

# Synthesis and Characterization of SiOH-Functionalized Polymer Latexes Using Methacryloxy Propyl Trimethoxysilane in Emulsion Polymerization

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**ABSTRACT:** Polystyrene latex particles carrying silanol groups on their surface have been synthesized in emulsion polymerization using 3-(trimethoxysilyl)propyl methacrylate (MPS) as a functional comonomer. We showed that the colloidal stability of the resulting latex suspensions was highly dependent on pH and on the nature of the surfactant. The structure of the hybrid copolymers was analyzed using infrared and solid-state NMR spectroscopies. Condensation reactions of the silane molecule were promoted at high and low pH and were also influenced by the silane content in the monomer mixture. No condensation products were formed when polymerization was performed at pH 7 using 10 wt % MPS (relative to styrene) indicating that it is possible to control the cross-linking process under these conditions. The functionalization reaction was extended further to poly(methyl methacrylate) and poly(butyl acrylate) latexes. In contrast to polystyrene, condensation products were identified in both cases presumably because of difference in comonomers reactivity ratios, and perhaps also because of difference in molecular mobility. Independent of the microstructure of the hybrid copolymers, AUGER electron spectroscopy and electrophoretic measurements gave evidence of the presence of silanol groups on the particle surface. The SiOH functionality is of great interest in applications where it can be necessary to control the surface properties of polymer colloids. The hybrid copolymers provide rigidity to the surface and can significantly influence mechanical properties of the material. In addition, the SiOH groups can be efficient primers for the subsequent growth of a mineral layer around the particles and can help compatibilize organic colloids with inorganic materials in nanocomposite structures or higher hierarchical devices.

## Introduction

The incorporation of functional groups into polymer latexes is of major interest in the field of colloidal science. A variety of chemical functions have been successfully introduced during the past 3 decades and there is still active work in this domain. The interest in functionalized latexes is mainly due to their potential applications as solid supports in catalysis, in chromatography, or in biotechnology.<sup>1,2</sup> Reactive groups, as for instance hydroxyl, carboxylic, or amino groups, can be introduced on the surface of organic or inorganic pre-formed nanoparticles by chemical derivatization of the particle surface. Inorganic oxides (mainly silica) can be easily functionalized by reaction of the silanol groups with alcohols, organoalkoxysilanes or chlorosilanes.<sup>3</sup> Highly hydrophobic inorganic supports, with applications in high-performance liquid chromatography, are obtained, for instance, by using alkylsilylating agents of different chain lengths.<sup>4</sup> Functionalization can also be carried out by using specific ingredients, such as functional initiators, reactive surfactants, or macromonomers, in the polymer particles formulation. For example, anionic or cationic charges can be imparted to the particle surface by using either anionic or cationic initiators.<sup>5</sup> However, direct polymerization of suitable functional comonomers is, in many instances, the best route for the design of many functional microspheres. A variety of functional comonomers (e.g., methacrylic acid, sodium styrenesulfonate, methacryloyl propyl tri-

methyammonium bromide, hydroxyethyl methacrylate, acrylamide, and so on...) have been reported in the literature.<sup>6–8</sup> The copolymerization approach is particularly well suited to control the surface properties of the functionalized latex particles. Surface charges and surface polarity, for instance, can be easily adjusted by the nature and concentration of the comonomer.

In the present study, we describe the incorporation of silanol groups (SiOH) on the surface of polystyrene latex particles using 3-(trimethoxysilyl)propyl methacrylate (MPS) as a functional (co)monomer in emulsion polymerization. Although, as mentioned above, organotrialkoxysilanes have been largely used to modify the surface of silica particles via silylation reactions, they have been more rarely involved in emulsion polymerization.<sup>9–11</sup> A reason may be that not only is MPS reactive in free radical polymerization but also it can undergo hydrolysis and polycondensation reactions in the aqueous phase. By reacting MPS at the polymer particles surface, we aim to produce hydrophilic polystyrene latexes with surface properties similar to those of silica microspheres (see Chart 1). Such hybrid nanoparticles open the route to many chemical derivatizations and provide new functional materials with potential applications in chromatography, catalysis, and coating. In addition, SiOH-functionalized colloids, with controlled size and chemical composition, can be used as elementary bricks for the elaboration of more sophisticated organic–inorganic nanostructures.<sup>12,13</sup> Functional building blocks are obviously of major importance with the aim to create new materials with new properties.

