the formation of the above-mentioned core−shell structure. In the meantime, cross-linking of the shell through siloxane bounds formation prevents the movement of chain segments and stabilizes therefore the core−shell morphology. Unfortunately, the core−shell structure cannot be identified by TEM as the core and shell materials display nearly the same contrast (see Figure 2). However, the fact that the particles exhibit a narrow size distribution (there is no formation of a secondary population of particles) and that their diameter, determined either

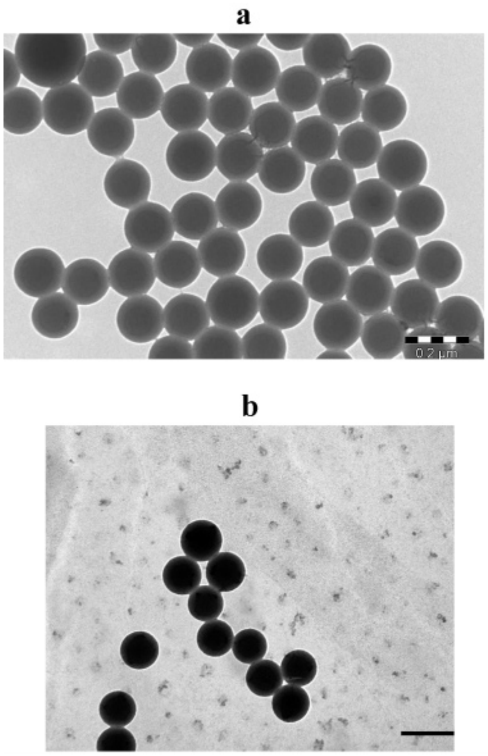

Figure 2. Transmission electron microscopy (TEM) pictures of the hybrid core−shell latex particles. (a) pH = 7 and (b) pH = 8.5. [MPS] = 10 wt % relative to styrene. Scale bar: 200 nm.

Table 1. Comparison of the Latex Particle Diameters Measured by DLS and by TEM (pH = 7 and [MPS] = 10 wt % Relative to Styrene)

particles diameter (nm)	before adding MPS	after copolymerization
DLS	126.8	155.7
TEM	115.3	146.4

by TEM or by DLS increases after copolymerization (see Table 1) strongly supports the assumption of formation of core−shell particles.

Although the copolymerization reaction occurring in/on the shell is expected to be the main reaction after the emulsion homopolymerization of styrene, a number of side reactions are likely to take place simultaneously with the copolymerization process. First, the MPS organosilane is easily hydrolyzed into silanetriols at appropriate pH conditions. Therefore, MPS is initially insoluble in water but becomes soluble as soon as the methoxy groups are converted into hydroxyl groups. The rate at which hydrolysis is taking place is expected to significantly influence consequently the partitioning of the silane molecule between the water phase and the latex seed particles. Silane partitioning is also dependent on the silane concentration. The silanetriols are metastable and self-condense in the water phase to yield cyclic molecules and higher molecular weight polysiloxane oligomers.[16] They can also undergo homopolymerization or copolymerization although the latter event is suspected to be marginal as most of the styrene monomer is contained into the latex particles and the remaining amount of styrene in the water phase is very low. The polysiloxane oligomers may either continue to grow in the water phase until the formation of water insoluble clusters and/or nanoparticles or may be captured by the seed particles where they can undergo further chemical reactions as for instance copolymerization with styrene. On the other hand, MPS molecules contained into the latex particles are suspected to be mainly involved into copolymerization reactions as their contact with water is greatly hindered.

The formation of the core−shell structure and possible microstructure of the hybrid copolymer shell is illustrated in Figure 3. It appears from Figure 3 that the copolymerization and hydrolysis−condensation reactions result in competitive mechanisms, which may be significantly influenced by the reaction conditions. It is therefore of great importance to understand how the reaction conditions affect the copolymer shell architecture and the balance between polymerization in/on the seed particles and in the water phase.

Study of the Influence of pH. To investigate the effect of pH, three experiments were realized at different pH values, corresponding to acidic (pH = 2), neutral (pH = 7), and basic (pH = 8.5) conditions. A relatively low concentration of MPS was chosen in order to minimize the influence of this second parameter, which will be discussed later.

