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Nitroxide-mediated polymerization of styrene initiated from the surface of fumed silica. Comparison of two synthetic routes

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Abstract

Nitroxide-mediated free radical polymerization of styrene was performed from 13 nm diameter fumed silica in two steps. First, an alkoxyamine, based on *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (DEPN) was covalently attached onto silica. Polystyrene chains with controlled molecular weights and narrow polydispersities were then grown from the alkoxyamine-functionalized nanoparticles surface in the presence of a 'free' sacrificial styrylDEPN alkoxyamine. Two strategies were investigated in order to immobilize the alkoxyamine initiator on the silica surface. In a first route, we synthesized a unimolecular alkoxyamine initiator carrying triethoxysilyl end groups reactive towards the silica surface. In a second route, the alkoxylamine was formed in situ by the simultaneous reaction of a polymerizable acryloxy propyl trimethoxysilane (APTMS), azobisisobutyronitrile (AIBN) and DEPN used as radical trap. In both cases, the grafting of both the initiator and the polystyrene chains was characterized and quantified by several techniques which allowed us to evaluate and compare the two strategies.

Keywords: Fumed silica; Nitroxide-mediated radical polymerization; Graft-from

1. Introduction

In recent years, there has been increasing interest in the grafting of polymers to inorganic surfaces. Grafting can be done in various ways using anionic [1], cationic [2] or free radical processes [3]. In order to achieve a high density of grafts with well-defined architectures and controlled molecular weights, living polymerization techniques are preferred. These techniques usually involve growth of the polymer from the solid surface by means of immobilized initiators using the so-called 'graft-from' method. Among the different methods, controlled free radical polymerization (CRP) has attracted considerable attention due to its simplicity and versatility compared to ionic processes [4]. CRP is usually divided into three categories: atom transfer radical polymerization (ATRP), reversible radical addition, fragmentation and transfer (RAFT) and nitroxide mediated polymerization (NMP). All three techniques permit the polymer molecular weight, the polydispersity and the polymer architecture to be accurately controlled, and have been used to build up highly dense polymer brushes from planar substrates [5–8] or from nanoparticles [9–13].

Recently, Parvole [10], Kasseth [11], Hawker [12] and ourselves [13], have demonstrated that NMP is well adapted to graft polymers on silica surfaces either in bulk or in solution. In these papers, various surface-immobilized initiators have been investigated to control the polymerization. These initiators are based either on unimolecular alkoxyamines carrying trichlorosilyl or triethoxysilyl end-groups [10b,c,12,13] or on bimolecular systems based on the strategy of Rühe in which the NMP process is initiated from surface-immobilized azo or peroxide initiators [10a,11].

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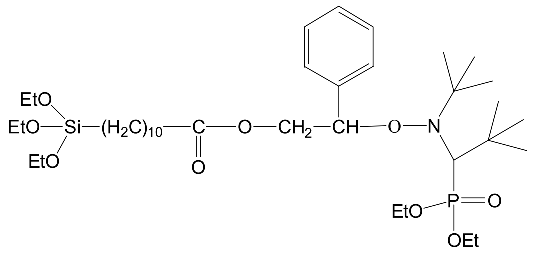
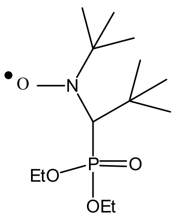
We report herein our recent efforts in this field which mainly focus in quantitative determination of the amount of alkoxyamine initiators that can be attached on the silica surface using strategies similar to those mentioned previously as well as some new alternative strategies. Such a determination is of major importance since the amount of surface initiator will control subsequently the amount of polymer chains that can be grown from the silica surface. Two routes were investigated in order to graft the alkoxyamine initiator (Scheme 1).

