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Silica-Polystyrene Nanocomposite Particles Synthesized by Nitroxide-Mediated Polymerization and Their Encapsulation through Miniemulsion Polymerization

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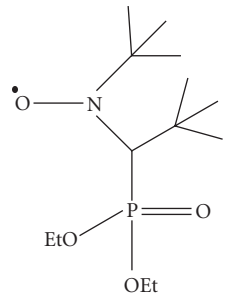
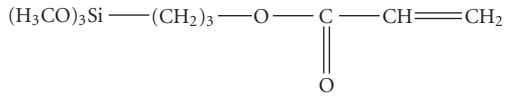
Polystyrene (PS) chains with molecular weights comprised between 8000 and 64000 $g \cdot mol^{-1}$ and narrow polydispersities were grown from the surface of silica nanoparticles (Aerosil A200 fumed silica and Stöber silica, resp.) through nitroxide-mediated polymerization (NMP). Alkoxyamine initiators based on N-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (DEPN) and carrying a terminal functional group have been synthesized in situ and grafted to the silica surface. The resulting grafted alkoxyamines have been employed to initiate the growth of polystyrene chains from the inorganic surface. The maximum grafting density of the surface-tethered PS chains was estimated and seemed to be limited by initiator confinement at the interface. Then, the PS-grafted Stöber silica nanoparticles were entrapped inside latex particles via miniemulsion polymerization. Transmission electron microscopy indicated the successful formation of silica-polystyrene core-shell particles.

1. INTRODUCTION

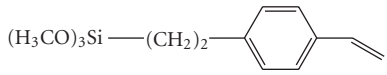
A key issue in the elaboration of organic/inorganic hybrids and nanocomposites is the creation of specific interactions at the interface of the organic and inorganic components. Among the large palette of existing techniques, living polymerizations offer versatile ways to engineer inorganic particle surfaces. Controlled radical polymerization allows the synthesis of polymers with various architectures (statistical copolymers, block copolymers, star polymers, etc.) with good control over the molecular weight and molecular weight distribution (polydispersities are typically less than 1.2-1.3). This chemistry was recently extrapolated to nanoparticles functionalization in order to elaborate well-defined nanocomposites which can be grown with the desired thickness and composition [1–12]. Recently, Parvole et al. [9], Kasseh et al. [7], and the authors et al. [10–12] have demonstrated that NMP is well adapted to the grafting of polymers from the surface of silica either in bulk or in solution. In these papers, various surface-immobilized initiators have been investigated to control the polymerization reaction. These initiators were based either on unimolecular alkoxyamines carrying trichlorosilyl or triethoxysilyl endgroups for further attachment on the silica surface [10–13] or on bimolecular systems based on the strategy of Rühe in which the NMP process is initiated from surface-immobilized azo or peroxide initiators [7, 9]. In most of these works, the resulting polymer-grafted silica particles were dispersed further into a polymer matrix by mechanical blending at high temperature or by lyophilization of the suspension mixture. However, to date, very little work has been devoted to the incorporation of polymer-grafted mineral particles into water borne polymers using for instance the miniemulsion polymerization technique although the later has found an increasing interest in recent literature [14–17]. Indeed, in miniemulsion, polymerization mainly occurs into small monomer droplets stabilized by the addition of a surfactant and a costabilizer. The polymer particles are thus the copy of the miniemulsion droplets. Therefore, if mineral particles can be successfully dispersed into the nanodroplets,



Structure 1: DEPN.



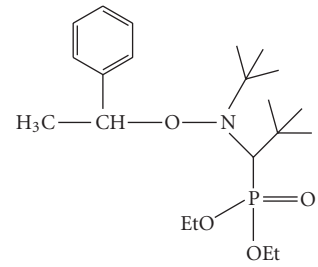
Structure 2: APTMS.



Structure 3: VETMSB.

composite particles made of for instance silica particles surrounded by a polymer shell will be obtained after polymerization.

Herein, we report two synthetic strategies in order to grow polystyrene chains from the surface of fumed silica (route I) and Stöber silica particles (route II), respectively using nitroxide-mediated polymerization. In the first route, the surface-alkoxyamine initiator was produced in a one step process by reacting simultaneously DEPN (Structure 1), AIBN, and acryloxy propyl trimethoxy silane (APTMS, Structure 2). The alkoxyamine was formed *in situ* by trapping of the acryloxy radicals produced by reaction of AIBN with APTMS and grafting of the resulting product onto silica according to the procedure previously described [12]. In the second route, a styrenic silane coupling agent (VETMSB, Structure 3) was first grafted onto the silica particles in a mixture of ethanol and water. Grafting of the alkoxyamine initiator was then performed by reacting styryl-DEPN (Structure 4) with the VETMSB-grafted silica in dimethylformamide (Scheme 1). The NMP of styrene from the grafted alkoxyamine silicas was performed in toluene for route I and in DMF for route II as this last solvent enabled us to maintain the silica particles colloidally stable all along during polymerization. In order to attest for the livingness of the free radical polymerization process, the monomer conversion, the polymer molecular weights and molecular weight distributions were analyzed as a function of



Structure 4: Styryl-DEPN.

time. The amount of grafted polymer chains was quantified and the bulk and surface compositions were compared for the two systems. In addition, dynamic light scattering (DLS) measurements and transmission electron microscopy (TEM) analysis were performed on the PS-grafted silica suspensions in order to examine the influence of the polymer molecular weight and the extent of grafting on the properties of the composite particles. At last, the polystyrene-grafted colloidal silicas were suspended into styrene and the resulting organic suspension was poured into water, emulsified and polymerized through miniemulsion in order to examine whether the silica particles could be encapsulated by polystyrene following this strategy.