Influence of pH on the Particle Size. The particle size and particle size distribution are a result of competitive mechanisms taking place during the reac-

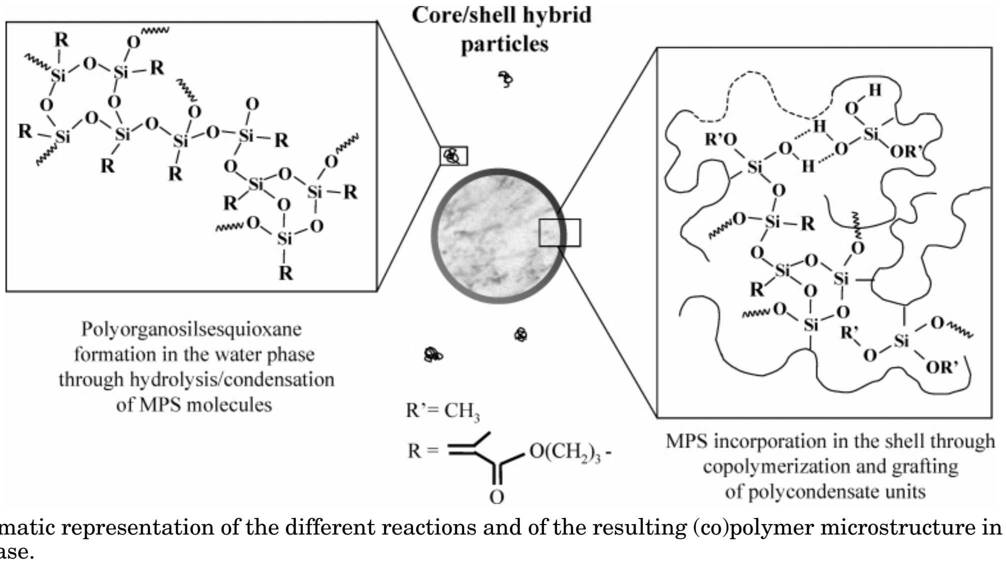

Figure 3. Schematic representation of the different reactions and of the resulting (co)polymer microstructure in the shell and/or in the water phase.

Table 2. Effect of pH on the Diameter and Number of the Latex Particles for a Constant MPS Concentration ([MPS] = 10 wt % Relative to Styrene)

		pH value			
		2	7[a]	8.5	7[b]
before adding MPS	diameter (nm)	137.5	126.8	132.9	144.3
	particle no./L	2.5×10^{17}	2.9×10^{17}	2.6×10^{17}	2.4×10^{17}
after copolymerization	diameter (nm)	*c*	155.7	211.8	152.3
	particle no./L	*c*	2.4×10^{17}	9.0×10^{16}	2.5×10^{17}
fractional reduction of the particle no. (%)		*c*	17.8	65.9	1.0

[a] Adjusted to 7 at the beginning of polymerization and allowed to cascade. [b] pH maintained at 7 all long during polymerization. [c] Gel formation.

tion. First of all, micellar or homogeneous nucleations give birth to new particles that grow by consuming the monomer. Coagulation might occur if the amount of surfactant is not sufficient especially with increasing solids content. The agglomeration phenomenon is evidenced experimentally by a discontinuous increase in the particle size or in other words by a decrease in the particle number while renucleation most often leads to a decrease in particles size (i.e., an increase of particles number). As will be shown below, the introduction of MPS into the latex suspension always give rise to a decrease of the particles number which effect depends, among other operating conditions, on pH. The effect of pH should be considered from two points of view. On one hand, the pH may influence the properties of the surfactant and its ability to adsorb on the particles surface, promoting therefore physicochemical coagulation of the latex. In the present study, a zwitterionic surfactant was used in order to reduce the influence of pH on surfactant adsorption. On the other hand, pH influences the hydrolysis/condensation rates, resulting in chemical cross-linking. As reported by Savard et al.,[16] MPS hydrolysis is catalyzed by both acid and alkali, the relative rate of the hydrolysis in acidic, basic, and neutral medium being of the order of 100:10:1.

The influence of pH on the latex stability can be monitored by following the evolution of particles size during the seeded-growth process. The particles diameter and the corresponding particles number, before, and after adding MPS are reported in Table 2. It can be seen in Table 2 that these two sets of values show some variation in the pH range from 2 to 8.5.

When the reaction is performed at low pH (i.e., pH = 2), the latex immediately turns to a gel as evidenced by a sudden increase in viscosity. This is probably due to chemical cross-linking allowed by the strong interaction of Si−OH groups at the surface of the particles. Indeed, under acidic conditions, hydrolysis is fast whereas condensation is relatively slow. This leads to the formation of open, extended chainlike structures that can play the role of chemical cross-linker in the suspension medium and promote bridging flocculation and gelation. In contrast, under basic conditions, condensation is more rapid resulting in the formation of dense clusters and/or particles. As mentioned before, these primary polycondensates may either stabilize (and form new particles) or precipitate on the latex seed and contribute to shell formation. At this point, we cannot differentiate between the two routes although the latter appears to be the most consistent with the observed data. The decrease of the particles number suggests however a limited stability of the resulting core−shell colloids. This may be related to the nature of the surface which displays less interaction with the surfactant than the original polystyrene latex particles. It is known from previous works in the literature that the nature of the surfactant is a determinant parameter that governs the colloidal stability of organo-alkoxysilane-functionalized polymer latexes.[13] The interaction of the surfactant molecule with the particle surface may be significantly influenced by the low surface energy profile associated with the presence of silicone bonds.