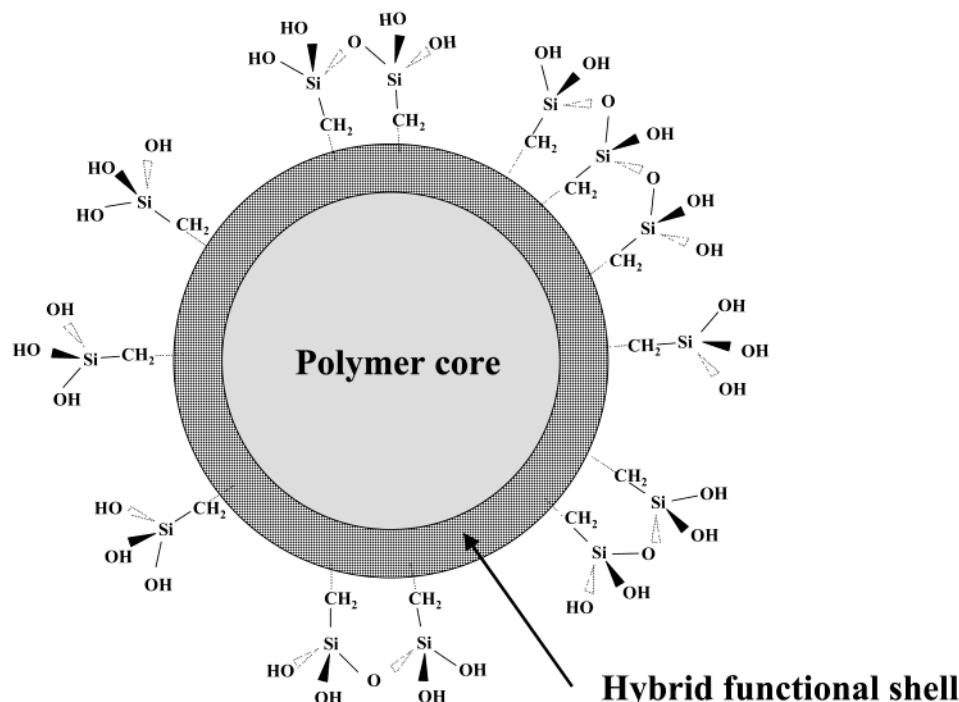
## Experimental Section

**Materials.** The monomers used, styrene, methyl methacrylate and butyl acrylate (from Aldrich), were distilled in a

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**Chart 1. Schematic Illustration of the Surface of the SiOH-Functionalized Polymer Latex Particles Obtained in Emulsion Polymerization**

vacuum before use. The initiator used, potassium persulfate (KPS, Acros Organics), was used as received. The surfactants used, sodium dodecyl sulfate (SDS, Acros Organics), poly-(oxyethylene) isooctylcyclohexyl ether (Triton X-405), and dodecyl dimethyl propylammonium sulfonate (Ralufon, Aldrich), were used as supplied. 3-(Trimethoxysilyl)propyl methacrylate (MPS, Aldrich) was used without purification. The water was deionized on mixed bed resins.

**Synthesis of the SiOH-Functionalized Polystyrene Latex Particles.** Latex particles having silanol groups on their surface were prepared in two steps. Emulsion polymerization of styrene was first carried out at 70 °C up to 80% conversion using KPS as initiator and three different surfactants, being anionic, nonionic, and zwitterionic, respectively. Once 80% conversion was achieved, known amounts of MPS were added to the reaction medium and the polymerization was continued at 70 °C for 5 h. The pH of the suspension was fixed at 8.5 by adding 0.2 g of sodium hydrogenocarbonate or at 7 by adding equivalent quantities of dihydrogenophosphate and dihydrogenocarbonate (typically 0.1 g of each per 100 g of water). A typical recipe is as follows: styrene, 10 g; KPS, 0.1 g; surfactant, 0.2 g; buffer, 0.2 g; water, 100 g; and various quantities of MPS (1 and 4 g).

**Characterization of the SiOH-Functionalized Latex Particles. (a) Monomer Conversions and Copolymer Particle Composition.** The monomer to polymer conversions were determined gravimetrically. Excess nonreacted MPS and free surfactant were removed by successive centrifugation/redispersion cycles. The composition of the SiOH-functionalized polymer particles after cleaning was determined by elemental analysis from the silicon and carbon contents.

**(b) Spectroscopic Analyses.** Infrared spectra were recorded using a Nicolet FTIR 460 spectrometer on powder-pressed KBr pellets. The hydroxyl region was observed on samples made into self-supporting wafers of around 20 mg/cm<sup>2</sup> and previously submitted to a thermal treatment under vacuum at 200 °C for 5 h. <sup>29</sup>Si solid-state NMR was performed on a Bruker DSX-300 spectrometer operating at 59.63 MHz by use of cross-polarization from proton. The contact time was 5 ms, the recycle delay 1 s, and the spinning rate 10 kHz. Auger electron spectroscopy (AES) data were acquired on a VG-MICROLAB 310-F Microprobe. The powder (the same as that used for chemical analysis, i.e., cleaned by serum replacement) was imprinted on the surface of an indium foil. The