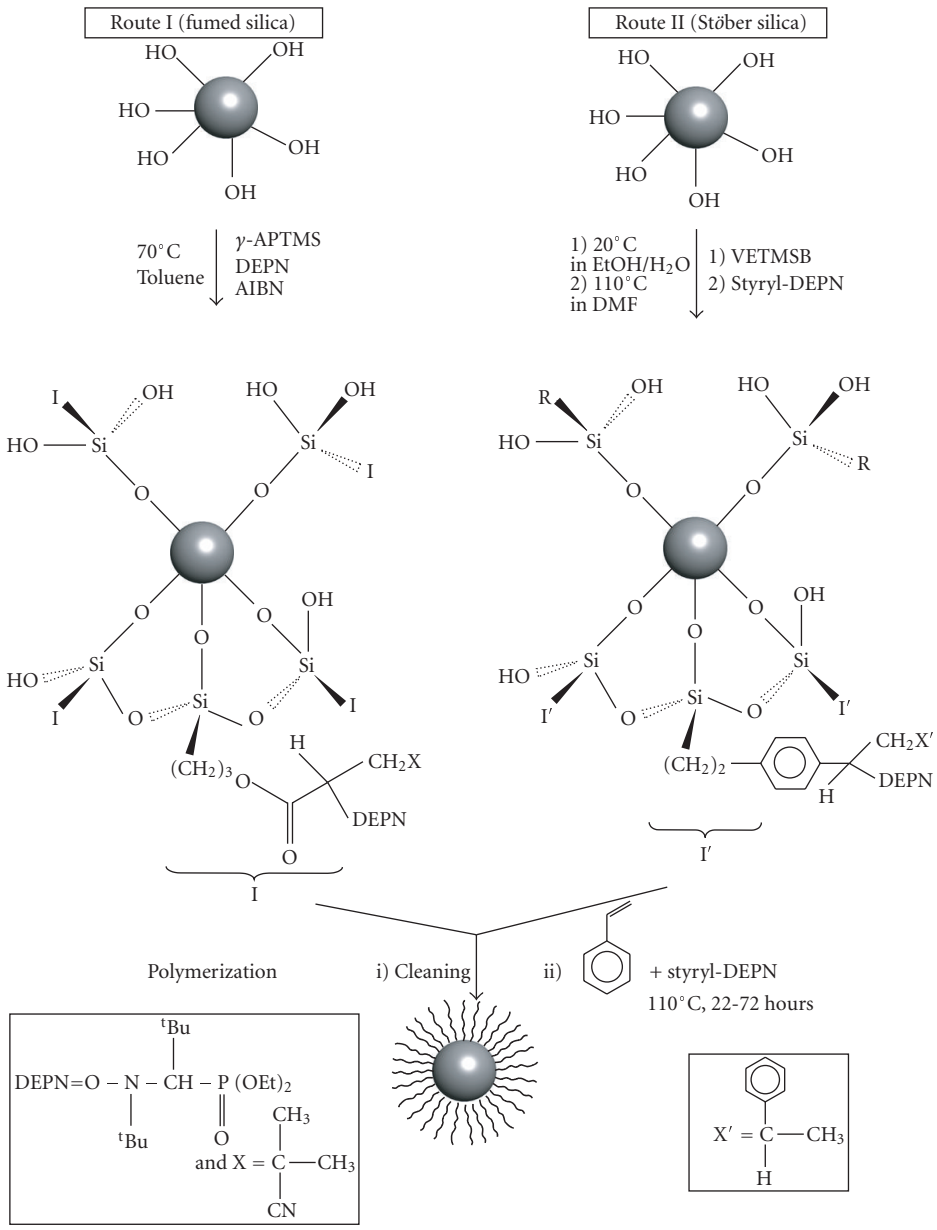
2. EXPERIMENTAL PART

2.1. Materials

Fumed silica (Aerosil A200V, Degussa) with an average diameter of 13 nm and a specific surface area of 228 m^2/g was dried four hours at 150°C under a vacuum before use. Styrene (99%, Aldrich), dimethylformamide (99%, Aldrich) and toluene (99.3%, Aldrich) were vacuum distilled on molecular sieve before use. Azobisisobutyronitrile (AIBN, 98%, Acros Organics) was recrystallized from methanol. Tetraethoxysilane (TEOS, Acros Organics), ethyl alcohol (Acros Organics), ammonia (29% in water, Carlo Erba), acryloxy propyl trimethoxy silane (APTMS, 95%, Gelest), and *p*-vinyl(ethyltrimethoxysilane) benzene (VETMSB, Structure 3, Acros Organics, 99%) were used as supplied. DEPN (88%) was kindly supplied by Atofina, and used as received. The free initiator, a DEPN-based alkoxyamine (styryl-DEPN, Structure 4), was prepared using a procedure described in the literature [18]. The initiator, potassium persulfate (KPS, Aldrich), cetyl alcohol (Aldrich), and sodium dodecyl sulfate (SDS, Aldrich) were of analytical grade and used as received.

2.2. Synthesis of the Stöber colloidal silica suspension

Monodisperse silica particles were synthesized in two steps. First, a silica seed suspension was prepared by introducing



Scheme 1: Chemical routes to polystyrene-decorated silica nanoparticles by nitroxide-mediated polymerization of styrene. Fumed silica are involved in the first route while Stöber silica particles have been employed in the second route.