In the case of pH = 7, the hydrolysis rate of the methoxy groups is about 1% of that which is expected in acidic conditions,[16,17] which drastically reduces the probability of hydrolysis and condensation reactions. However, although the suspension medium was buffered, the pH decreased to around 5.3 during polymerization (see Supporting Information) which slightly affected the particles size evolution (the particles number decreased of around 17%). The diminution of pH is mainly due to KPS decomposition in the water phase which process is known to generate acidic free radicals.[18] Therefore, to keep a constant pH, an additional experiment was launched in which the amount of initiator was halved and that of the buffer was increased by a factor of 2. In these conditions, the latex particles reached the size predicted from monomer feed, solids content, and seed size data (see Table 2).

The propensity of organo-trialkoxysilanes to form gels, particles, or precipitates depends on various parameters such as the nature of the organic substituent, the suspension pH, the silane concentration, the solvent, etc., and may vary significantly according to the experimental conditions.[19,20] Trimethoxysilanes, for instance, are much more sensitive to hydrolysis than triethoxysilanes and polymerize to form gels more readily and at lower concentrations. Similarly, monomers with small organic groups are more reactive toward hydrolysis than those with bulkier substituents. They would be expected therefore to react more quickly and be more prone to form highly cross-linked polymers capable of forming gels.[21]

So, for purposes of comparison and since no data were available in the literature for our system, we performed the hydrolysis/condensation reaction of MPS alone in the absence of polystyrene latex seeds under otherwise identical experimental conditions. While stable, but relatively large, particles ($D_p = 806$ nm) were obtained under neutral conditions after 3 h, the polymerization performed under basic conditions gave rise to insoluble solid precipitates visible to the naked eye. It can be thus concluded from these experiments that the emulsion polymerization reaction of MPS is made easier in the case of neutral conditions than in basic or acidic conditions, in agreement with the previous observations.

Effect of pH on the Copolymer Microstructure. It could be seen from the last paragraph that pH is a key parameter which affects the hydrolysis and condensation reaction rates. Therefore, to better character-

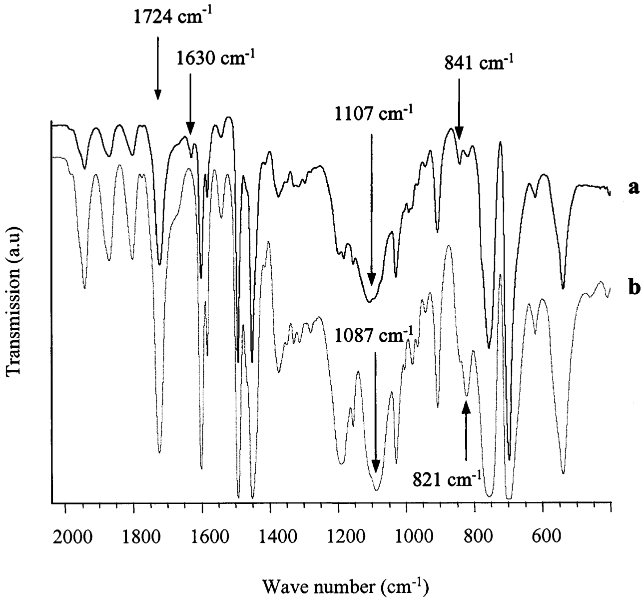

Figure 4. Fourier transform infrared spectra of the core−shell latex particles produced at different pH values with 10 wt % MPS relative to styrene. (a) pH = 8.5 and (b) pH = 7.

Table 3. Results of the Deconvolution of the ^{29}Si NMR Spectra of a Series of Hybrid Core/Shell Latexes ([MPS] = 20 wt % Relative to Styrene)

pH		T^0	$T^1 + T^2$	T^3	$100(T^1 + T^2 + T^3)/T^0$
7	before cleaning	100	0	0	0
8.5	before cleaning	18	22	60	82
	after cleaning	22	14	64	78

ize the different species formed in the suspension medium and establish the role of pH on the copolymer microstructure, further characterizations were performed by FT-IR and solid-state NMR spectroscopy.