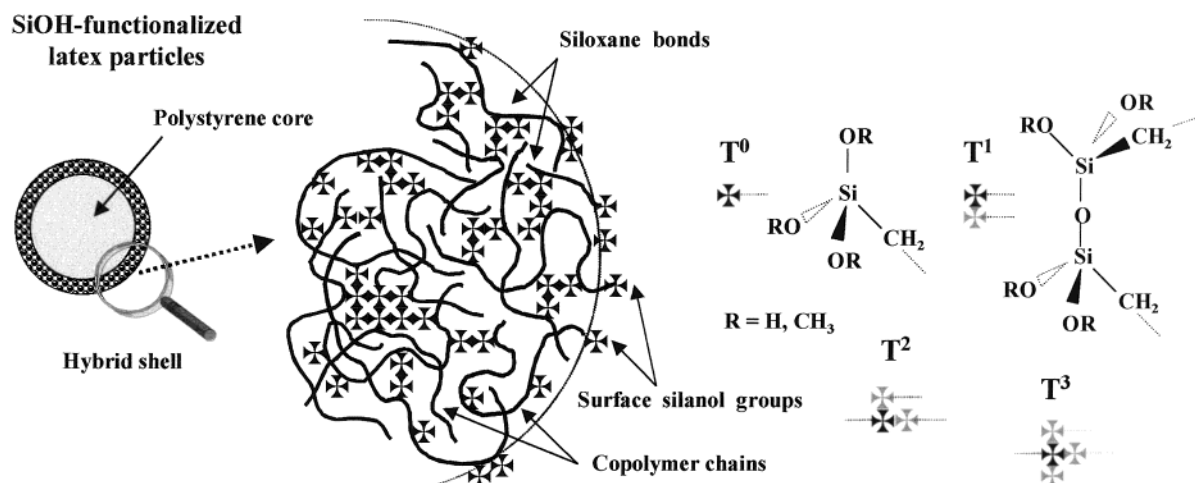
applied analysis conditions were an acceleration voltage and beam current of 10 keV and 2 μA, respectively. The data were taken in the conventional EN(E) mode. The energy windows scanned in this multiplexing technique were, for each element: O, 490–530 eV; C, 240–290 eV; Si, 1590–1630 eV. The analysis area was 5 μm in diameter. Ionic etching was performed with Ar<sup>+</sup> ions accelerated at 4 keV, 0.2 μA absorbed current, onto an area of 0.8 mm × 0.8 mm. In such conditions, the etching rate is about 0.2 nm·s<sup>-1</sup> on a SiO<sub>2</sub> standard.

**(c) Particle Sizes and Morphologies.** The diameter, *D<sub>p</sub>*, of the latex particles was determined by dynamic light scattering (DLS) using a Malvern Autosizer Lo-C instrument. Transmission electron microscopy analysis (TEM) was performed with a Philips CM10 electron microscope operating at 80 kV. In a typical experiment, one drop of the colloidal dispersion was put on a carbon film supported by a copper grid and allowed to air-dry before observation.

**(d) ζ Potential Measurements.** The electrophoretic mobility was determined using a laser electrophoresis ζ potential analyzer (Zetasizer III from Malvern Instruments). The analyses were carried out at 20 °C, and the ζ potential was an average of three measurements. The ionic strength was kept constant by dilution into a 0.001 mol/L sodium chloride solution. The pH of the suspension was controlled by adding 0.1 N standard hydrochloric acid or sodium hydroxide aqueous solutions. The ζ potential was calculated from the electrophoretic mobility (*μ*), using the Henry equation after determination of the function *f(κa)*.<sup>14</sup>

## Results and Discussion

**Colloidal Stability and Spectroscopic Characterizations of the SiOH-Functionalized Polystyrene Latex Particles. (a) Effect of the Nature of the Surfactant.** A first series of experiments was performed at pH 7 using 10 g of MPS per 100 g of styrene (denominated as 10 wt % MPS) and three different surfactants. The monomer conversions and the latex particle diameters before and after functionalization are reported in Table 1. From the data in Table 1, it appears that the colloidal stability and the diameters of the latex particles after functionalization are strongly

**Scheme 1. Schematic Representation of the Organic–Inorganic Network Formed on the Latex Particle Surface in Acid- or Base-Catalyzed Systems****Table 1. Characterization of the MPS-functionalized Polystyrene Latex Particles Prepared Using Three Different Surfactants. Monomer Conversions, Particle Sizes and Particle Numbers before and after Functionalization<sup>a</sup>**

surfactant	SDS	Ralufon	TX 405
nature	anionic	zwitterionic	nonionic
Before the Addition of MPS			
[styrene] (g/L)	98.5	97.2	98.0
conversion (%)	80	78	85
diameter (nm)	61	117	285
particle no./L	$6.4 \times 10^{17}$	$8.7 \times 10^{16}$	$6.6 \times 10^{15}$
After Functionalization			
[styrene + MPS] (g/L)	108.9	107.9	108.3
overall convn (%)	100	98	84
diameter (nm)	67	135	715
particle no./L	$6.6 \times 10^{17}$	$7.8 \times 10^{16}$	$4.5 \times 10^{14}$

<sup>a</sup> The polymerizations were performed at pH 7 using 10 wt % MPS relative to styrene and 2 g/L surfactant.

