# Nitroxide-Mediated Polymerizations from Silica Nanoparticle Surfaces: "Graft from" Polymerization of Styrene Using a Triethoxysilyl-Terminated Alkoxyamine Initiator

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ABSTRACT: Nitroxide-mediated stable free radical polymerization of styrene was performed from 13 nm diameter silica nanoparticles in two steps. First, an alkoxyamine, based on *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (DEPN) carrying a terminal triethoxysilyl functional group was synthesized and covalently attached onto silica. Polystyrene chains with controlled molecular weights and narrow polydispersities were then grown from the alkoxyamine-functionalized nanoparticles surface. The grafting of both the initiator and the polystyrene was qualitatively evidenced by FTIR spectroscopy and solid-state NMR and quantified by thermogravimetric and elemental analysis. More than 40% of the surface bound alkoxyamine initiator participated in the growth reaction. Polymer graft densities of around 110 chains per particle were obtained by this technique.

## Introduction

In recent years, an increased interest has been devoted to the elaboration of organic/inorganic nanocomposites. Owing to the major technological and fundamental applications of this new class of materials, processing techniques based on either physicochemical routes or polymerization methods have been described in the literature.[1−4] A key feature in the construction of hybrid systems is the development 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 particles' surfaces. Three main routes are usually reported to chemically attach a polymer to a surface: (i) the "grafting onto" method, where end-functionalized polymers react with appropriate surface sites;[5] (ii) the "grafting from", where chains grow in situ from preformed surface-grafted initiators;[6−8] and (iii) surface copolymerization through a covalently linked monomer.[9] The "grafting from" approach is the most appropriate method to grow high densities of grafts because of easy access of the reactive groups to the chain ends of the growing polymer. This technique, combined with controlled free radical polymerization, has therefore been used to build up highly dense polymer brushes from planar surfaces[10] and was recently extrapolated to nanoparticle functionalization in order to elaborate well-defined nanocomposites that can be grown to the desired thickness and composition.[11−18] Von Werne and Patten[11−13] described for instance the atom transfer radical polymerization (ATRP) of methyl methacrylate and styrene from colloidal silica particles by using monoethoxysilane-terminated ATRP initiators. Boettcher[14,15] focused on the same ATRP process and reported on the graft density of a first and a second generation of polystyrene grafted from silica. He showed that approximately 10−15% of the first generation of grafts was not active for reinitiation of the second monomer feed. Although there are many recent examples of ATRP in the literature, it appears that examples of "graft from" polymerizations by the so-called "stable free radical polymerization" (SFRP) process are scarce. Recently, Parvole[16] and Kasseh[17] reported the nitroxide-mediated polymerization reactions from azo or peroxide initiators attached to fumed silica. One major drawback of this method, however, is the low initiation efficiency. Blomberg[18] described the elaboration of shell cross-linked polymeric capsules in a multistep procedure by templating colloidal silica with polymeric compounds and cross-linking the polymer shell. Micrometric silica beads were first modified by grafting a chlorosilane alkoxylamine initiator on their surface, and copolymers were then grown from the surface-attached initiator using an appropriate amount of sacrificial "free" alkoxylamine. However, the emphasis was put on material aspects, and nearly no mention was made of the quantitative aspects of the grafting reaction (graft density and grafting yield).

Herein, we report the grafting of a novel triethoxysilyl-terminated alkoxyamine initiator based on DEPN[19] (structure **1**, Scheme 1) onto silica and the subsequent SFRP reaction of styrene from the functionalized surface in the presence of a "free" sacrificial styrylDEPN alkoxyamine (structure **2**). The functional alkoxyamine **1** was designed to contain a cleavable ester group in order to facilitate degrafting of the polymer chains for analytical purposes. The grafted and free polymers could be thus characterized separately and compared (Scheme 2).

This first paper emphasizes the quantitative determination of the graft density in order to get optimal surface coverages. A subsequent paper will describe an alternative procedure to elaborate a surface-tethered SFRP initiator by in situ trapping carbon radicals