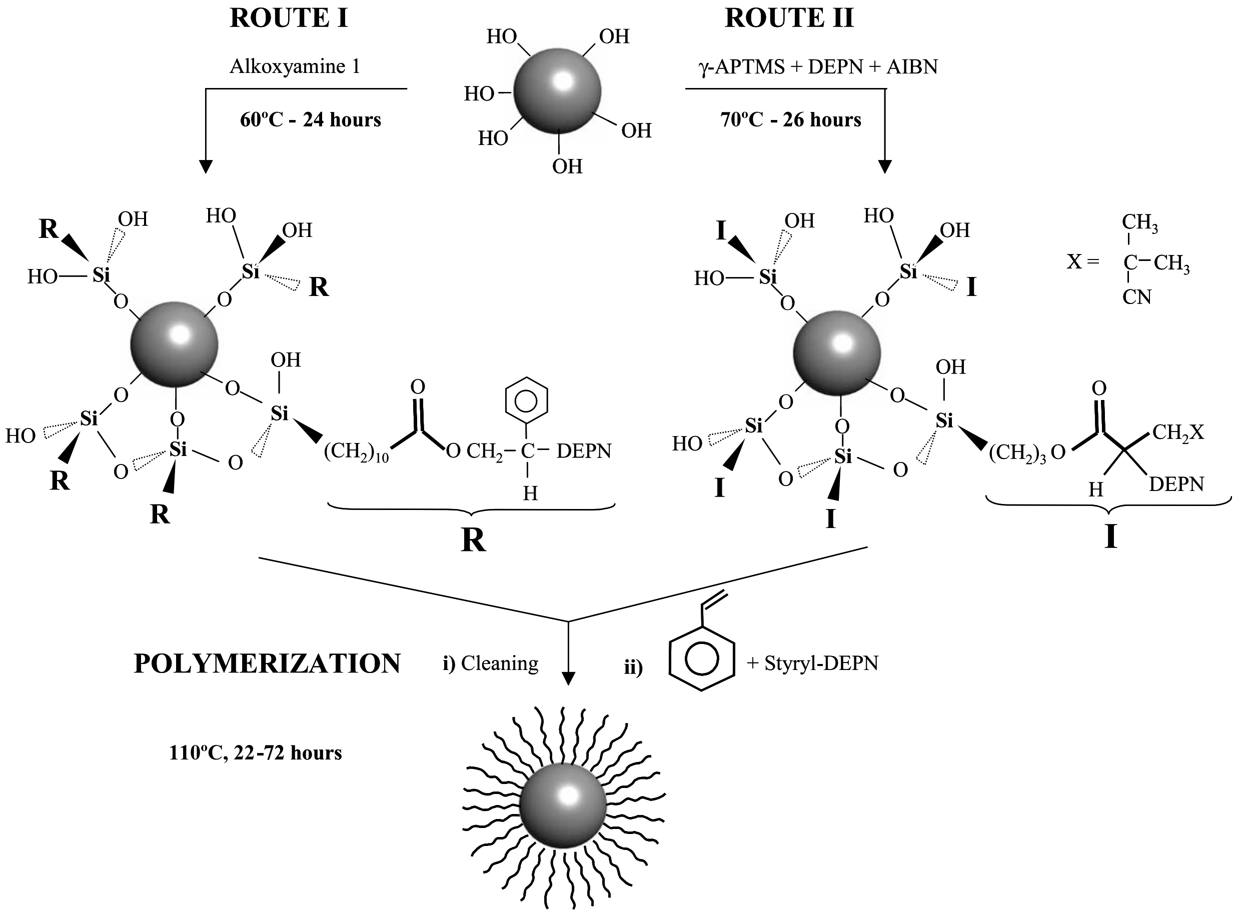
In a first route, a triethoxysilyl-functionalized alkoxyamine (structure **1**) based on *N-tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethylpropyl) nitroxide (DEPN, structure **2**) was synthesized and reacted with the silanol groups of silica. In a second route, a surface-alkoxyamine initiator was produced in a one step process by reacting simultaneously DEPN, AIBN and acryloxy propyl trimethoxy silane (APTMS, structure **3**). 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. In both cases, the alkoxyamine compound carried an hydrolysable ester group that enabled us to isolate and characterize the grafted PS chains. The polymer chain grafting density obtained in the two routes could be then compared. In a last experiment, we have tested the ability of the polymer chains to reinitiate a second monomer feed and we have determined the efficiency of the re-initiation process.



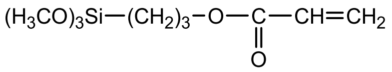
Structure 1. Triethoxysilyl-terminated alkoxyamine initiator.



Structure 2. DEPN.



Scheme 1. Reaction scheme for the covalent bonding of the DEPN-based alkoxyamine initiator onto silica and subsequent grafting of polystyrene from the functionalized silica surface.



$$(H_3CO)_3Si{-}(CH_2)_3{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH_2$$

Structure 3. APTMS.