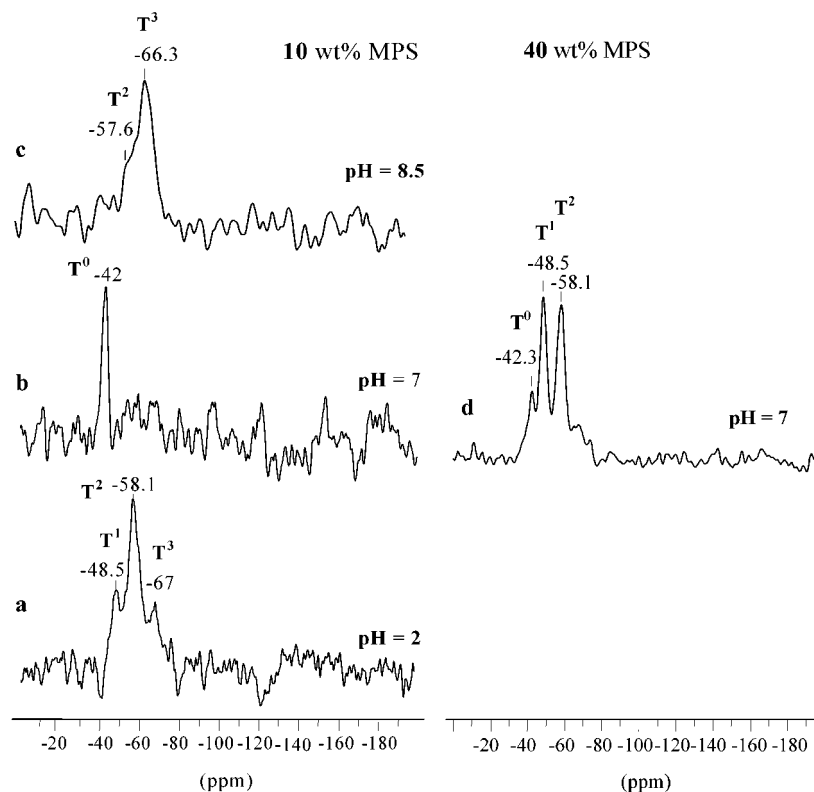
influenced by the nature of the surfactant. When the ionic surfactants, either SDS or Ralufon, were involved in the polymerization reaction, the diameters of the latex particles increased from 61 to 67 and from 117 to 135 nm, respectively, in agreement with the increase in the solid content of the suspension (i.e., the particle number remained constant). In contrast, the polymerization performed in the presence of the nonionic polyoxyethylenic surfactant turned out to be unstable as attested by the increase in particle size from 285 to 715 nm which is much more than expected assuming a constant particle number and 84% overall conversion of MPS and styrene monomers (the particle number decreased from  $6.6 \times 10^{15}$  to  $4.5 \times 10^{14}$ ). It can be therefore concluded that the polyoxyethylenic nonionic surfactant is not suitable for stabilization of the functionalized latexes in the present system. A reason may be that the polyether molecules strongly adsorb on the silanol groups of the copolymers through hydrogen bonding and act as a bridge between two adjacent particles. Therefore, in the following, we decided to use dodecyl dimethyl propylammonium sulfonate as the surfactant although sodium dodecyl sulfate also appeared to satisfactorily stabilize the functional polystyrene particles under our experimental conditions.

**(b) Effect of pH.** When MPS is involved in the emulsion polymerization reaction, different events can take place simultaneously. On one hand, the functional

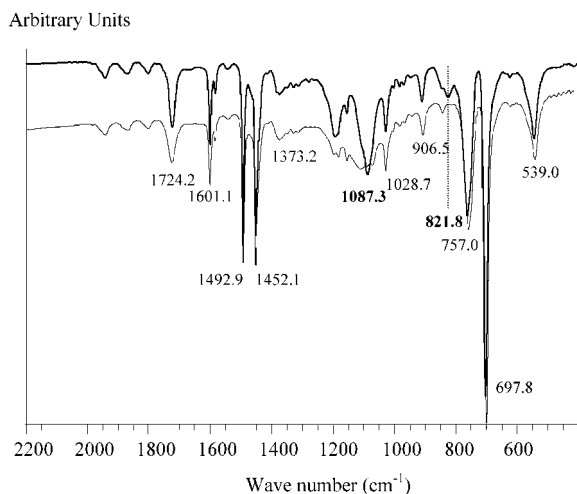
monomer can be incorporated into the polystyrene chains by copolymerization of the methacrylate moiety with styrene. On the other hand, the organoalkoxysilane may hydrolyze into silanetriol molecules and condense into inorganic polysilsesquioxane networks via the sol-gel process. An hybrid copolymer structure is then expected to be formed at the particle surface from the combination of vinyl radical polymerization with the hydrolysis and condensation of the trimethoxysilyl groups as schematically represented in Scheme 1. It can be anticipated that the microstructure of the organic–inorganic copolymers will be essentially dependent on the polymerization rates of the two systems. While the reactivity of MPS in free radical polymerization is mainly controlled by the reactivity ratios of the (co)-monomers, the hydrolysis and condensation reactions are highly dependent on the pH of the suspension medium.<sup>15</sup>

To investigate this parameter, the polymerization reaction was performed at three different pH, corresponding to acidic (pH 2), neutral (pH 7), and basic (pH 8.5) conditions, respectively, using otherwise the same recipe (ca. 10 wt % MPS relative to styrene and 2 g/L Ralufon). The <sup>29</sup>Si CP MAS NMR spectra of the latex particles synthesized at pH 2, pH 7 and pH 8.5 are reported in Figure 1, parts a–c, respectively. A unique and sharp resonance at –42 ppm corresponding to monomeric T<sup>0</sup> units and at the same position as in the starting MPS is observed in Figure 1b, indicating that no condensation reactions occurred at all in neutral medium (see Scheme 1). In contrast, resonances at –48.5, –58.1 and –67 ppm, characteristics of trifunctional silicon atoms with one (T<sup>1</sup>), two (T<sup>2</sup>) and three (T<sup>3</sup>) siloxane bonds, respectively, are clearly identified on the NMR spectra of Figures 1a and 1c. Concurrently, the <sup>13</sup>C NMR spectrum (not shown) gave evidence that MPS has copolymerized since the signal of the carbonyl group (C=O) was shifted to a higher frequency while the peaks at 137.4 and 124.7 ppm, attributed to the double bond have disappeared. These results are supported by infrared spectroscopic analysis (see Figure 2 and Table 2). We can identify in Figure 2 the presence of bands specific to polystyrene at 1601, 1492, 1452, 1028, 906, 757, and 697 cm<sup>–1</sup> as well as absorption bands corresponding to MPS (1724 and 1087 cm<sup>–1</sup>). We note the absence of the ν(C=C) band at 1634 cm<sup>–1</sup> which indicates complete conversion of the (co)monomers in