41.6 g of TEOS in a mixture of absolute ethanol (667.8 g), water (101.3 g) and ammonia (8.4 g) according to the procedure first described by Stöber et al. [19]. The mixture was stirred for 24 hours at room temperature and yielded silica particles with an average diameter of 61.3 nm and a 1.8 wt% solid content. Seeded growth of the silica suspension was then performed by the addition of a solution of TEOS (96 g) in ethanol (113.5 g) at the rate of 20 mL per hour and stirring for 48 hours. The final suspension had an average particle diameter of 79.7 nm determined by DLS and a solid content of 5.4 wt%. Figure 1 shows the TEM image of the thus produced silica particles.

2.3. *Initiator attachment on the silica surface and stable free radical polymerization of styrene from the functionalized silica surface*

The graft polymerization of styrene from the surface of silica involves two steps (Scheme 1): (i) in situ grafting of a triethoxysilyl-terminated alkoxyamine initiator [12], and (ii) controlled growth of polystyrene chains from the silica surface in the presence of free alkoxyamine initiator. In the first route, 1.22 g of the APTMS coupling agent (5.2 mmoles corresponding to 12 μmol/m^2 of silica) was added to a suspension of silica (1.9 g) in toluene (93 g) and stirred for 30

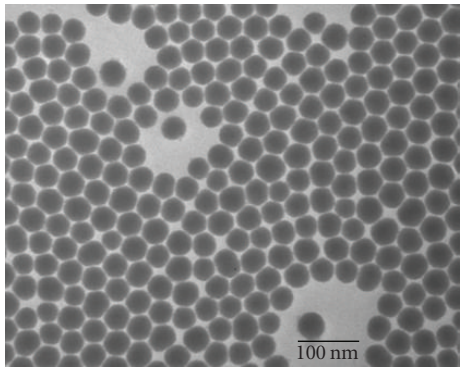


Figure 1: TEM image of the Stöber silica sample. Scale bar=100 nm.

minutes at room temperature. Then, 1.1 g of **3** (corresponding to 3.65 mmoles) and 0.4 g of AIBN (2.6 mmoles) were introduced in the reaction flask. The suspension was degassed by 4 freeze-pump-thaws, and the mixture was heated to 70°C for 26 hours. The grafted silica was extensively washed by successive centrifugation/redispersions in toluene in order to remove the excess reagents before characterization. The nitroxide-mediated polymerization experiments were then conducted as follows. The alkoxyamine-functionalized silica (0.3 g), toluene (57.3 g, 0.62 mol), styrene (60.4 g, 0.58 mol), and 0.2 g (0.68 mmol) of the "free" alkoxyamine initiator (styryl-DEPN, Structure 4), corresponding to a total styrene-to-initiator molar ratio of 800, were introduced in a predried Schlenk flask under an argon atmosphere. After stirring for a few minutes, the suspension was degassed by 4 freeze-pump-thaw cycles, and the polymerization mixture was heated to 110°C for 5 to 30 hours. The conversions were determined gravimetrically by precipitation in methanol. The free nongrafted polystyrene was removed from the silica suspension by successive centrifugation/redispersion cycles in toluene. The polymer grafting density was then determined by carbon elemental analysis as described in our previous work [10–12].

In the second route, 2.8 g of VETMSB (11 mmoles or 5.5 μmoles/m^2) was first added to a suspension of silica (48.2 g) in EtOH/H_2O 50/50 v/v (1058 g) and stirred for 78 hours at room temperature. The free nongrafted VETMSB was discarded by successive centrifugation/redispersion cycles. A small part of the grafted silica powder was dried in a vacuum oven at 50°C before characterization while the remaining part (2.24 g) was redispersed in DMF (80.6 g, 1.1 mol). The surface alkoxyamine was then formed *in situ* by introducing 0.32 g (0.80 mmol, 8.5 μmol/m^2) of styryl-DEPN (Structure 4) in a predried Schlenk flask under an argon atmosphere. The suspension was degassed by 4 freeze-pump-thaw cycles and heated to 110°C for 72 hours. The graft-from polymerization was pursued in the same reactor by adding 66.5 g of styrene (0.64 mol) corresponding to a total styrene-to-initiator molar ratio of 800. After stirring for a few minutes, the suspension was degassed by 4 freeze-pump-thaw cycles, and the polymerization mixture was heated to 110°C for 5 to 30 hours. The conversions were determined as described above for route I while the free nongrafted polystyrene was removed from the silica suspension by successive centrifugation/redispersion cycles in DMF.

2.3.1. Synthesis of silica-polystyrene core-shell particles through miniemulsion polymerization

The PS-grafted Stöber silica (1.5 g) was dispersed into 15 g of styrene and the resulting suspension was introduced into 150 g of an aqueous solution containing the surfactant (SDS, 0.45 g) and the hydrophobe (cetyl alcohol, 1.2 g). The overall mixture was finally sonified for 1 minute (90% output power) to create the silica-loaded miniemulsion droplets. The polymerization was carried out in a double-wall thermostated reactor at 70°C for 5 hours. The reactor was first purged with nitrogen for 1 hour and potassium persulfate (0.15 g) was used as initiator to start polymerization. The silica, droplet, and composite particles number per unit volume of water was calculated by the following equation:

$$\frac{N_p}{L} = \frac{M/\rho}{(\pi/6)Dp^3 \cdot V} \times 10^{19}, \tag{1}$$

where M (g) is the total mass of silica or silica plus monomer, ρ(g·cm^{-3}) is the particles or droplets density, Dp (nm) is, respectively, the diameter of the silica, the monomer droplets or the composite latex particles determined by DLS, and V (in liter) is the total volume of water.