IR spectra of the products obtained at different pH and 10 wt % MPS are shown in Figure 4. Whatever the suspension pH, bands specific of the aromatic ring of polystyrene at 1601, 1492, 906, 757, and 697 cm^{-1} are observed as well as absorption bands corresponding to MPS ($\nu_{C=O}$ at 1724 cm^{-1}). A band characterizing nonreacted Si−OR groups (symmetrical Si−O−C at 821 cm^{-1}) is observed at pH 7 while this signal is not visible at pH 8.5. Concurrently, the absorption at 1087 cm^{-1}, corresponding to asymmetrical Si−O−C (ν_{Si-O-C}), is shifted to a higher frequency ($\nu_{Si-O-Si}$,1107 cm^{-1}), indicating the formation of siloxane units. In addition, no C=C bond of MPS (1630 cm^{-1}) appears at pH = 7 unlike the case of pH = 8.5. This indicates that, under basic conditions, a part of MPS did not copolymerize with styrene but was only involved in condensation reactions. We presume that these polymers are formed in the earlier stage of polymerization when hydrolysis and condensation predominate. In the later stages, these species may either graft onto the shell by reaction with previously incorporated alkoxysilane moieties or stay in the continuous phase as free-standing clusters and/or nanoparticles depending on their size and colloidal stability. The possibility that these polymers simply adsorb to the latex seed cannot be also completely ruled out. To summarize, evidence is given here of the formation under basic conditions of a cross-linked polyorganosilsesquioxane network containing entrapped nonreacted methacryloyl groups, while under neutral conditions FTIR showed the presence of residual nonhydrolyzed methoxy groups.

To estimate the extent of polycondensation in the water phase and discriminate between the different aforementioned mechanisms, the latex suspension was characterized by TEM. Close examination of the particles obtained at pH = 8.5 indicates the formation of small dark and diffuse objects with a diameter of a few nanometers in the suspension medium surrounding the core−shell latex particles (Figure 2, right). These nanosize objects are speculated to originate from the condensation of alkoxysilane molecules in the aqueous phase and supports the view of formation of stable clusters although the two other hypothesis may also be valid and coexist. At neutral pH, in contrast, we did not find any evidence of formation of free-standing polycondensate species as no dark spots could be visualized around the latex particles. In addition, the MPS units appeared to be uniformly distributed in the shell as no phase segregation could be identified on the TEM picture even at a magnification of 200000×. A similar conclusion was reached by Jang and Park during the sol−gel synthesis of polystyrene/silica hybrids using MPS as compatibilizing agent.[22]

To get further insight into possible side reactions occurring in the continuous phase, the latexes were submitted to a series of centrifugation and redispersion in ethanol. The centrifugation is expected to remove all the oligomers and small cyclic compounds contained in the water phase or weakly adsorbed to the latex particles surface. The resulting particles were analyzed for determination of their composition which was compared to that of the original latexes. As expected, the carbon and silicon percentages obtained from the elemental analyses of the original latex samples were in reasonable agreement with the theoretical values whatever the suspension pH. However, it should be noticed that we did not observe a significant difference in the carbon and silicon contents before and after cleaning which suggests the formation of only a minor proportion of polycondensates in the water solution surrounding the latex particles. To get further insight into the copolymer microstructure at different pH values and 20 wt % MPS, NMR experiments were performed on the core−shell particles before and after removal of the oligomeric compounds. The different silicon-based species are called according to the conventional T^j nomenclature where T is the trifunctional alkoxysilane and j designates the number of siloxane groups bounded to the silicon atom. Under basic conditions, most of the hydrolyzed species have condensed to form mainly T^3 (−68 ppm) and T^2 (−60 ppm) sites, whereas under neutral conditions, only T^0 (−44 ppm) species are identified in the NMR spectrum of the original latexes. Similar results have been reported by our group in previous investigations.[5,6] Considering now the evolution of the NMR signals after cleaning of the core−shell latex particles, we observed a decrease of the proportion of condensed species as estimated by determining the area under each of the three peaks. The percentages of the different T^j species are reported in Table 3, and the corresponding NMR spectra are included in the Supporting Information. This results thus indicates the removal of oligomers from the latex suspension.

In summary, NMR and TEM analysis confirm the formation of free-standing polysiloxane clusters and/or oligomers at pH 8.5, the presence of which may affect the colloidal stability of the polymer latexes by forming for instance bridges between adjacent particles.

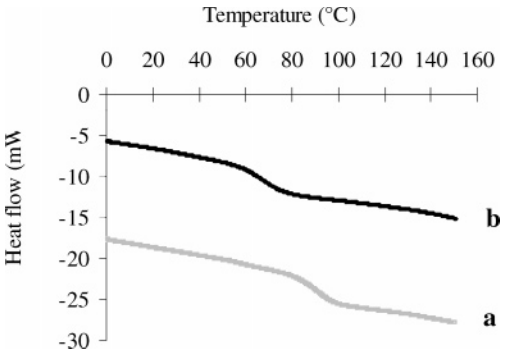

Figure 5. Differential scanning calorimetry (DSC) thermograms of the hybrid core−shell latex particles produced at different pH values with 10 wt % MPS relative to styrene. (a) pH = 8.5 and (b) pH = 7. The curves have been shifted vertically for clarity.