**Figure 1.**  $^{29}\text{Si}$  solid-state NMR analysis of MPS-functionalized latex particles as a function of pH, (a) pH = 2, (b, d) pH = 7, and (c) pH = 8.5, and of the MPS concentration, (a–c) 10 wt % MPS and (d) 40 wt % MPS.



**Figure 2.** FTIR spectra of 10 wt % MPS-functionalized polystyrene latex particles: (a) pH = 7; (b) pH = 8.5.

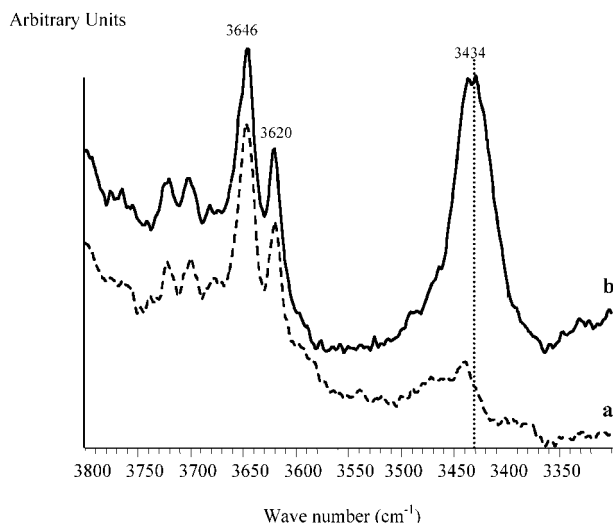
agreement with elemental and gravimetric measurements. We also observe in Figure 2a a signal at  $821\text{ cm}^{-1}$  (symmetric  $\delta(\text{Si}-\text{O}-\text{C})$ ) characteristic of nonreacted SiOR groups that disappeared in Figure 2b while, simultaneously, the signal at  $1087\text{ cm}^{-1}$  was shifted to a higher frequency ( $1111\text{ cm}^{-1}$ ), indicating the formation of siloxane units<sup>16</sup> in agreement with  $^{29}\text{Si}$  NMR analysis. The pH also had a drastic effect on the colloidal stability of the latex particles. While particle sizes were not affected by the increase of pH in the range 7–8.5, the latex suspension immediately turned into a gel when the functionalization reaction was performed at pH 2, indicating that aggregation of the MPS-functionalized latex particles was promoted under acidic conditions. This is presumably due to the difference in the structure of the inorganic network formed in acidic conditions.

**Table 2. Wave Numbers and Assignments of the Infrared Bands of the MPS-Functionalized Polystyrene Latex Particles**

wavenumbers ( $\text{cm}^{-1}$ )	polystyrene	MPS
3024	C–H arom	
2921, 2847	–CH <sub>2</sub>	–CH <sub>2</sub>
1601	–C=C arom	
1492, 1452	–C <sub>6</sub> H <sub>5</sub>	
1200	–CH= arom, out of plane	
906, 697	–CH= arom, in plane	
1724		$\nu(\text{C}=\text{O})$
1634		$\nu\text{ C}=\text{C}$
1111		$\nu\text{ Si}-\text{O}-\text{Si asym}$
1087		$\delta\text{ Si}-\text{O}-\text{C asym}$
821		$\delta\text{ Si}-\text{O}-\text{C sym}$

While acid catalysis promotes the formation of weakly cross-linked polymeric structures, more highly cross-linked, even fully dense inorganic networks are formed in alkaline solutions.<sup>17</sup> The “extended” fractal structure of the copolymers formed at low pH could promote interactions of two adjacent latex particles and explain the aggregation phenomenon observed in acidic media (so-called bridging flocculation). Aggregation can also be explained by a decrease in the surface charge density with decreasing the pH which has for direct consequence an increased number of effective collisions between two latex particles. At higher pH, in contrast, the functionalized latexes are stabilized by the negative ionic charges formed on their surface, and particles aggregation is prevented.

**(c) Infrared Spectroscopy Analysis.** Further insights into the structure of the organic–inorganic copolymers were obtained by FTIR spectroscopy analysis. Indeed, silanol groups can be successfully observed by this technique after removal of adsorbed water by thermal treatment under vacuum and looking at the

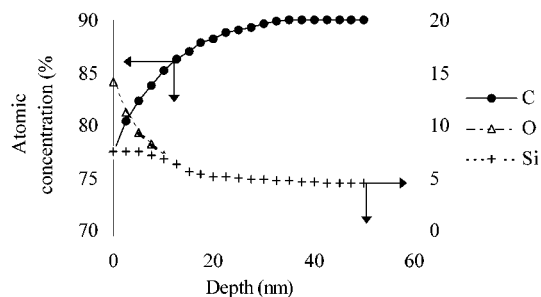


**Figure 3.** FTIR spectra: (a) pure polystyrene latex particles; (b) 40 wt % MPS-functionalized latex particles after removal of water at 200 °C under vacuum.