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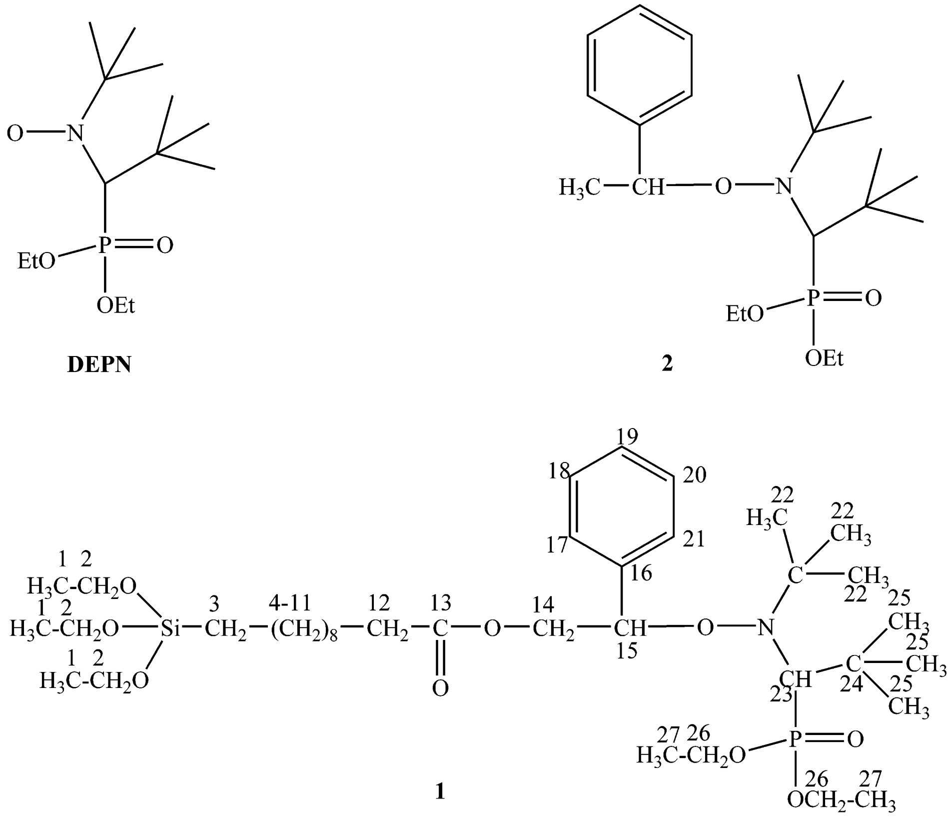
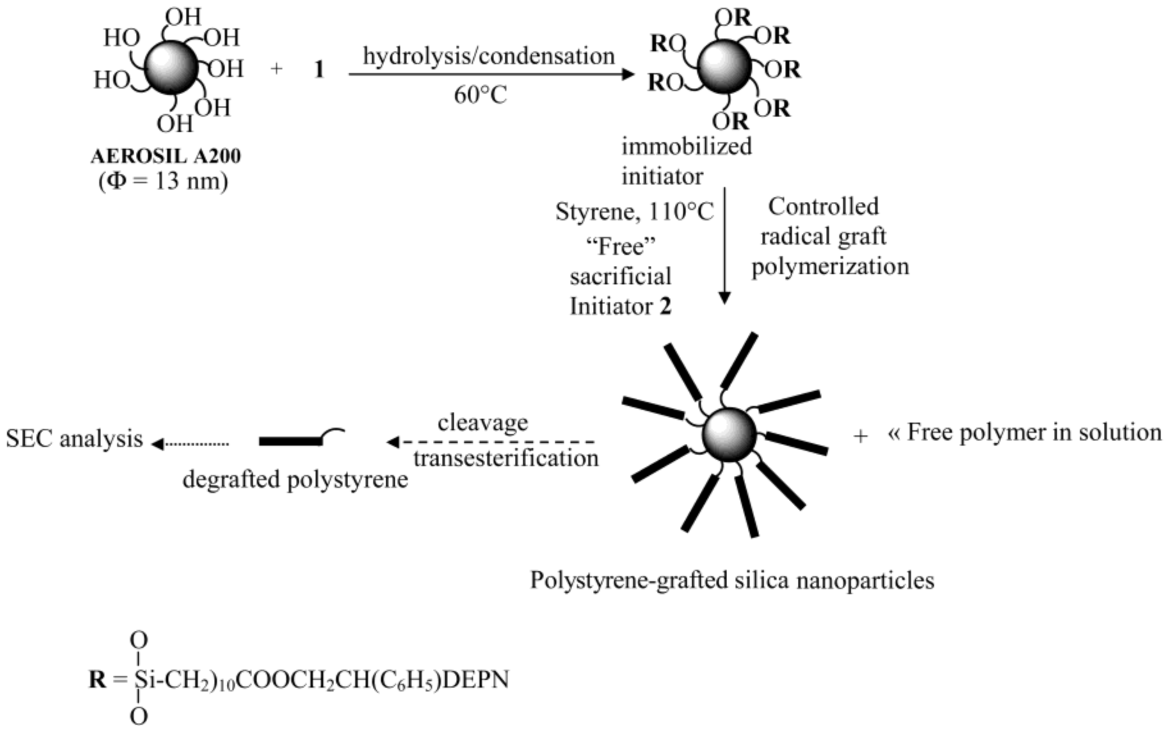
**Scheme 1. Chemical Structures of the DEPN Counter Radical, the Functional Alkoxyamine 1, and the Free Sacrificial Alkoxyamine Initiator 2**