In a last effort to characterize the copolymer microstructure, we determined the glass transition temperature of the copolymers. The DSC curves, shown in Figure 5 indicate that the T_g of the hybrid nanoparticles produced at pH = 8.5 (Figure 5a) is much lower than that of the hybrid copolymer obtained at pH = 7 (Figure 5b). T_g = 69.7 and 91.0 °C, respectively. Again, this result is consistent with the previous conclusions. The incorporation of siloxane units into the shell contributes to lowering of the glass transition temperature of the hybrid material. Indeed, experiments performed on MPS alone under basic conditions indicate that the T_g of the resulting hybrid polymer is low and close to −61.7 °C. This is presumably due to the nature of the polymer which contains flexible Si−O−Si segments. The silsesquioxane oligomers thus play the role of plasticizer for the polystyrene matrix. Incorporation of pendant alkoxysilyl groups in the copolymer is also expected to give rise to a significant decrease of T_g as reported in a previous work on the synthesis of poly(styrene-*co*-MPS) hybrids.[23] The lower T_g observed for base-catalyzed samples can also be due to the fact that the later contain a notably higher proportion of siloxane-rich domains than those produced at neutral pH for which the MPS units are suspected to be more homogeneously distributed along the copolymer chain.

Study of the Influence of the MPS Concentration. To investigate the effect of the amount of MPS, the polymerization reaction was performed at three different MPS concentrations corresponding to 5, 10, and 20 wt % MPS relative to styrene under both neutral and basic conditions.

Effect of the MPS Concentration on the Particle Size. Figures 6 and 7 show the evolution of the particles diameter and particles number as a function of conversion at different MPS concentrations and different pH. The predicted particle diameter is calculated from the particle diameter determined before adding MPS combined with the overall monomer conversion determined by GC, assuming constant particle number in the system.

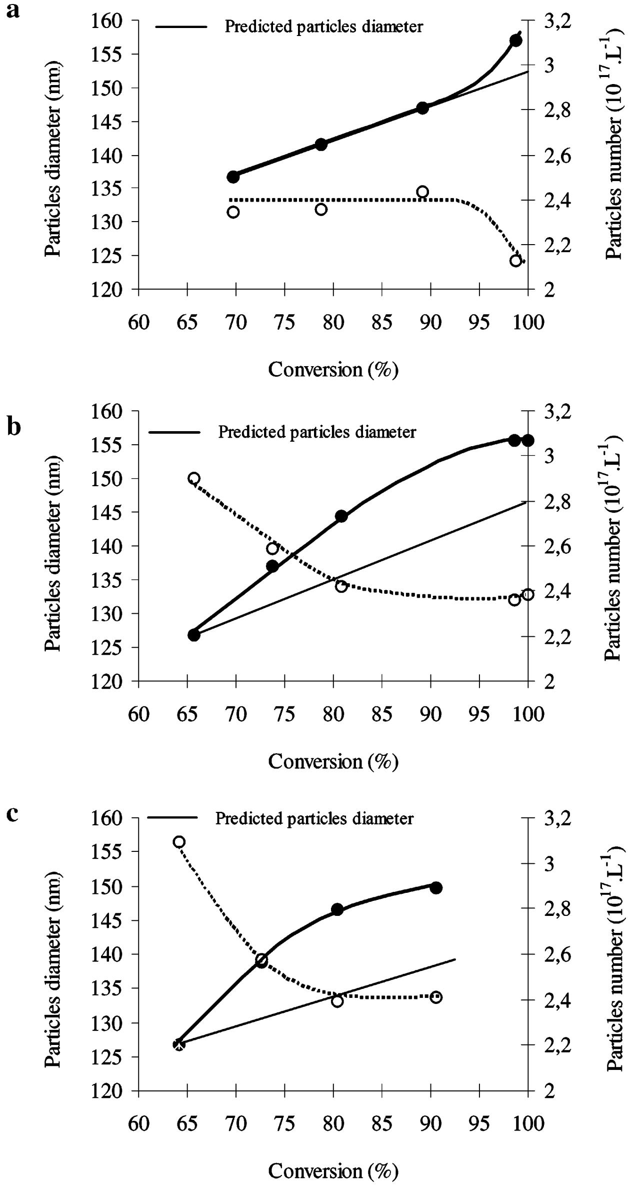

Figure 6. Particles diameter (●) and particles number (○) as a function of the overall conversion determined by GC. pH = 7. [MPS] = 5 (a), 10 (b), and 20 wt % (c) relative to styrene.