2. Experimental section

2.1. Materials

The silica particles (Aerosil A200V, Degussa) have an average diameter of 13 nm and a specific surface area of 228 m^2/g. They were dried for 3 h at 150 °C under vacuum before use. Toluene (Aldrich) was dried on molecular sieve and stored under an argon atmosphere. DEPN (88%, a gift from Atofina) and APTMS (95%, Gelest) were used as received. The alkoxyamine **1** was prepared in four steps according to a method described elsewhere [14]. The free initiator, a DEPN-based alkoxyamine (structure **4**), was prepared using a procedure described in the literature [15]. AIBN was recrystallized and styrene was purified upon distillation before use.

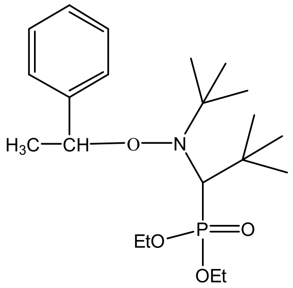
2.2. Alkoxyamine initiators immobilization

2.2.1. First route

1.36 g of **1** (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 non-reacted 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 during 4 h before analysis.

2.2.2. Second route

1.28 g of the APTMS coupling agent (5.47 mmol 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 min at room temperature. Then, various amounts of **2** (from 1.01 to 2.54 g corresponding to 3.5–8.6 mmol) and 0.43 g of AIBN (2.6 mmol) were introduced in the reaction flask. The suspension was degassed by four freeze–pump–thaw cycles, and the mixture was heated to 70 °C for 26 h. The grafted silica was extensively washed before characterization as reported above.



Structure 4. Styryl-DPEN.

2.3. Polymerization

In a typical run (Table 1), 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’ alkoxyamine initiator **4** (comprised between 0.05 and 0.27 g), corresponding to a total styrene-to-initiator molar ratio in the range 200–800, 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–thaw cycles, and the polymerization mixture was heated to 110 °C for 23–55 h. Monomer conversions were determined gravimetrically by precipitation in methanol. The recovered polymer was characterized by size exclusion chromatography (SEC). A kinetic study was performed by taking aliquots as a function of time and precipitating the polymer.

Table 1

TGA and elemental analysis of alkoxyamine-grafted silica particles for increasing concentrations of **1**

[**1**] (μmol/m^2)[a]	TGA	Elemental analysis (EA)		Grafting density (μmol/m^2)		Grafting yield (%)[b]	
	Weight loss (%)[c]	Carbon content (%)	ΔC (wt%)[d]	TGA[e]	EA[f]	TGA	EA
0	1.2	0.3	0	–	–	–	–
1.1	8.1	5.3	5.0	0.57	0.63	52.1	57.1
4.0	9.9	6.9	6.5	0.73	0.85	18.3	21.1
8.0	12.3	7.2	6.9	0.96	0.89	12.0	11.1
11.7	13.2	7.3	7.0	1.05	0.90	9.0	7.7
15.9	13.5	7.9	7.6	1.08	1.00	6.8	6.3

[a] Initial alkoxyamine molar concentration in the feed per unit area of silica surface.

[b] Determined using Eq. (3).

[c] W_{60-730} corrected from the decomposition profile of **1**.

[d] Difference in carbon content after and before grafting.

[e] Determined using Eq. (1).

[f] Determined using Eq. (2).

Degrafting of the polystyrene (PS) chains from the silica surface was performed as described elsewhere [13].

2.4. Chain extension experiments

Reinitiation experiments were performed under the same conditions as for the formation of the first generation of polystyrene chains. In a typical experiment, the grafted silica sample, synthesized according to the procedure reported above (M_n of the grafted polymer chains = 50,400 g/mol), was first extensively cleaned by successive centrifugation/redispersion in toluene to remove the free polymer. The polystyrene-functionalized silica particles (0.8 g) were then suspended into a mixture of toluene (10.2 g) and styrene (10.9 g) and the required amount of the 'free' alkoxyamine initiator **4** (i.e. 47.3 mg corresponding to a total monomer to initiator molar ratio of 793) was introduced in the suspension medium. The polymerization was conducted for 54 h at 110 °C as described previously. The free polymer chains were again separated from the grafted silica samples and characterized as reported above. The grafted polystyrene chains (first plus second generation) were cleaved by transesterification, and the recovered polymer chains were isolated and characterized by SEC.