**Scheme 2. Schematic Representation of the “Grafting from” Procedure**



attached to the surface. Future works will concentrate on the potential of these “graft from” procedures for the elaboration of nanocomposite materials.

## Experimental Section

**Materials.** Nonporous silica particles (Aerosil A200V, Degussa), with an average diameter of 13 nm and a specific surface area of 228 m$^2$ g$^{-1}$, were dried for 3 h at 150 °C under vacuum before use. Toluene (99.5%, Aldrich) was dried on molecular sieve (3 Å) and stored under an argon atmosphere. Methyl alcohol (99.9%, Aldrich) and *p*-toluenesulfonic acid monohydrate (98.5%, Aldrich) were used as received. DEPN (85%) was kindly supplied by Atofina and used as received. The alkoxyamine **1** was prepared in four steps according to the method previously described.[19] The free initiator, a DEPN-based alkoxyamine (styrylDEPN, **2**), was prepared using a procedure described in the literature.[20]

**Characterization.** The Fourier transform infrared (FTIR) spectra were recorded on powder pressed KBr pellets using a Nicolet 460 spectrometer with a resolution of 4 $cm^{-1}$.

$^{29}Si$ and $^{13}C$ solid-state NMR was performed at magic angle spinning (MAS) on a Bruker DSX-300 spectrometer operating at 59.63 and 75.47 MHz, respectively, by use of cross-polarization from a proton. The contact time was 5 ms, the recycle delay 1 s, and the spinning rate 10 kHz. The $^{29}Si$ MAS NMR spectra were referenced to tetramethylsilane (TMS). Size exclusion chromatography (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. It was equipped with a set of two Waters microstyragel columns (HR1 and HR4, weight range 5000−600 000 g/mol) working at 45 °C under a flow rate of 1 mL/mn. THF was used as eluent. Polymer molecular weights were derived from a calibration curve based on polystyrene standards.

Thermogravimetric measurements were performed using a 2950 TGA analyzer (DuPont instruments) by heating the sample in a flow of helium (50 mL/h) at 10 °C/min from room temperature to 800 °C.

Carbon elemental analysis was performed on a homemade microanalyzer by combustion of the sample at 1050 °C in a stream of oxygen followed by infrared detection.

**Grafting of 1 onto Silica.** Under a dry argon atmosphere, the required amount of the functional triethoxysilyl capping agent **1** (1.36 g, 1.8 mmol) dissolved in toluene (1 g) was added to a suspension of silica (1 g) in toluene (28.5 mL). The mixture was stirred for 24 h at 60 °C. The modified silica particles were isolated by centrifugation (Beckman Avanti 30, 18 000 rpm), resuspended in fresh toluene, and centrifuged again. This washing procedure was repeated five times to ensure complete removal of the nonreacted coupling agent as checked by gas chromatography analysis of the supernatant solution. The recovered grafted silica powder was dried in a vacuum oven at 50 °C for 4 h before analysis.

The graft density of the alkoxyamine initiator on the silica surface was determined by thermogravimetric analysis (TGA) using eq 1:

$$\text{graft density } (\mu\text{mol/m}^2) = \frac{\left(\dfrac{W_{60-730}}{100 - W_{60-730}}\right) \times 100 - W_{\text{silica}}}{M \times S_{\text{spec}} \times 100} \times 10^6 \quad (1)$$

where $W_{60-730}$ is the weight loss between 60 and 730 °C corresponding to the decomposition of the silane molecule *corrected* from the thermal degradation profile of **1** established in a separate blank experiment, and $M$ is the molecular weight of the grafted silane. $S_{\text{spec}}$ and $W_{\text{silica}}$ are respectively the specific surface area and the weight loss of silica determined before grafting.