It can be seen in Figure 6 that the difference between the real and predicted particle sizes increases with increasing conversion and with increasing the MPS concentration; i.e., the FRPN increases. As anticipated from the previous data, this effect is more pronounced at pH = 8.5 than at pH = 7. Indeed, the higher the pH and/or the MPS concentration, the more important the amount of MPS remaining in the water phase and the greater therefore the probability that these molecules undergo hydrolysis/condensation reactions. Another possibility is that the higher the amount of MPS that undergoes condensation in the shell, the lower the affinity of the surfactant for the functionalized particles surface and the poorer therefore the colloidal stability of the resulting copolymer latexes. Table 4 shows the fraction of MPS groups which are effectively hydrolyzed at different MPS concentrations. The amount of hydrolyzed methoxy groups increases with increasing the MPS concentration in agreement with the above assumption: the rate of hydrolysis depends on two parameters: the solution pH and the initial silane concentration.[16]

Effect of the Concentration of MPS on the Copolymer Shell Microstructure. As before, FTIR and solid-state NMR spectroscopies were used to characterize the shell microstructure. FTIR analysis (spectra not shown) indicates the presence of residual double bonds for 20% MPS and pH 7 (see Supporting Information). This result, allied with the previous data, illustrates that the microstructure of the alkoxysilane-based polymers is largely determined by the hydrolysis/

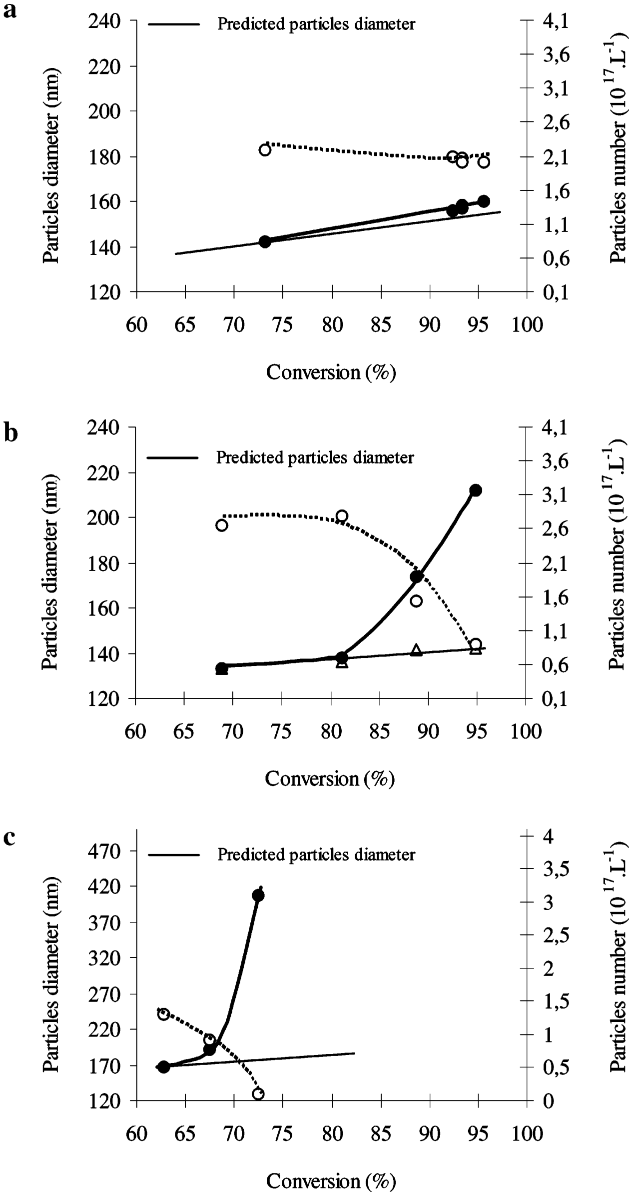

Figure 7. Particles diameter (●) and particles number (○) as a function of the overall conversion. pH = 8.5. [MPS] = 5 (a), 10 (b), and 20 wt % (c) relative to styrene.

Table 4. Extent of Hydrolysis Obtained by Gas Chromatography at Various MPS Concentrations and a Given pH Value (pH = 7)

MPS concn (wt % relative to styrene)	5	10	20
amt of methanol (g/100 g emulsion)	0.026	0.083	0.288
% of hydrolyzed Si−OMe groups	4.5%	7.3%	12.6%

condensation rates of the MPS molecule. Independently of the suspension pH, the increase of the MPS concentration accelerates both hydrolysis and condensation, which promotes therefore the formation of a cross-linked network. As before, under basic conditions, unreacted MPS monomers are trapped within this polysiloxane network and can no longer react in the free radical polymerization. This is also supported by ^{29}Si NMR which shows the appearance of T^2 and T^3 signals which proportion increases with increasing the silane concentration. Concurrently, the T_g of the hybrid products decreased from 91.0 to 86.3 °C when the MPS concentration was increased from 5 to 20 wt % relative to styrene (see Supporting Information) as the copolymers contained more and more siloxane units.