2.5. Characterizations

^{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 proton. 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 thermogravimetric analysis (TGA, DuPont Instruments, heating rate: 10 °C/min) using Eq. (1) below:

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

where $W_{60\text{–}730}$, is the weight loss data measured between 60 and 730 °C, and M is the molecular weight of the grafted molecule. $S_{\text{spec.}}$ and W_{silica} are, respectively, the specific surface area and the weight loss of silica determined before grafting.

In route I, the alkoxyamine initiator grafting density was also determined by elemental analysis from the difference of carbon content (ΔC, wt%) after and before grafting, using Eq. (2) below

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

where N_c and M designate, respectively, the number of carbon atoms and the molecular weight of the grafted alkoxyamine molecule ($N_c = 32$ and $M = 659$ g/mol), and $S_{\text{spec.}}$ (m^2/g) has the same meaning as previously. From the grafting density, one could determine the grafting yield which corresponds to the fraction of **1** which effectively participated to the coupling reaction:

$$\text{Grafting yield } (\%) = \frac{\text{Grafting density} \times 100}{[\mathbf{1}]} \qquad (3)$$

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

In order to provide more accurate data in route II, phosphorous elemental analysis was used in this particular case to determine the alkoxyamine grafting density using Eq. (4) below:

$$\text{Alkoxyamine grafting density } (\mu\text{mol/m}^2) = \frac{10^6 \text{P}}{[(3100 - \text{P}(M-1)) \times S_{\text{spec.}}]} \qquad (4)$$

where P (wt%) designates the phosphorous content, M is the molecular weight of the grafted alkoxyamine molecule ($M = 552$ g/mol), and $S_{\text{spec.}}$ (m^2/g) has the same meaning as previously.

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. Particle size was 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.

3. Results and discussion

3.1. Surface immobilization of the alkoxyamine initiator

Grafting of the alkoxyamine initiator on the silica surface was qualitatively evidenced by FTIR and solid state NMR spectroscopies which attested for covalent attachment of the silane molecules. The FTIR spectra of the hydroxyl region of aerosil and alkoxyamine-functionalized silica are reported in Fig. 1. One can see signals assigned to

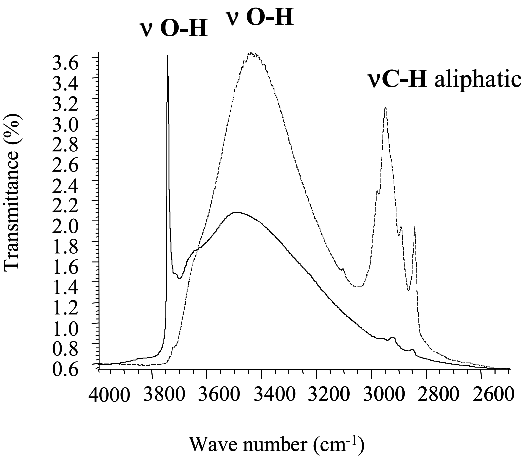


Fig. 1. FTIR spectra of the hydroxyl region of the A200V silica before grafting (full line) and after grafting (dotted line).

physisorbed water and hydrogen-bonded silanols at around 3450 cm^{-1} and a sharp peak at 3740 cm^{-1} corresponding to terminal non-reacted silanols. Both signals are characteristic of hydrated silica. Upon grafting of the alkoxyamine initiator, the latter peak disappeared while new bands corresponding to aliphatic carbons appeared in the 3000–2800 cm^{-1} region attesting for grafting [16]. Similar FTIR responses were obtained in the two routes.

A quantitative approach by TGA and carbon elemental analysis allowed us to accurately determine the grafting density of the initiator units on the surface.

The data reported in Table 1 for route I indicate a good agreement between the two sets of data. The grafting density increases with the silane content and reaches a maximum value of around 1 μmol of **1** per square meter of silica for an initial silane concentration of around 16 μmol/m^2. This result suggests that the alkoxyamine grafting density is limited by steric hindrance which is a reasonable assumption in view of the bulky dimensions of the molecule [13].