2.3.2. Characterizations

SEC analysis was performed using a 410 Waters differential refractometer, a 996 Waters photodiode array detector, a 717 Waters autosampler, and a 515 Waters HPLC pump. THF was used as eluent. Polymer molecular weights were derived from a calibration curve based on polystyrene standards. The initiators and polymer grafting densities were determined by elemental analysis from the difference of carbon content (ΔC, wt%) after and before grafting, using (2) below:

$$\text{Grafting density } (\mu\text{mol/m}^2) = \frac{10^6 \Delta C}{[(1200Nc\text{-}\Delta C(M\text{-}1)) \times S_{spec}]}, \tag{2}$$

where Nc and M designate, respectively, the number of carbon atoms and the molecular weight of the grafted molecule, and S_{spec}(m^2·g^{-1}) is the specific surface area of silica.

TEM analysis was performed on 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. The particle and droplet sizes were determined by DLS using a Malvern autosizer Lo-c apparatus with a detection angle of 90°. The measurements were carried out at 23°C on highly diluted samples in order to rule out interaction and multiple scattering effects. The intensity average diameter was computed from the intensity autocorrelation data using the cumulant analysis method.

Table 1: Polymer grafting densities for a series of "graft-from" polymerization reactions performed in the presence of fumed silica (route I) and Stöber silica (route II), respectively.

Route	Run	Styrene/Initiator (molar ratio)[(b)]	Time (h)	Conversion (%)	Mn_{th} (g/mol)[(c)]	Grafting density[(d)]	Free polymer in solution	
							Mn (g/mol)	Mw/Mn
I[(a)]	**1**	800	22	33	27490	0.33	30700	1.22
	2	800	54	63	52416	0.32	55500	1.20
II[(a)]	**3**	800	30	38	31616	0.10	64000	1.45
	4	400	30	68	28288	0.14	37000	1.34

[(a)]The alkoxyamine grafting density is of approximately 0.75 μmol/m^2 for route I and 2 μmol/m^2 for route II.
[(b)]Initiator = surface-grafted initiator + free initiator.
[(c)]$Mn_{th} = ([M]_0/[I]_0) \times$ Mw of styrene $\times$ conv/100.
[(d)]Determined by carbon elemental analysis using (2) and the molecular weight of the free polymer in solution.

3. RESULTS AND DISCUSSION

3.1. Initiator immobilization

Grafting of the alkoxyamine initiators on the silica surface was qualitatively evidenced by FTIR and solid state NMR spectroscopies which attested for covalent attachment of the silane coupling agents [11, 12]. The density of the initiator units, determined by carbon elemental analysis, was around 0.75 μmol/m^2 in the case of route I [12] which value is from two to three times lower than the values given in the literature for the grafting of a series of organotrialkoxysilane and chlorosilane molecules [5]. In our experiments, approximately 12.5% of the original amount of silanol groups had reacted, which suggests the occurrence of steric hindrance limitations and physisorption of the DEPN moiety onto the silanol groups of silica during the grafting reaction. In the second route, the grafting density of VETMSB on the Stöber silica surface was also calculated from carbon elemental analysis using (2). It was found that around 5 μmol/m^2 of the silane coupling agent were grafted onto silica which value excluded the possibility of the formation of a single monolayer. Indeed, VETMSB molecules can condense with one another before condensing on the silica surface and form multilayers of VETMSB molecules as described in the literature for trimethoxysilyl-terminated silane coupling agents [8, 20–22]. After the grafting of VETMSB on the silica surface, we performed the insertion of Styryl-DEPN to create an alkoxyamine by *in situ* trapping of carbon radicals. This reaction was conducted in dimethylformamide at 110°C. The amount of the resulting grafted alkoxyamine was determined again by carbon elemental analysis. The grafting density calculated from (2) is around 2 μmol/m^2. This result is in good agreement with the grafting density (2.4 μmol/m^2) reported by Von Werne and Patten [2] for the grafting of an ATRP initiator but is twice higher than the value given in the literature for *in situ* grafting of alkoxyamine initiators [8, 9]. It is likely that some physisorption may also occur here together with the coupling reaction. In addition, DLS measurements revealed that the initiator-coated silica particles were perfectly dispersed in DMF as their diameter remained almost unchanged after grafting.

3.2. Surface initiated polymerization

The polymerizations were conducted in a 50/50 (v/v) styrene/toluene solution for route I and in a 50/50 (v/v) styrene/DMF solution for route II in the presence of 1 wt% of silica and a known amount of "free" sacrificial initiator. The addition of "free" alkoxyamine creates an overall concentration of nitroxide in the polymerization mixture, which controls the chain growth of both the immobilized and soluble initiators, and allows one to achieve a good molecular weight control. According to previous studies [1, 2, 8, 10–12, 23–25], it can be reasonably assumed that the molecular weight of the free polymer chains is similar to that of the grafted polymer. Thus, the "living" character of the polymerization reaction can be assessed by following the molar mass and the polydispersity indexes of the free polymer only.

For route I, the data in Table 1 indicates a good agreement between the experimental molecular weights and the theoretical ones as expected for a controlled polymerization reaction. This result suggests that steric constraints around silica particles have no influence on the livingness of the free radical process. Moreover, a maximum polymer grafting density (determined from the molecular weight, Mn, of the free polymer in solution) of around 0.32 μmol/m^2 was achieved under optimal conditions whatever the polymer molecular weight comprised between 30000 and 60000 g·mol^{-1}. From this data, we can calculate that approximately 40% of the grafted alkoxyamine underwent polymerization which value is in close agreement with the data reported by Böttcher et al. [5] or Kasseh et al. [7] on silica nanoparticles. However, this value is inconsistent with the observed agreement between the theoretical and the experimental molecular weights (runs 1 and 2 in Table 1). This discrepancy can be reasonably attributed to the desorption of physically adsorbed initiator molecules during polymer chain growth as stated in a previous report [12]. Indeed, some alkoxyamine molecules are suspected to be only physically attached to the silica surface. Therefore, these physisorbed molecules could progressively desorb from the surface during polymerization as the growing polymer chains are becoming more and more hydrophobic and displays consequently less affinity for the inorganic surface.