For comparison, the graft density was also determined by elemental analysis from the difference of carbon content ($\Delta C$, wt %) after and before grafting, using eq 2:

$$\text{graft density } (\mu\text{mol/m}^2) = 10^6\Delta C/[(1200N_c - \Delta C(M - 1)) \times S_{\text{spec}}] \quad (2)$$

where $N_c$ and $M$ designate the number of carbon atoms and the molecular weight of the grafted alkoxyamine molecule ($N_c = 32$ and $M = 659$ g/mol), respectively, and $S_{\text{spec}}$ ($m^2$ $g^{-1}$) has the same meaning as previously.

From the graft density, one could determine the grafting yield which corresponds to the fraction of **1** that effectively participated in the coupling reaction:

$$\text{grafting yield } (\%) = \text{graft density} \times 100/[\mathbf{1}] \quad (3)$$

where [**1**] ($\mu$mol/$m^2$) designates the initial concentration of **1**, expressed in mole number of the functional alkoxyamine molecules introduced per square meter of silica surface.

**Polymerization Procedure.** A series of polymerization experiments have been conducted with various styrene-to-initiator molar ratios comprised between 200 and 600 (targeted molecular weight comprised between 4000 and 30 000 g/mol). In a typical experiment, the alkoxyamine-grafted silica (0.3 g), toluene (14.7 g, 0.16 mol), styrene (15.5 g, 0.15 mol), and a known amount of the "free" sacrificial alkoxyamine initiator **2** (0.27 g, 0.7 mmol), corresponding to a total styrene-to-initiator molar ratio in the range 200 (total initiator = $I_0$ = surface-grafted initiator + free initiator **2**), were introduced in a predried Schlenk flask under an argon atmosphere. After stirring for a few minutes, the suspension was degassed by four freeze−pump−thaws, and the polymerization mixture was heated to 110 °C for 23 h. Monomer conversions were determined gravimetrically by precipitation of the polymer in methanol. The recovered polymer (11.45 g, 74% conversion) was characterized by SEC ($M_n$ = 15 500 g/mol, $I_p$ = 1.3). A kinetic study was performed by taking aliquots as a function of time and precipitating the polymer as reported above.

**Recovery of the Free and Grafted Polymer Chains.** The free polymer, formed in solution, was isolated from the grafted silica particles by successive centrifugation/redispersion cycles in toluene. After each cycle, the solvent was discarded and replaced by fresh toluene (15 mL per 0.3 g of polymer-grafted silica). The polymer content of the supernatant cleaning solutions (determined gravimetrically) decreased from 38 to 0 wt % after six cycles, indicating complete removal of the physisorbed polymer chains from the surface. Then, the recovered silica powder and the free polymer (obtained after precipitation of the supernatant in MeOH) were collected separately and dried at 50 °C for 4 h, and at 60 °C overnight, respectively, prior to characterization. The grafting was characterized by FTIR and NMR spectroscopies. TGA analysis was used to assess the amount of grafted polymer onto silica. The grafted polymer chains were cleaved from the silica surface by acid-catalyzed transesterification with methanol according to a procedure reported elsewhere.[4] Namely, 150 mg of the polymer-modified silica gel was suspended in 30 mL of toluene. Then, 3 mL of MeOH and 15 mg (0.079 mmol) of *p*-toluenesulfonic acid monohydrate were added to the grafted silica suspension, and the mixture was heated to reflux overnight. The polystyrene chains, cleaved from the surface, were finally isolated as described above for nonbonded polymer.

Molecular weights of free and grafted polymers were determined by SEC.

## Results and Discussion

**Grafting of 1 onto Silica.** The grafting of the functional alkoxyamine initiator onto silica was qualitatively confirmed by FTIR and NMR spectroscopies. The FTIR spectra of bare and grafted silica are reported in Figure 1. The spectrum of Figure 1b shows characteristic vibrations of the carbonyl ($\nu_{C=O}$, 1734 $cm^{-1}$) and the aliphatic groups ($\nu_{CH}$, 2850, 2920, and 2980 $cm^{-1}$; $\delta_{CH}$, 1384 $cm^{-1}$) of the alkoxyamine molecule.