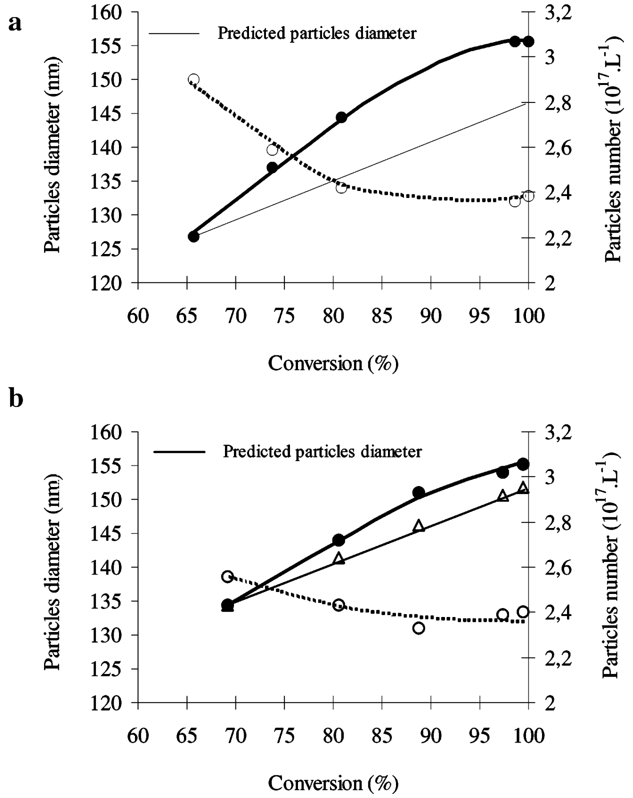

Figure 8. Particles diameter (●) and particles number (○) as a function of the overall conversion. (a) MPS is introduced at once, and (b) MPS is introduced semicontinuously. pH = 7. [MPS] = 10 wt % relative to styrene.

Study of the Influence of the Addition Mode of MPS. To study the influence of the addition mode of MPS, two experiments were realized with different MPS flow rates (4.5 and 6 g/h). These experiments were compared to an experiment where MPS was introduced as a shot at a fixed pH (pH = 7) and a constant MPS concentration (MPS = 10 wt % relative to styrene).

Effect of the MPS Addition Strategy on the Particle Size. Figure 8 shows the evolution of the particle size and the particle number for different addition modes of MPS (MPS added continuously to the reactor with an inlet flow rate of 4.5 g/h or MPS introduced as a shot). The data plotted in Figure 8 indicate that the latex particles have a greater colloidal stability when MPS is added semicontinuously. The particle number is almost constant, and the particle size is close to the predicted value. Such an effect may be due to a decrease of the MPS concentration in the water phase. Indeed, slow MPS addition promotes incorporation of the MPS monomer in the latex seed. Therefore, not only is the nature of the surface different but less polysiloxane oligomers are formed in the continuous phase which two effects contribute to an increased stability of the core−shell latex particles.

Effect of the MPS Addition Policy on the Copolymer Microstructure. In view of the previous results, we anticipate that cross-linking will be greatly reduced through semicontinuous addition of MPS. This was confirmed indeed by FT-IR which indicates less cross-linking (signals at 1087 and 821 cm^{-1}) when MPS is added semicontinuously than when it is introduced as a shot (see Supporting Information). The analysis was done on a latex synthesized at pH 8.5 since we know that cross-linking is promoted under these conditions.

Table 5. Copolymer Compositions in the Shell for Different MPS Addition Modes (pH = 7 and [MPS] = 10 wt % Relative to Styrene)

adding MPS at once	time after adding MPS (min)	30	60	120
	MPS in the copolymer (wt %)	43.5	33.1	21.3
MPS addition rate: 4.5 g/h	time after adding MPS (min)	30	60	120
	MPS in the copolymer (wt %)	20.9	27.4	32.1
MPS addition rate: 6 g/h	time after adding MPS (min)	30	60	120
	MPS in the copolymer (wt %)	26.0	28.5	31.3