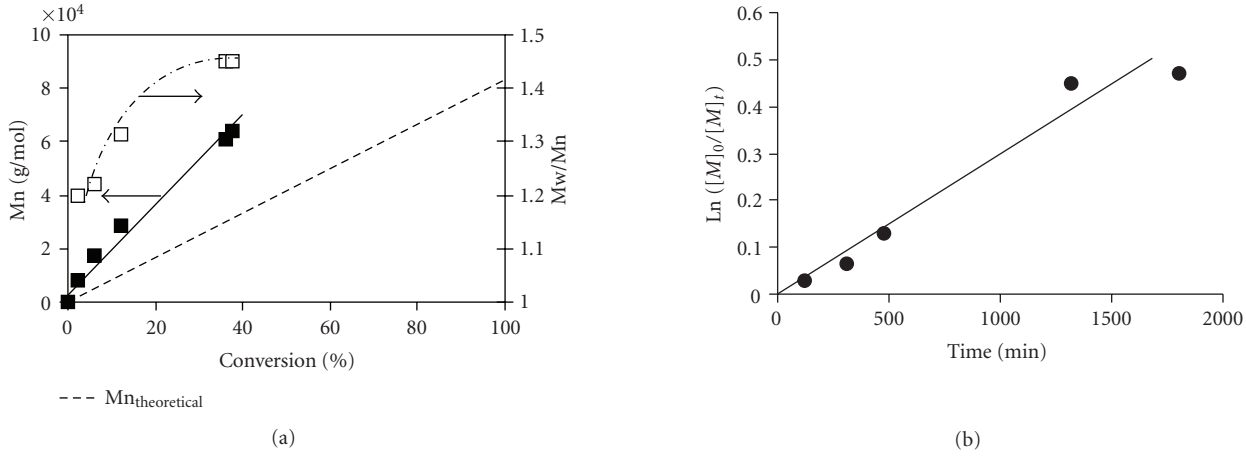


Figure 2: (a) Variation of Mn with conversion and (b) first-order kinetic plot for the DEPN-mediated stable free radical polymerization of styrene in the presence of alkoxyamine-grafted Stöber silica particles (route II). *Initiator-to-styrene molar ratio* = 800.

In route II, the polymerization was conducted in DMF in order to keep a colloidally stable system all along during the growth process. As shown in Figure 2(b), the polymerization exhibited first-order kinetics with respect to total monomer conversion. In addition, Mn evolved linearly with conversion while the polydispersity was lower than 1.5 and increased with increasing conversion. All these results confirm that the graft polymerization of styrene from the Stöber silica surface exhibits all the characteristics of a controlled/"living" polymerization.

However, it can be seen in Figure 2 and in Table 1 that the experimental molecular weights are higher than the theoretical values, Mn_{theo}, determined from the polymerization conversion and the monomer to initiator ratio. The discrepancy between the experimental and theoretical molecular weights may have different origins. First, it may be argued that the steric hindrance of the grafted alkoxyamine is responsible for a loss of initiator efficiency by blocking the access of monomer to all the initiator sites as already observed by Von Werne and Patten [2] and El Harrak et al. [24] for the ATRP of styrene from the surface of Stöber silica particles. But, according to Böttcher et al. [5], this can most likely be ascribed to chain termination reactions promoted on the silica surface by the close proximity of the propagating "living" radicals or by the termination between a free chain formed in solution and a surface-bound polymer at the initial stage of the radical polymerization. However, in the present system, this can be mostly attributed to undesirable side reactions occuring during the formation of the surface alkoxyamine initiator by the reaction of styryl-DEPN with the VETMSB-grafted silica. Indeed, part of the styryl-DEPN molecules could be lost during this coupling step. In order to check if our hypothesis is correct, we doubled the styryl-DEPN concentration into the polymerization medium (run 4 in Table 1). The styrene-to-initiator molar ratio was thus decreased from 800 to 400. The data in Table 1 and the kinetics plots of Figure 3 show