$^{13}C$ and $^{29}Si$ NMR spectroscopies clearly attest the covalent attachment of the alkoxyamine initiator on the silica surface. The $^{29}Si$ NMR spectrum of Figure 2a shows $Q^4$ [Si(4OSi)] and $Q^3$ [Si(3OSi, 1OH)] signals centered at −109 and −105 ppm, attributed to framework silicon atoms and surface silanol groups, respectively, along with a broad signal at around −58 ppm corresponding to $T^2$ [Si(2OSi, 1R, 1OR′] species, indicating the occurrence of grafting. The predominance of $T^2$ units in the grafted silicate layer indicates that the alkoxyamine molecules have been attached by two siloxane bonds, either by reaction of **1** with two vicinal SiOH groups of the surface or by reaction of **1** with a surface silanol and a neighboring alkoxysilane molecule. The $^{13}C$ NMR spectrum of Figure 2b provides further

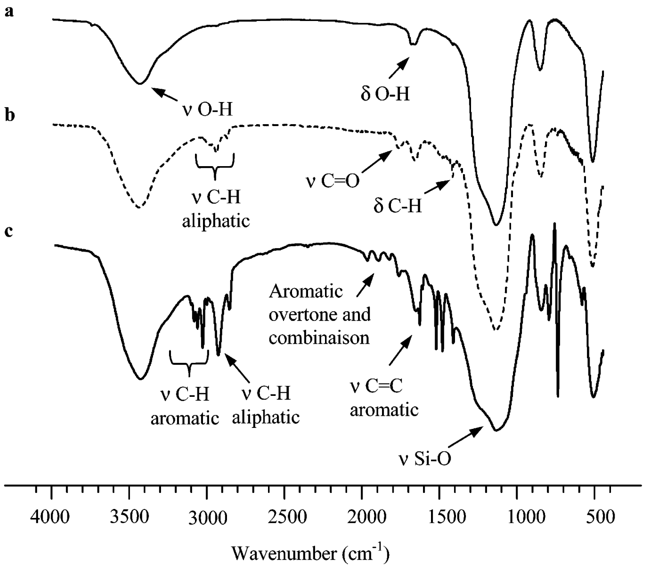


**Figure 1.** FT-IR spectra of (a) unmodified silica, (b) alkoxyamine-grafted silica, and (c) poly(styrene)-grafted silica (run 4, Table 2).

confirmation of the formation of Si−O−Si linkages. The assignments reported in the figure are based on the proton-coupled $^{13}$C NMR spectrum of **1**, recorded in solution.[20] The $^{13}$C NMR spectrum exhibits all the signal characteristics of **1**, and only the carbonyl group (C13) and the carbon directly attached to the silicon atom (C3) were shown to be affected by the variation of the silicon environment. The C13 and C3 carbon atoms resonate at 177.2 and 15.4 ppm, respectively, while the same carbons appear at 173.4 and 18.3 ppm in the corresponding free unbonded triethoxysilane molecule. According to previous studies in this field, the shift of the C3 carbon resonance to a lower frequency is indicative of a chemical reaction between the functional alkoxyamine and the silica surface.[21]

To gain more insight into the grafting reaction, and also to find optimum grafting conditions, increasing amounts of **1** were introduced in the silica suspension. The graft density was calculated using both TGA and carbon elemental analysis. A typical TGA curve is given as Supporting Information. As shown in Table 1, the two techniques gave very similar results, attesting for the validity of our quantitative approach as already pointed out in the literature for similar investigations.[22]

Figure 3 shows the evolution of the graft density and the grafting yield (determined by TGA) as a function of the silane concentration. The graft density increases with increasing the silane content and reaches a plateau at high concentrations while, concurrently, the grafting yield decreases. The surface coverage at saturation, i.e., 0.95 $\mu$mol/m$^2$, is 2−3 times lower than the values given in the literature for the grafting of a series of organotrialkoxysilane and chlorosilane molecules.[23,24] For example, Boettcher[15] reported a surface coverage of around 2 $\mu$mol/m$^2$ for the grafting of a monochlorosilane-terminated ATRP initiator under conditions very similar to ours. However, grafting reactions are very sensitive to experimental conditions (moisture content, silane chemical composition and functionality, washing procedures and curing treatments, etc.). Such a sensitivity makes it difficult to ensure reproducible surface coverages,[25] which may account for the large disparity of literature data. Nevertheless, the fact that we obtained a plateau level and that only 12.5% of the original amount of silanol groups had reacted under our experimental conditions[26] suggests the occurrence of steric hindrance limitations. Indeed, surface concentrations of bonded organosilanes on inorganic substrates are highly dependent on the conformation of the grafted molecule in the surface monolayer.[27] An estimation of the molecular cross-sectional area of the silane compound can be obtained from the surface coverage at saturation.[28] These data are available in the literature for some frequently encountered organosilane compounds and were found to vary from 33 Å$^2$/molecule for the smallest coupling agents to more than 100 Å$^2$/molecule for more bulky compounds.[24] As an illustration, the substitution of one methyl group by a bulky phenyl group attached to the silicon atom decreases the surface coverage by a factor of 2.[24] It is likely that this type of steric restrictions may occur in the present system. Moreover, the polar phosphonic ester moiety of the DEPN-based alkoxyamine initiator **1** may also be physisorbed onto the silanol groups of silica during the grafting reaction which reduces the grafting yield.