In the second route, preliminary experiments performed on APTMS alone enabled us to determine the optimal grafting conditions. A maximum grafting density of 2 μmol/m^2 (as determined by TGA) was achieved for a silane content of 12 μmol/m^2 in agreement with the literature data [17]. Therefore, in the following, all the coupling experiments will be performed using 12 μmol of APTMS per square meter of silica surface. The simultaneous reaction of **2**, AIBN and APTMS is expected to give a large number of products [18], among which the surface alkoxyamine can be readily isolated by sedimentation of silica and cleaning of the surface. In fact, characterization of the functionalized silica by ^{13}C, ^{31}P and ^{29}Si solid state NMR indicated the formation of the targeted alkoxyamine compound together with the presence of non-reacted APTMS molecules [19]. The alkoxyamine was evidenced by the appearance on the ^{31}P NMR spectra of a signal at 22.93 ppm characteristics of the DEPN moiety, while APTMS was identified on the ^{13}C NMR spectra by a signal at 123 ppm characteristic of ethylenic carbons. Considering the presence on the silica surface of non-reacted APTMS, we next decided to use phosphorous elemental analysis to determine the alkoxyamine grafting density. Indeed, both TGA and carbon elemental analysis are expected to give overestimated values of the alkoxyamine grafting density since not only the targeted alkoxyamine compound but also APTMS are quantified by these techniques. The alkoxyamine grafting density determined by phosphorous elemental analysis decreased from 0.75 μmol/m^2 for low DEPN concentrations to 0.4 μmol/m^2 for higher DEPN concentrations (Table 2). It is likely that increasing the amount of DEPN results in a decrease of the efficiency of the coupling reaction because of the competition that might exist between addition of the radicals formed upon thermal decomposition of AIBN to the APTMS double bonds and trapping of these radicals by DEPN.

Table 2
Alkoxyamine grafting densities determined by TGA and P elemental analysis as a function of the DEPN concentration

[DEPN] μmol/m^2	TGA	Phosphorous elemental analysis (wt%)	Grafting density (μmol/m^2)	
	Weight loss (%)		TGA	EA
8	5.9	0.48	1.00	0.74
12	4.3	0.29	0.85	0.43
14	3.2	0.27	0.76	0.40
20	2.6	0.26	0.6	0.38

[APTMS] = 12 μmol/m^2 and [AIBN] = 6 μmol/m^2.

If we now compare the results obtained in the two routes, we note that the alkoxyamine grafting density obtained in route II under optimized conditions (e.g. 0.74 μmol/m^2) is slightly lower than the optimal value measured in route I (that is 1.0 μmol/m^2). Since the two alkoxyamine molecules have very similar sizes, this is obviously related to the competitive events mentioned above occurring during in situ formation of the alkoxyamine compound. In spite of these small differences, it is worth mentioning, however, that the second route is very convenient from an experimental point of view since the alkoxyamine is produced directly in the suspension medium in a one step process, which constitutes a clear advantage in comparison to the multi-step synthesis of the functional alkoxyamine 1. As such, we largely recommend this second route since it allows the grafting of the alkoxyamine compound in high amounts under convenient conditions.

3.2. Kinetics

Fig. 2 shows the kinetics of the grafting reaction performed using route I. Only the molecular weight of the free polymer chains is considered here. It will be compared later to that of the grafted polystyrene chains. The polymerization exhibits all the criteria of a controlled process. M_n increases linearly with conversion, the plot of

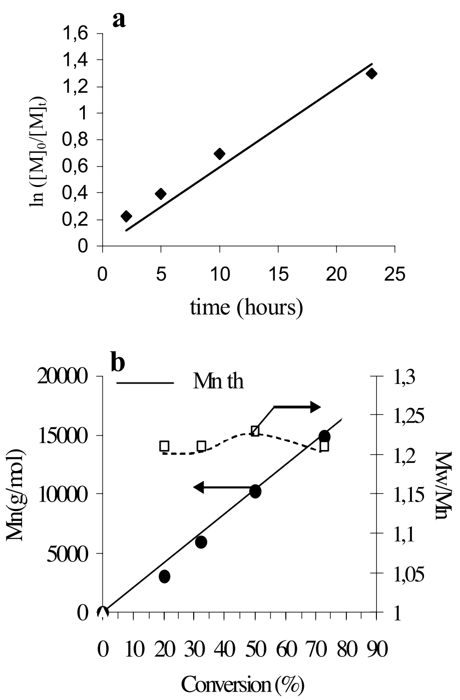


Fig. 2. (a) First order kinetic plot and (b) variation of M_n with conversion for the DEPN-mediated stable free radical polymerization of styrene in the presence of alkoxyamine-grafted silica particles (route I). Initiator-to-styrene molar ratio = 200.