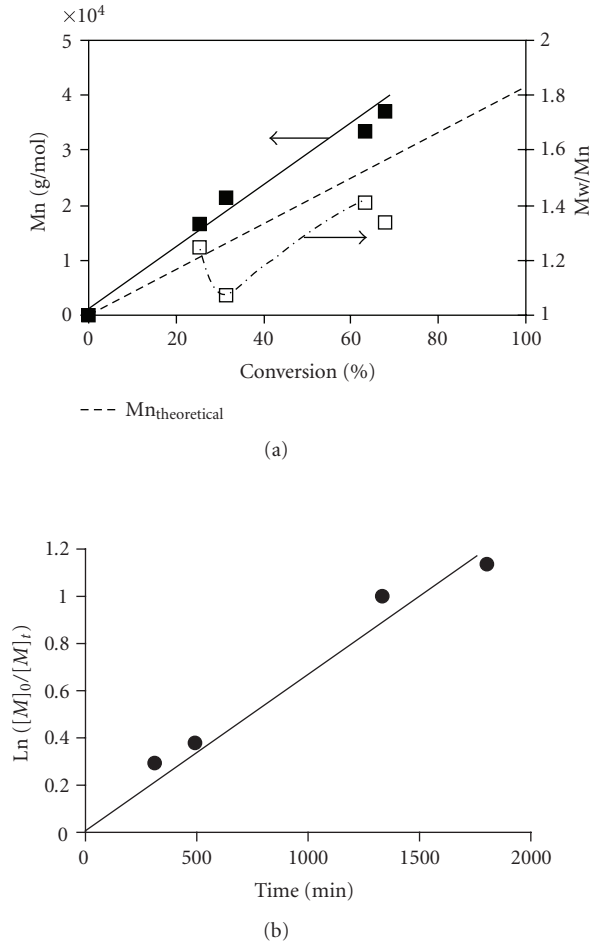
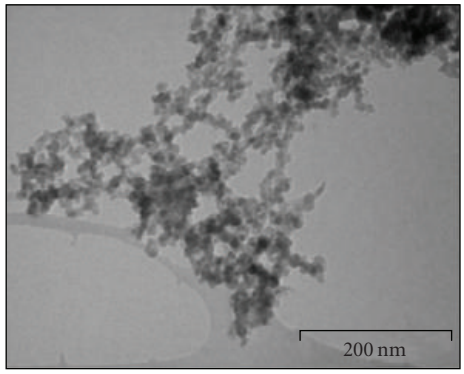
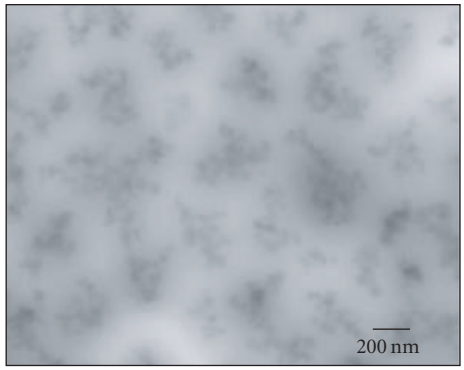


Figure 3: (a) Variation of Mn with conversion and (b) first-order kinetic plot for the DEPN-mediated stable free radical polymerization of styrene in the presence of alkoxyamine-grafted Stöber silica particles (route II). *Initiator-to-styrene molar ratio* = 400.



(a)



(b)

Figure 4: TEM images of (a) bare fumed silica particles and (b) PS-grafted silica particles cast from dilute toluene suspensions (route I). Mn of free PS = 55500 g·mol^{-1} (sample 2 in Table 1).

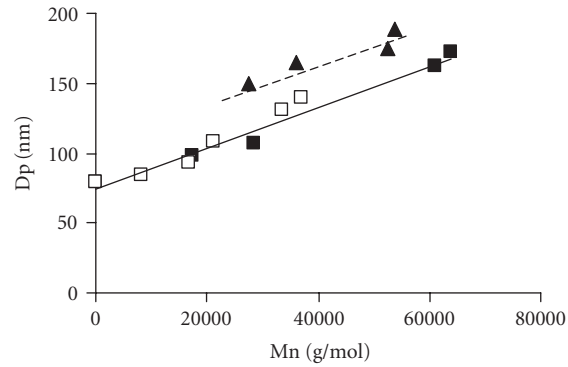


Figure 5: Hydrodynamic diameter of the polystyrene-grafted silica particles as a function of the molecular weight of the grafted polystyrene chains. □ route II, Table 1, *Initiator-to-styrene molar ratio* = 400, ■ route II, *Initiator-to-styrene molar ratio* = 800, ▲ route I, *Initiator-to-styrene molar ratio* = 800.

that the experimental molecular weight, Mn, is closer to the theoretical one in agreement with the above arguments.

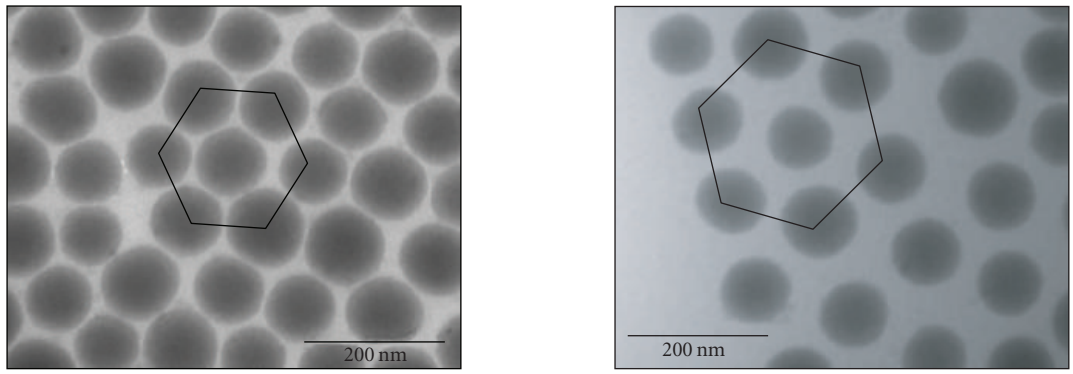
Further insight into the grafting mechanism was obtained by determining the polymer chains grafting density. The data in Table 1 indicate that the polystyrene grafting densities estimated from carbon analysis are close to 0.1 μmol/m^2 independently of the styrene-to-initiator molar ratio (runs 3 and 4 in Table 1). This value is three times lower than the polystyrene grafting densities obtained for fumed silica (0.3 μmol/m^2) and confirms the hypothesis according to which termination reactions are promoted on the silica surface due to confinement of the initiator radicals.