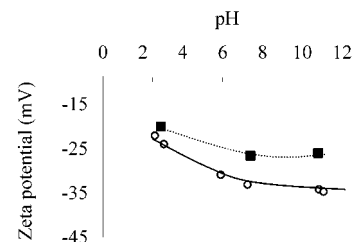
hydroxyl region, i.e., in the range 3000–4000  $\text{cm}^{-1}$ . While pure polystyrene latex particles (Figure 3a) show no adsorption between 3300 and 3550  $\text{cm}^{-1}$ , a sharp band at 3434  $\text{cm}^{-1}$  characteristic of hydrogen-bonded Si–OH groups is clearly identified in the spectrum of Figure 3b. The shift of the peak position toward lower wavenumbers (SiOH are normally identified at 3730  $\text{cm}^{-1}$ ) suggests strong interactions between neighboring silanol groups or between silanol groups and the methacrylate ester moiety of the coupling agent via inter- or intra-hydrogen bonding.

**(d) Effect of the MPS Concentration.** The  $^{29}\text{Si}$  CP/MAS NMR spectrum of Figure 1d shows the influence of the MPS loading on the copolymer microstructure. While the polymerization performed at pH 7 using 10 wt % MPS gave hybrid copolymers without siloxane linkages,  $\text{T}^2$  and  $\text{T}^1$  condensed products are identified on the NMR spectrum when the MPS concentration is increased to 40 wt %. This result illustrates the important role of the comonomer feed composition on the MPS reactivity. Indeed, since condensation is second order in silane concentration, doubling the concentration of silanol species multiplies the rate of formation of condensed products by 4-fold.<sup>17</sup> Condensation reactions are therefore promoted with increasing the MPS concentration, and a polyorganosilsesquioxane network is formed simultaneously to the organic copolymers. Another possible interpretation is that condensation reactions are promoted by the increased fraction of incorporated MPS monomer on the latex particles surface. The increase in MPS concentration increases the probability of coupling reactions and can also significantly influence chain mobility. It should be noticed however the absence of signal in the  $\text{T}^3$  region and the presence of a small peak at  $-42.3$  ppm corresponding to  $\text{T}^0$  units, which both indicate an uncompleted condensation scheme even for large MPS concentrations presumably because of the concurrent copolymerization reaction which interfere with the cross-linking process.

**Evidence of the Presence of Silanol Groups on the Latex Particle Surface.** The above spectroscopic analysis showed that MPS has been successfully incorporated into the polystyrene latex particles. Owing to the hydrophilic character of the molecule and considering that MPS has been introduced at the end of



**Figure 4.** Silicon-, oxygen-, and carbon-related AES depth profiles of 40 wt % MPS-functionalized polystyrene latex particles after removal of the surfactant by extensive cleaning as described in the experimental part.

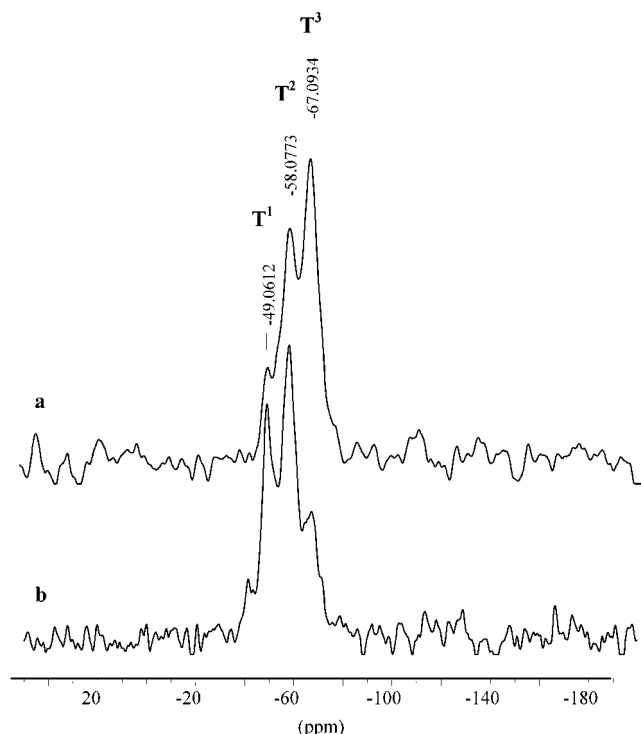


**Figure 5.** Variation of  $\zeta$  potential as a function of pH (NaCl:  $10^{-3}$  M): (■) pure polystyrene latex particles; (○) 10 wt % MPS-functionalized latex particles.

polymerization, the particle surface is expected to contain a large proportion of silanol groups. In that section, several techniques have been used to attest for the presence of SiOH functions on the polymer particle surface.