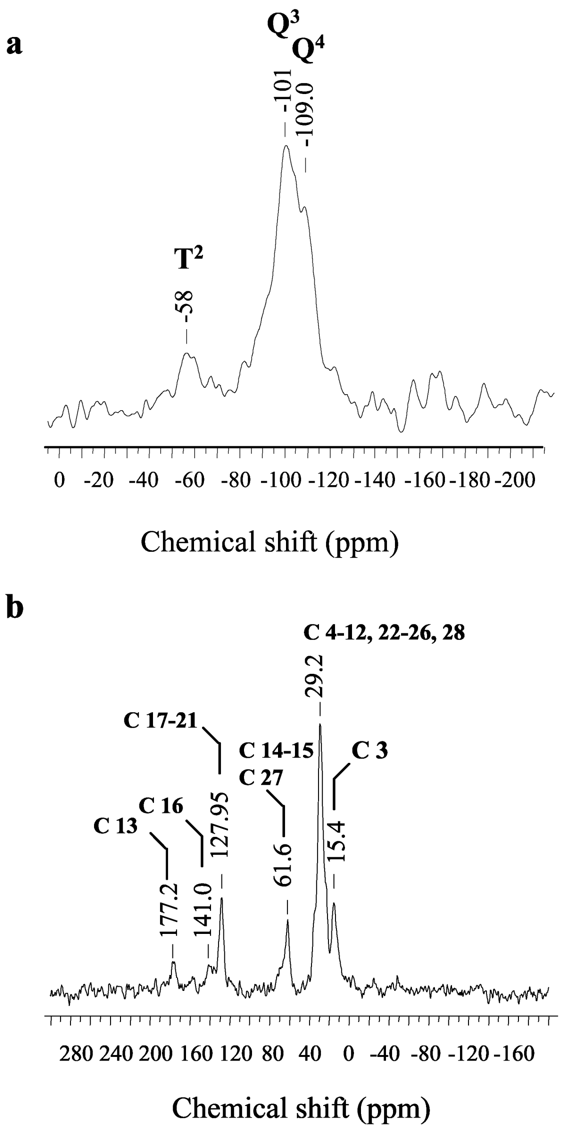


**Figure 2.** $^{29}$Si (a) and $^{13}$C (b) CP/MAS solid-state NMR spectra and chemical shift assignments of the alkoxyamine-functionalized silica particles.

**Polymerization of Styrene Initiated from the Alkoxyamine-Functionalized Silica Surface.** Con-

**Table 1. TGA and Elemental Analysis of Alkoxyamine-Grafted Silica Particles for Increasing Concentrations of 1**

| | | thermogravimetric analysis | | | elemental analysis | | | |
|---|---|---|---|---|---|---|---|---|
| entry | [silane] ($\mu$mol/m$^2$)[a] | weight loss (%)[b] | graft density ($\mu$mol/m$^2$)[c] | grafting yield (%)[d] | carbon content (%) | $\Delta C$ (wt %)[e] | graft density ($\mu$mol/m$^2$)[f] | grafting yield (%)[d] |
| 1 | 0 | 1.2 | / | / | 0.3 | 0 | / | / |
| 2 | 1.1 | 8.1 | 0.50 | 46.0 | 5.3 | 5.0 | 0.62 | 56.4 |
| 3 | 4.0 | 9.9 | 0.65 | 16.2 | 6.9 | 6.5 | 0.85 | 21.2 |
| 4 | 8.0 | 12.3 | 0.85 | 10.6 | 7.2 | 6.9 | 0.89 | 11.1 |
| 5 | 11.7 | 13.2 | 0.93 | 8.0 | 7.3 | 7.0 | 0.91 | 7.8 |
| 6 | 15.9 | 13.5 | 0.96 | 6.0 | 7.9 | 7.6 | 1.00 | 6.3 |

[a] Initial silane molar concentration in the feed per unit area of silica surface. [b] $W_{60-730}$ corrected from the decomposition profile of **1**. [c] Determined using eq 1. [d] Determined using eq 3. [e] Difference in carbon content after and before grafting. [f] Determined using eq 2.