3.3. Characterization of the PS-grafted silica suspensions

TEM images of starting silica gel particles and PS-grafted silicas are shown in Figure 4. According to manufacturer's specifications, the diameter of the aerosil silica particles is around 13 nm. However, TEM clearly indicates that the particles form micrometer-sized domains of stringy-shaped aggregates when cast from diluted toluene suspensions (Figure 4(a)). After grafting of the polystyrene chains (Figure 4(b)), the silica particles appear regularly distributed within the polymer film which indicates that the agglomerates have been partly destroyed. It is then clear from these results that the formation of a hairy polymer layer around silica provides a steric barrier against particles aggregation in organic medium.

The above observations were confirmed by DLS measurements which indicated that the dispersability of the silica gel particles in toluene was greatly improved after grafting. The hydrodynamic diameter of the PS-grafted silica increased from 150 nm to 190 nm with increasing the molecular weight of the grafted polymer from 27500 to 55500 g·mol^{-1} (Figure 5) as expected for spherical particles coated with a layer of densely grafted polymer chains [26]. A similar behavior was observed in route II for which the hydrodynamic diameter of the polystyrene-grafted silica particles increased from 80 nm to 170 nm with increasing the polymer molecular weight from 0 to 64000 g·mol^{-1} (Figure 5). It is worthwhile to notice that the two lines have identical slopes.

The linear increase of particles size with the polymer molecular weight indicates the formation of a densely grafted polymer brush on the silica surface. Indeed, as recently argued by Zhao and Brittain [26], the fact that the polymer thickness varies linearly with the degree of polymerization constitutes a strong argument in favor of a polymer brush conformation at the mineral surface. Let us consider for instance PS-grafted silica particles with a hydrodynamic diameter of 98 nm (Figure 5, route II), the average thickness of the polymer shell (whose number average molecular weight is around 17450 g·mol^{-1}) is thus of around 9 nm. Considering that the radius of gyration of polystyrene chains with a molecular weight of 14300 g·mol^{-1} in THF is about 4 nm [2], the thickness of the hairy polymer layer is more than twice the radius of gyration of the polystyrene chains indicating that the later has adopted an extended brush conformation at the silica surface.



(a) (b)

Figure 6: TEM images of PS-grafted colloidal silica. (a) Mn = 8340 g·mol^{-1} (b) Mn = 61000 g·mol^{-1}.

The TEM images of the PS-grafted Stöber silica with different molecular weights are shown in Figure 6. The silica nanoparticles core appears as dark spheres uniformly dispersed throughout the polymer film (in gray). It can be seen that the interparticle distance increases with increasing the polymer molecular weight as already demonstrated by several authors [2, 22, 27]. This indicates that the film characteristics can be readily manipulated by varying the degree of polymerization of the grafted polymer chains and the silica particles diameter. The regular arrangement of the silica spheres within the film is again in favor of the formation of a well-defined high density polymer brush at the silica surface.

3.4. Miniemulsion polymerization

Although there have been many reports in recent literature on the incorporation of surface-functionalized mineral particles in miniemulsion recipes including clay [17], ZnO, and silica colloids [16], to the best of our knowledge, there are no reports mentioning the utilization of polymer-coated mineral particles. Therefore, in the following, we aim to demonstrate that PS-grafted silica particles can be successfully encapsulated by polystyrene through miniemulsion polymerization according to the procedure detailed in the experimental section. Indeed, as shown in the previous paragraphs, grafting of polystyrene chains to the silica surface is an effective way to enhance their hydrophobicity, prevent particles floculation, and make them compatible with most organic media. As expected, the PS-grafted Stöber particles could be thus successfully dispersed into styrene without particles aggregation which constitutes a key issue of the miniemulsion polymerization process as schematically represented in Figure 7(a). Figure 7(b) displays TEM images of the resulting composite latex particles. The top image shows the formation of a large number of unfilled polystyrene spheres with only one encapsulated silica particle. The ratio between the number of empty and filled latex spheres can be estimated to be around 400 by manually counting directly on the TEM micrograph. The bottom image of Figure 7(b) shows a selected enlarged region on the copper grid. The PS-grafted silica particles appears as dark spheres surrounded by a polystyrene shell in an excentered core-shell morphology. A careful examination of a large number of particles allows us to testify that there are no composite particles containing more than one silica bead. This is presumably due to the diameter of the PS-grafted silica spheres (e.g., around 173 nm) which is close to that of the monomer droplets (see Table 2). It is thus hardly conceivable to have two silica spheres dispersed in a single droplet. In addition, the fact that we did not observe more than one silica particle per composite particle strongly suggests the absence of coalescence during polymerization. It is worth mentioning also that there are no free silica beads in the suspension medium as all the silica particles are surrounded by polymers. Quantitative information on the respective population numbers (e.g., the silica, the silica-loaded monomer droplets, and the composite particles) can be obtained from their respective diameters determined by DLS. The data are shown in Table 2. It can be seen from Table 2 that the number of droplets is two orders of magnitude higher than the silica particles number which is mainly due to the low silica concentration used in this particular experiment. Increasing the silica concentration should allow us to generate a higher proportion of silica-filled particles. In addition, it should be mentioned also that the composite particles number is one order of magnitude higher than the number of droplets which indicates the occurrence of renucleation. The ratio between the number of composite and silica particles is therefore of around 700 in agreement with the above TEM analysis.