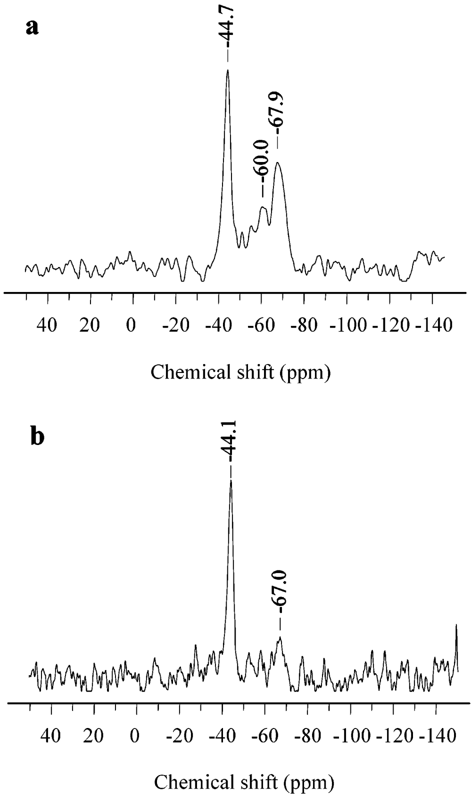

Figure 9. ^{29}Si solid-state NMR analysis of the hybrid core/shell latex particles. pH = 8.5 and [MPS] = 10 wt % relative to styrene. (a) MPS is introduced as a shot, and (b) MPS is introduced semicontinuously.

This was also corroborated by ^{29}Si solid-state NMR which showed that under such conditions the latex sample mostly contained nonreacted T^0 species and only a minor proportion (less than 5%) of T^1 units (Figure 9).[24]

The semicontinuous process not only allowed to control the copolymer microstructure but also enabled to maintain a constant composition of the copolymer chains in the shell. Table 5 shows the copolymer compositions deduced from the conversion data determined by GC after various MPS addition policies. As MPS is more reactive than styrene[23] (reactivity ratios: $r_1 = 0.9$, $r_2 = 0.45$), MPS is consumed first when the reaction is performed in batch which leads to a drift in the copolymer composition. Consequently, more MPS units are incorporated into the shell at the beginning of the reaction than at the end of polymerization. To control the copolymer microstructure and obtain a homogeneous composition in the shell, MPS was introduced semicontinuously using different flow rates. The results of Table 5 indicate, as expected, that semicontinuous addition of MPS enables to reach a more random distribution of the alkoxysilane units in the copolymer. Although these results are satisfactory, the flow rate could be further optimized in order to yield a better control over the shell composition.

As anticipated from the above data, the T_g of the hybrid polymer is slightly higher when MPS is added semicontinuously (T_g = 95.5 °C) than when it is introduced as a shot (T_g = 91.0 °C). This is due again to a better incorporation of the MPS units into the copolymer chains, resulting in a minor proportion of Si−O−Si bonds.

Conclusion

Organic−inorganic hybrid core−shell nanoparticles were synthesized in a two steps process: emulsion polymerization of styrene and subsequent copolymerization of unreacted styrene with γ-methacryloxypropyltrimethoxysilane. Along with the copolymerization process, hydrolysis and polycondensation reactions are taking place in the presence of the aqueous phase, resulting in cross-linking of the alkoxysilane monomer which chemical process has a strong influence on the latex particles size (which is to say on the colloidal stability) and on the shell microstructure.

The pH value is the main factor influencing the cross-linking reaction and consequently the properties of the latex suspension. The latex is more stable in neutral conditions, while it rapidly turns to a gel after the addition of MPS under acidic conditions. Under basic conditions, although the latex is stable, the particle number significantly decreases, demonstrating thus the occurrence of agglomeration phenomena. As the hydrolysis and condensation reactions are promoted at high pH value, many Si−OR groups turn into a Si−O−Si network containing nonreacted entrapped methacryloyl groups. The resulting polysiloxane network can either be incorporated into the shell by grafting or copolymerization with styrene or remain in the continuous phase in the form of low molecular weight cyclic oligomers and/or clusters. In neutral conditions, the free radical reaction dominates the system and almost all the MPS is copolymerized into the polymer chains so that only few cross-linking reactions are allowed to take place in the water phase and in the particles as attested by ^{29}Si solid-state NMR.

Increasing concentrations of MPS also promotes hydrolysis and condensation reactions so that the formation of Si−O−Si segments is made easier. As before, for low MPS concentrations and basic conditions, polysiloxane-rich domains are incorporated into the shell which promotes latex particles aggregation.

Uniform copolymer compositions and more stable lattices could be obtained through the semicontinuous addition of MPS to the reactor. Although the conditions still need to be improved, one can expect to perfectly control both the copolymer shell microstructure and the latex stability with this operating policy.

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Supporting Information Available: Evolution of pH with conversion during the semibatch emulsion polymerization of MPS (10 wt % relative to styrene) at pH 7; ^{29}Si NMR spectra of the core−shell particles produced at pH 8.5 and 20% MPS before and after cleaning of the latex suspension; FTIR spectra and DSC thermograms of the hybrid core−shell latexes produced at different MPS concentrations and pH 7; FTIR spectra of the core−shell particles obtained at pH 8.5 and 10% MPS for different MPS addition modes. This material is available free of charge via the Internet at http://pubs.acs.org

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