**Table 2. SEC Analysis of the Grafted and Free Polystyrene Chains for a Series of "Graft from" Polymerization Reactions[a]**

| | | | | | free polymer in solution | | surface-grafted polymer | |
|---|---|---|---|---|---|---|---|---|
| run | molar ratio styrene/initiator[b] | time (h) | conv (%) | $M_{n,th}$ (g/mol)[c] | $M_n$ (g/mol) | $M_w/M_n$ | $M_n$ (g/mol) | $M_w/M_n$ |
| 1 | 200 | 4 | 21 | 4 368 | 4200 | 1.30 | 4 400 | 1.28 |
| 2 | 199 | 23 | 74 | 15 315 | 15 500 | 1.30 | 15 250 | 1.30 |
| 3 | 354 | 24 | 55 | 20 249 | 20 300 | 1.21 | 20 600 | 1.19 |
| 4 | 600 | 30 | 47 | 29 328 | 29 200 | 1.19 | 29 300 | 1.21 |

[a] The alkoxyamine surface graft density of the silica particles is of approximately 0.85 $\mu$mol/m$^2$ (entry 4 in Table 1). [b] Initiator = surface-grafted initiator + free initiator. [c] $M_{n,th}$ = (([M]$_0$/[I]$_0$) × $M_w$ of styrene × conv)/100.

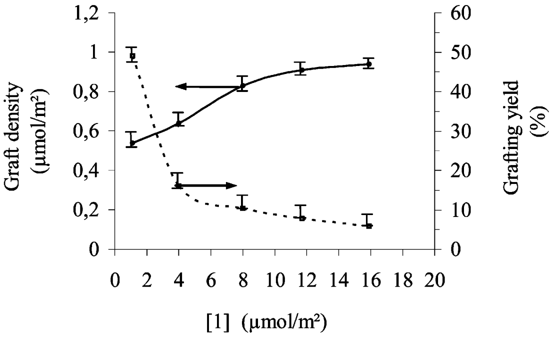


**Figure 3.** Graft density and grafting yield of **1,** as determined from TGA analysis using eqs 1 and 3, respectively (see the text), as a function of the silane content in the feed.

trary to other nitroxide-based systems, and particularly those using TEMPO as counter radical, DEPN-based alkoxyamine initiators offer the advantage of providing an accurate control of molecular weights and polydispersities for a large variety of monomers including acrylates and acrylamide, and at temperatures as low as 90−110 °C, which drastically reduces the risk of thermal initiation.[29] The versatility of this system makes it particularly attractive for the elaboration of polymer layers with controlled architectures. The polymerization was conducted in a 50/50 (v/v) styrene/toluene solution, containing 1 wt % silica. Such experimental conditions present several advantages. First, the viscosity of the polymerization mixture is reduced, and the purification procedures are easier.[18] "Free" sacrificial initiator was also added in the reaction medium to ensure a good level of control. Although we introduced a cleavable ester group in our functional initiator to facilitate polymer degrafting, the possibility to follow kinetics of the growing polymer chains by simple analysis of the polymer formed in the volume is obviously advantageous for easy and rapid characterizations. After quantitative removal of the free polymer chains by extensive washings, as attested by the decrease of the solid content of the supernatant cleaning solutions down to 0 wt %, analysis of the recovered silica powder by FTIR gave clear evidence of polymer grafting with absorption bands at 3020−3090 cm$^{-1}$ ($\nu_{CH}$) and 1450−1600 cm$^{-1}$ ($\nu_{C=C}$) characteristic of the aromatic ring of poly(styrene), and a strong absorbance at 1110 cm$^{-1}$ was attributed to silica ($\nu_{Si-O-Si}$) (Figure 1c). The $^{13}$C solid-state NMR spectrum (not shown) also supports the presence of polymer on the surface (see Supporting Information).

**Surface Graft Densities and Molecular Weights of the Free and Grafted Polymer Chains.** In the following, a series of growth experiments with varying styrene-to-initiator molar ratios were carried out in order to obtain further insight into the growth process by comparing molecular weights and polydispersity indexes of the grafted and free polymer chains. Table 2 indicates a good agreement between the two sets of data as already reported by many authors.[11,18,30,31] Experimental molecular weights agreed well with the theoretical ones as expected for controlled polymerization. All these results indicate that steric constraints around silica particles have no influence on the livingness of the free radical process.