$\ln([M]_0/[M]_t)$ versus time is linear and the polydispersities of all the polymers obtained are very low.

3.3. Polymer grafting densities

In order to gain insights into the grafting process for the two routes, the polymer chains were cleaved from the surface and characterized by SEC. Table 3 shows the results obtained for a series of polymerization experiments performed with different styrene to initiator molar ratios, different reaction times and a predetermined amount of surface alkoxyamine. Remarkably, the molecular weight of the grafted polymer chains is similar to that of the free polymer and close to the theoretical values calculated from the feed ratio of styrene to total initiator (i.e. the free alkoxyamine plus the grafted alkoxyamine determined by either carbon (route I) or phosphorous (route II) elemental analyses).

As could be expected for a controlled polymerization, the amount of polymer deposited on the surface increased with increasing the monomer to initiator ratio and with increasing conversion. From the weight loss and the M_n of PS, we could estimate the polymer chains grafting density and compare it to the density of initiator groups reported above. The present analysis indicates that only a fraction of the initial amount of initiator (comprised between 23 and 50% molar) effectively participated to the growth reaction. Indeed, a maximum polymer grafting density of around 0.35 μmol/m^2 was achieved for both routes under optimized conditions. Although this value is in close agreement with the data previously reported by Böttcher [20] or Kasseth [11] on silica nanoparticles, it is inconsistent with the observed agreement between the theoretical and the experimental molecular weights (Table 3). Indeed, if we assume that only a part of the grafted alkoxyamine has participated to the initiation reaction, one should expect molecular weights significantly larger than the ones determined experimentally. For instance, a calculation performed on run 2 (Table 3) indicates that the molecular weight should be of 36,000 g/mol instead of 29,300 g/mol if you assume an initiation efficiency of 42 mol%. This

Table 3
SEC analysis of the grafted and free polystyrene chains, weight loss data, polymer grafting densities and hydrodynamic diameters of the PS/grafted silica for a series of 'graft-from' polymerization reactions using route I and route II

Route	Run	Styrene/initiator (molar ratio)[a]	Time (h)	Conversion (%)	$M_{n\ th}$ (g/mol)[b]	Free polymer in solution		Surface-grafted polymer		Weight loss (%)[c]	Grafting density[d]	Hydro dynamic diameter (nm)[e]
						M_n (g/mol)	M_w–M_n	M_n (g/mol)	M_w–M_n			
I[f]	1	199	23	74	15,315	15,500	1.30	15,250	1.30	52.2	0.27	–
	2	600	30	47	29,328	29,200	1.19	29,300	1.21	71.2	0.35	134
	3	802	22	31	24,862	28,900	1.23	29,000	1.23	42.2	0.22	126
	4	805	54	65	54,418	58,500	1.29	60,500	1.26	79.3	0.27	181
II[f]	5	801	22	33	27,490	30,700	1.22	30,900	1.22	71.3	0.33	150
	6	789	33	44	36,105	38,400	1.21	38,700	1.20	77.4	0.37	165
	7	800	54	63	52,416	55,500	1.20	56,000	1.21	80.7	0.32	175
	8	806	72	64	53,647	57,900	1.20	60,000	1.18	79.9	0.28	189

[a] Initiator = surface-grafted initiator + free initiator.

[b] $M_{n\ th} = ([M]_0/[I]_0) \times (M_w \text{ of styrene} \times \text{conv})/100$.

[c] Determined by TGA.

[d] In μmol/m^2—calculated using Eq. (1).

[e] Determined by DLS.

[f] The alkoxyamine grafting density is of approximately 0.95 μmol/m^2 for route I and 0.75 μmol/m^2 for route II.

Table 4
Grafting densities, molecular weights and molecular weight distributions of the first and first plus second generation of grafts

Generations	Styrene/initiator (molar ratio)[a]	Time (h)	Conversion (%)	$M_{n\ th}$ (g/mol)[b]	Free polymer in solution		Surface-grafted polymer		Weight loss (%)[c]	Grafting density[d]
					M_n (g/mol)	M_w–M_n	M_n (g/mol)	M_w–M_n		
First generation	800	54	63	52,416	50,700	1.3	50,400	1.3	82.3	0.39
Second generation	793	54	66	54,430	53,400	1.5	105,400[e]	1.5	88.8	0.32[e]

[a] The alkoxyamine grafting density is of 0.95 μmol/m^2. Initiator = surface-grafted initiator + free initiator.