In summary, although the experimental conditions need to be optimized in order to get a better agreement between the droplet and particle sizes (by changing, e.g., the nature and/or concentration of the costabilizer) and improve the efficiency of the encapsulation reaction (by increasing the silica particles concentration), the above preliminary experiment has opened a new route to polymer-encapsulated minerals. As a matter of fact, this method should be in principle applicable to various polymer-grafted minerals and thus

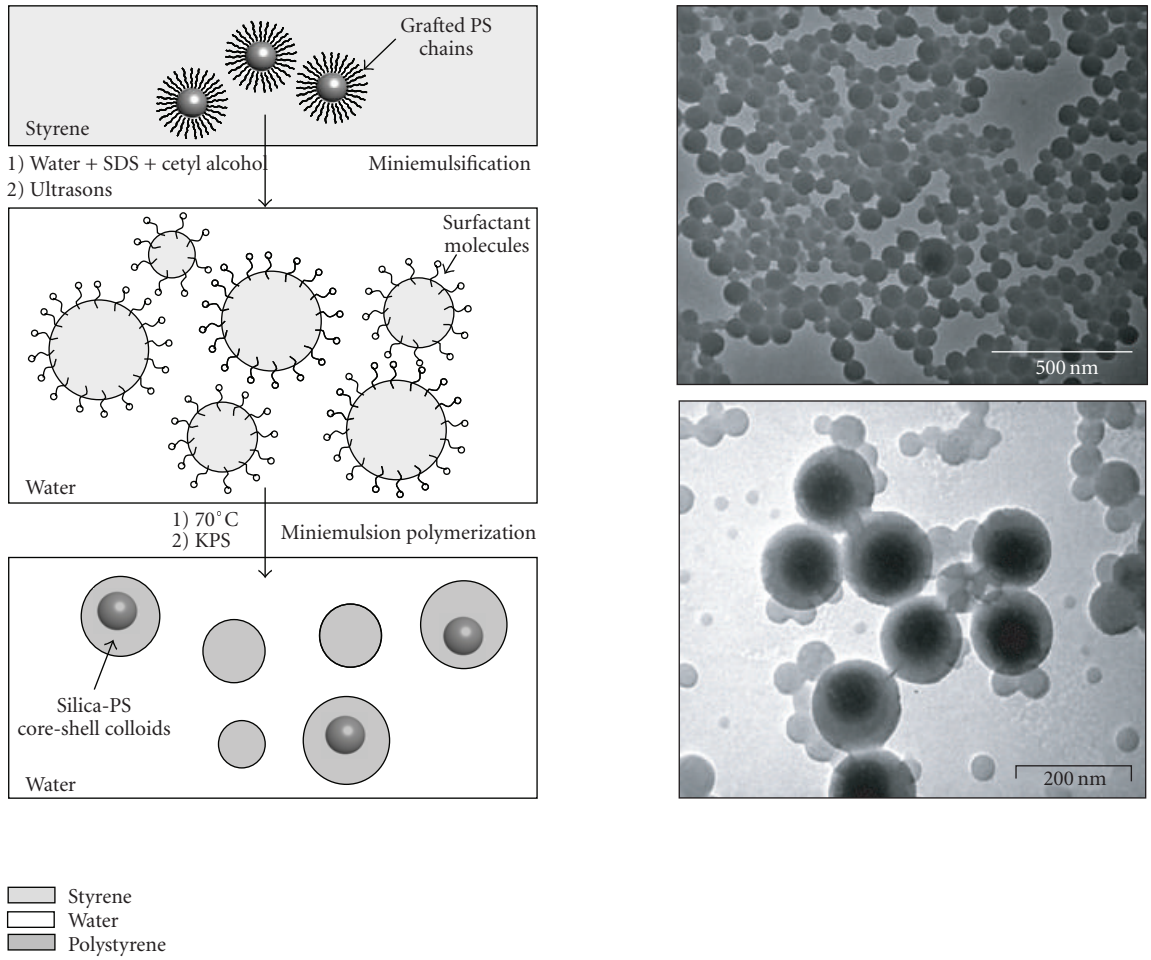


Figure 7: (a) Scheme illustrating the principle of PS-grafted silica particles encapsulation through miniemulsion polymerization and (b) transmission electron micrographs of the thus-produced silica-polystyrene core-shell latex particles. Mn of the grafted polymer chains is around 64000 g·mol^{-1} (run 3 in Table 1); the arrow points out one encapsulated silica particle within unfilled polystyrene spheres.

Table 2: Silica, droplets, and composite particle sizes and numbers during the encapsulation reaction of PS-grafted Stöber silica colloids through miniemulsion polymerization. The molecular weight of the grafted polymer chain is around 64000 g·mol^{-1}, while the diameter of the PS-grafted silica is around 173 nm in DMF.

Particles diameter (nm)[a]			Particles number (per liter of water)		
Silica	Droplets	Composite particles	Silica[b]	Droplets[c]	Composite particles
70.7	212	114.2	$5.2\ 10^{14}$	$6.6\ 10^{16}$	$4.2\ 10^{17}$

[a] Determined by DLS.
[b] Determined using (1) with $[SiO_2] = 10\ g \cdot L^{-1}$.
[c] Determined from the droplet size by considering the overall amount of silica plus monomer.

extendable to other miniemulsion formulations including polar acrylic monomers by correctly defining the nature of the grafted polymer chains. Indeed, polymer-encapsulated minerals are of potential interest in coating applications. The inorganic particles are incorporated into the composite material to improve the mechanical properties of the coating while a good dispersion of the mineral into the polymer matrix ensures the obtention of transparent films.

4. CONCLUSION

Polystyrene chains with molecular weights comprised between 8000 and 64000 g·mol^{-1} and narrow polydispersities were successfully grown from the surface of silica nanoparticles. TEM analysis showed that it was possible to control nanoparticles ordering, interparticles distance, and spatial organization of the inorganic particles within the polymer

matrix by varying the polymer molecular weight. In addition, the PS-grafted silica particles could be successfully redispersed into styrene to generate silica-loaded monomer droplets by miniemulsification. The resulting nanodroplets were polymerized in miniemulsion giving rise to the formation of silica-polystyrene core-shell particles.

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