As before, thermogravimetric analysis was used to evaluate the amount of grafted polymer (see Supporting Information). The graft density of polystyrene was determined from the weight loss and the molar mass of the grafted polymer chains after subtracting the contribution of adsorbed water and bonded initiator. The calculation performed on run 4 (see Table 2) gave a polymer graft density of 0.35 $\mu$mol/m$^2$ (e.g., around 110 chains per particle), which corresponds to about 42 mol % of the initial amount of grafted alkoxyamine initiator. The above value is nearly 3 times larger than the initiator efficiency reported by Boettcher[15] in bulk ATRP and also much more higher than the results published by Kasseh[17] for similar molecular weights polymers produced by nitroxide-mediated polymerization of styrene on fumed silicas. As mentioned by Von Werne and Patten,[11] there may be many reasons for such limitations. In the context of the present study, however, one plausible explanation is particles aggregation, which reduces the accessible surface area for polymer grafting. Steric hindrance limitations due to a larger average cross-sectional area of a polymer chain (~180−200 Å$^2$) than the surface area of an initiator molecule (~20−

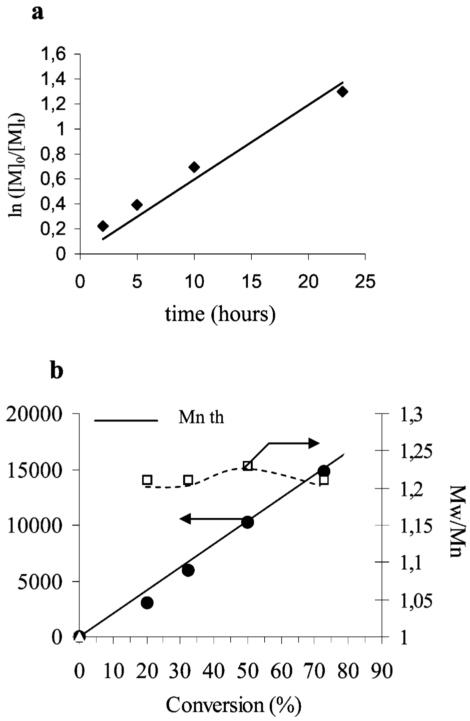


**Figure 4.** First-order kinetic plot (a) and variation of $M_n$ with conversion (b) for the DEPN-mediated stable free radical polymerization of styrene in the presence of alkoxyamine-grafted silica particles. Initiator-to-styrene molar ratio = 200. The theoretical molecular weight, $M_{n,th}$, was calculated according to $M_{n,th} = (([M]_0/[I]_0) \times M_w$ of styrene $\times$ conv)/100.

180 Å$^2$) can also inhibit polymer chains growing from every single initiator.[32] Such a crowding effect of the initiating end groups on the surface, responsible for low initiation efficiencies, has already been observed by Kasseh[17] and Zhou.[33]

**Polymerization Kinetics.** To demonstrate the controlled character of our polymerization process, we performed a kinetic study by following the molar mass and the polydispersity index of the free polymer since we proved in the preceding section that surface and volume polymers have identical molecular weights. The graft polymerization of styrene from the functionalized silica particles exhibits all of the characteristics of a controlled polymerization. The kinetic plot of ln($[M]_0/[M]_t$) vs time and the corresponding $M_n$ vs monomer conversion are linear, while polydispersity indexes are lower than 1.3 (Figure 4). Similar kinetic results were obtained for polymerizations performed without silica or in the presence of nonfunctionalized silica, which indicates that silica gel has no effect on polymerization rates.

## Conclusion

Well-defined polystyrene-coated silica nanoparticles were prepared by nitroxide-mediated polymerization using a novel triethoxysilyl-functionalized alkoxyamine initiator. The chain growth process from the alkoxyamine-grafted silica surface exhibits all criteria of controlled radical polymerization. Polymer molecular weights agree well with the theoretical ones, and the free and grafted polymer chains have nearly the same molecular weights and molecular weight distributions in agreement with previous studies in this field. Using our "graft from" procedure, the nature and composition of the hairy polymer layer around silica (chemical structure, chain length, and graft density) can be precisely controlled and adjusted, which is of major importance for the elaboration of stable colloidal suspensions of the inorganic particles into good solvents for the polymer being formed. The versatility of the "graft from" technique, combined with the advantages of controlled radical polymerization processes, obviously open the route to the elaboration of a new family of nanocomposite colloids with potential applications in materials science.

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**Supporting Information Available:** $^{13}$C NMR spectrum of polystyrene-grafted silica particles and TGA curves of alkoxyamine- and polystyrene-grafted silica particles. This material is available free of charge via the Internet at http://pubs.acs.org.

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