**(a) AUGER Electron Spectroscopy Analysis.** AES measurements have been performed on a sample containing 40 wt % MPS relative to styrene. The elemental composition of the particles surface was compared to that of the core after etching the sample by argon ion beam sputtering. The carbon, oxygen, and silicon concentration depth profiles are reported in Figure 4. From the data in Figure 4, it is clear that the particles surface is enriched in silicon and oxygen atoms in comparison to the bulk. The oxygen and silicon signals, however, do not completely drop to zero because the analysis was performed on particle multilayers and on a 5  $\mu\text{m}$  diameter area. Nonetheless, the chemical composition of the surface is in good agreement with the theoretical one (i.e., 77% carbon, 17% oxygen, and 6% silicon atoms assuming a MPS to styrene weight ratio equal to 2 on the particle surface).<sup>18</sup>

**(b)  $\zeta$  Potential Measurements.** Electrophoresis is a convenient method to characterize the surface properties of polymer and metal oxide colloids. The evolution of  $\zeta$  potential as a function of pH is plotted in Figure 5 for SiOH-functionalized latex particles containing 10 wt % MPS and pure polystyrene latex particles.  $\zeta$  potential measurements qualitatively attest for the presence of silanol groups at the latex particles surface.  $\zeta$  potential increases with increasing the pH in agreement with the surface silanol groups dissociation equilibrium. It is worth pointing out that the higher the pH, the higher is the difference between the surface potential before and after functionalization. At pH 2, which corresponds to the isoelectrical point of a silica surface,<sup>19</sup> the contribution of the silanol groups to the surface potential is zero and the  $\zeta$  potential of the functionalized latexes corresponds to that of pure polystyrene latex particles.  $\zeta$  potential is still negative at this point since sulfate



**Figure 6.**  $^{29}\text{Si}$  CP MAS NMR analysis of 10 wt % MPS-functionalized PBuA (a) and PMMA (b) latex particles at pH 7 using Ralufon as stabilizer.

groups of initiator residues are also present at the surface of the functional latexes. These groups are negatively charged over a large range of pH and contribute to a decrease in  $\zeta$  potential. Consequently, the isoelectrical point of the functionalized latex particles is lower than the value expected for pure silica particles.

**Functionalization of Poly(methyl methacrylate) (PMMA) and Poly(butyl acrylate) (PBuA) Latex Particles.** The above modification procedure has been extended to PMMA and PBuA polymer latexes. With the aim to control condensation reactions of the silane molecule, functionalization was performed at pH 7 following the same recipe as that described previously for polystyrene (i.e., using Ralufon and employing the shot growth method for MPS). Figure 6 shows the  $^{29}\text{Si}$  CP/MAS NMR spectra of the resulting hybrid copolymers. Both spectra exhibit broad signals in the  $T^1$ ,  $T^2$ , and  $T^3$  regions at  $-49$ ,  $-58$ , and  $-67$  ppm respectively, indicating the formation of a siloxane network. It is to be underlined however the predominance of the  $T^3$  and  $T^2$  signals in the NMR spectrum of the P(BuA-*co*-MPS) copolymers while the spectrum of the P(MMA-*co*-MPS) hybrids preferentially displays  $T^2$  and  $T^1$  signals. The formation of  $T^3$  units seems thus more difficult for PMMA than for PBuA. However, in view of the reactivity ratios for butyl acrylate ( $M_1$ ) and MPS ( $M_2$ ) comonomers, (i.e.,  $r_1 = 0.005$  and  $r_2 = 0.007$ , respectively),<sup>20</sup> and those for methyl methacrylate and MPS (e.g.,  $r_1 = 0.74$  and  $r_2 = 1.33$ , respectively),<sup>21</sup> it can be stated that MPS is much more reactive toward the PBuA macroradicals than toward the PMMA radicals. The P(BuA-*co*-MPS) macromolecules are expected therefore to be constituted of alternate units of MPS and BuA while the P(MMA-*co*-MPS) hybrids is presumed to be composed rather of large blocks of MPS units with randomly distributed organic monomeric moieties. Because of the high local concentration of the MPS molecules in the

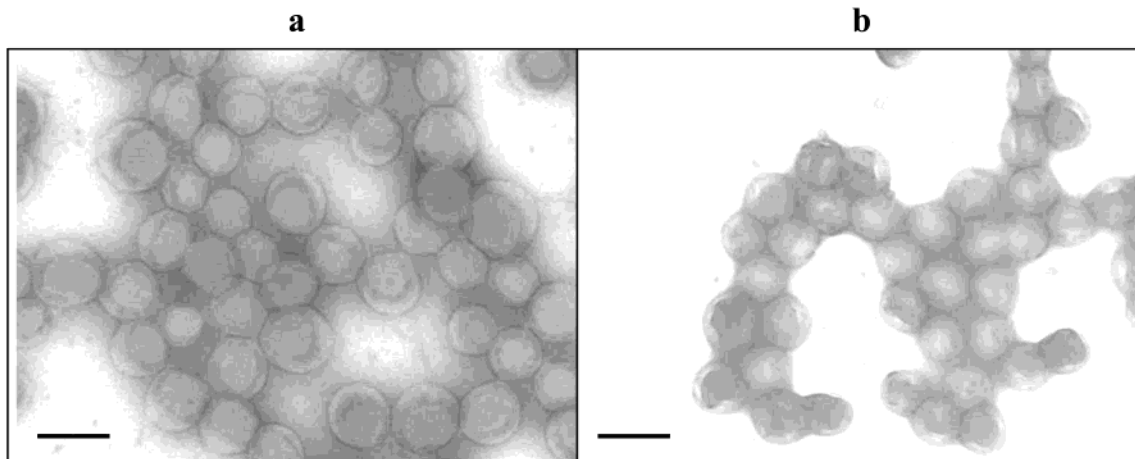
case of the P(MMA-*co*-MPS) copolymers, the probability that MPS would condense under these conditions should be higher than for the P(BuA-*co*-MPS) copolymers. The above data suggest therefore that the inorganic network formation is also largely dependent on the glass transition temperature of the copolymers. When MPS is reacted with butyl acrylate, condensation reactions are promoted because of the high molecular mobility of the polymer chains ( $T_g$  of PBuA is  $-49$  °C).<sup>22</sup> Nonetheless, condensation of MPS also occurs in the PMMA-based hybrids because of the low reactivity of the silane molecule toward PMMA radicals. Since MPS slowly copolymerizes in this case, it remains for a longer time in the water phase and can freely hydrolyze and condense. As soon as MPS is copolymerized, however, the rigid nature of the polymer chains along with the fact that the silane units are trapped inside the latex particles, afford an efficient protection against hydrolysis and condensation reactions which can no longer take place. This is presumably the reason no condensation products were formed when styrene was involved as the comonomer. MPS is indeed more reactive toward polystyryl radicals than toward PMMA. The reactivity ratios for the copolymerization reaction of styrene (monomer 1) and MPS (monomer 2) were reported to be  $r_1 = 0.45$  and  $r_2 = 0.9$ , respectively.<sup>21</sup> The silane units are expected consequently to be readily incorporated in the polymer chains in this case and be thus protected against further cross-linking reactions.

Silanol groups incorporation also has some consequences on the overall aspect of the resulting material. In the case of poly(butyl acrylate), for instance, which is a film forming polymer, the rigid inorganic network formed at the latex particle surface has a direct influence on coalescence and film formation. Despite the formation of a siloxane framework, an homogeneous, transparent and cohesive film was obtained after drying the latex suspension at  $70$  °C for 12 h. The latex film, however, was more rigid (somewhat brittle) and less tacky than pure poly(butyl acrylate), attesting to the presence of the inorganic phase in the hybrid material. The particle rigidity was confirmed by TEM analysis. Indeed, as shown in Figure 7a, the copolymer latex particles could be easily visualized under standard conditions (i.e., at ambient temperature and without any contrasting agent) meanwhile pure PBuA particles would have completely coalesced under the same conditions. It is worth reminding that because of their low  $T_g$ , PBuA latexes can only be observed by freeze-drying the particles and using specific equipments. These results again attest for the formation of an organic-inorganic network at the latex particles surface even though this polymeric network seems to be not rigid enough or too thin and too irregular to provide a dense barrier for polymer interdiffusion in the latex film. As shown in Figure 7b, the functionalization method is also very helpful for poly(methyl methacrylate) latex particles since it provides again a practical way to visualize the polymer beads without using any staining agents which are, in this particular case, necessary to enhance contrast and help reduce the radiation damage caused by exposure of the particles to the accelerating voltage.

## Conclusion

In this work, polystyrene latex particles carrying silanol groups on their surface have been synthesized in emulsion polymerization using MPS as a functional





**Figure 7.** TEM micrographs of SiOH-functionalized PBuA (a) and PMMA (b) latex particles. Scale bar: 100 nm.

comonomer. We showed that the colloidal stability of the latexes was highly dependent on the nature of the surfactant and on the pH of the suspension. Stable polymer particles were obtained using ionic surfactants under neutral or basic conditions. As expected, condensation of the silane molecule was promoted at low and high pH but no condensation occurred at all when the polymerization was performed at pH 7 except for large MPS concentrations. Residual nonreacted methoxy groups were identified into the copolymer latexes while spectroscopic analysis and  $\zeta$  potential measurements were used to attest for the presence of silanol groups on the particle surface. The functionalization technique was next extended to poly(methyl methacrylate) and poly(butyl acrylate) latexes. An inorganic polysilsesquioxane network was formed for both monomers at pH 7 and low MPS concentrations. In view of the reactivity ratios of the comonomers, it appeared that condensation reactions were promoted first by a decrease in reactivity of the silane molecule for the polymer radicals and second by the increase in the molecular mobility of the copolymer chains in the latex particles.

The hybrid structure of the resulting colloids obviously offers interesting perspectives in several applications where a compatibility between organic polymers and minerals is required. The SiOH functionality is also of major interest in various fields of material science as for instance catalysis, chromatography and biotechnology. Moreover, we showed, in a recent work, that the silanol group density can be finely tuned by varying the MPS concentration.<sup>13</sup> One could take benefit of the amphiphilic character of the organic–inorganic surface of the particles, therefore, to stabilize emulsions. In addition, our technique provides a versatile method to control the surface hardness of soft polymer latexes with significant consequences on coalescence and film formation. Finally, the hybrid copolymers could also find industrial applications as cross-linker agents and in room-temperature vulcanization of silicone rubbers.

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