[b] $M_{n\ th} = ([M]_0/[I]_0) \times (M_w$ of styrene $\times$ conv$)/100$.

[c] Determined by TGA.

[d] In μmol/m^2—calculated using Eq. (1).

[e] First plus second generation of grafts.

corresponds to approximately 20% difference between the actual and the predicted molecular weights, which is more than the experimental uncertainty of GPC. Even an estimated 10% errors on the determination of the nitroxide grafting density could not account for this result as we can calculate that, under such conditions, the theoretical molecular weight (ca. 30,155 g/mol) would be still much lower than the predicted one [21]. Therefore, the observed discrepancy between predicted and actual molecular weights could not be explained by experimental errors only. Thus, to explain this result, one must admit that part of the alkoxyamine is only physisorbed on the silica surface presumably via hydrogen-bonds formation between the carbonyl or the phosphonyl moieties of the alkoxyamine compound and the silanol groups of silica. These physisorbed molecules are strongly anchored to the surface, as they could not be displaced by a series of five centrifugation/redispersion cycles in toluene. However, desorption of these physically adsorbed initiator molecules might take place during polymer chains growth. Indeed, the growing polymer becomes more and more hydrophobic and displays therefore less affinity for the surface.

3.4. Reactivation of the grafted polymer chains

In order to check the ability of the nitroxide end groups of the grafted polymer to reinitiate the polymerization of a second monomer feed, the surface polystyrene was chain-extended under conditions similar to those used for synthesis of the first generation of grafts (see run 4 in Table 3). The characteristics of the first polystyrene sequence are indicated in Table 4.

After addition of a second monomer charge, the extended polymer chains were isolated and analysed by SEC (Fig. 3). The shift of the SEC trace towards lower elution volumes (i.e. higher molecular weights) indicates that the nitroxide end-groups remained active and could reinitiate the polymerization of styrene. Remarkably, the molecular weight of the free polymer is close to the theoretical one calculated on the basis of the monomer to initiator ratio. Also noteworthy, the observed increase in molecular weight of the surface polymer (e.g. 105,400 g/mol) corresponds to the expected increase on the basis of the molecular weights of the first and second generation of grafts (i.e. 50,400 and 54,430 g/mol, respectively). Although, there was no indication of bimodality on the SEC trace of the final polymer, the molecular weight distribution slightly broadened suggesting that termination reactions have been minimized but not completely eliminated. Quantitative determination by TGA of the amount of surface polymer at the end of this chain-extension experiment enabled us to calculate the polymer grafting density using Eq. (1). The data given in Table 4 indicate a re-initiation efficiency of 83% which result is consistent with the above observations and is in close agreement with the previous work of Böttcher and Hallensleben on the graft polymerization of styrene from the surface of silica using the ATRP technique [20].

4. Morphological characterization of the polystyrene-grafted silica particles

Insights into the silica/polystyrene composites nanostructure were provided by DLS measurements and TEM analysis. While the original silica aggregates settled down in toluene, the polystyrene-grafted silica samples formed a stable suspension with a mean diameter comprised between 125 and 190 nm depending on the polymer molecular weight (Table 3). These data prove that the dispersability and stability of the silica particles in toluene are

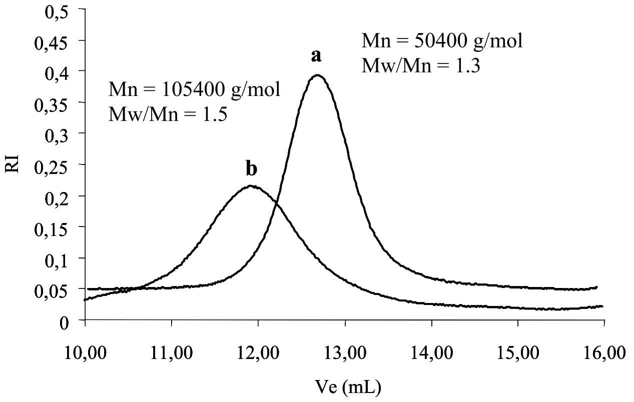


Fig. 3. SEC traces of (a) first generation of polystyrene and (b) first plus second generation of polystyrene.

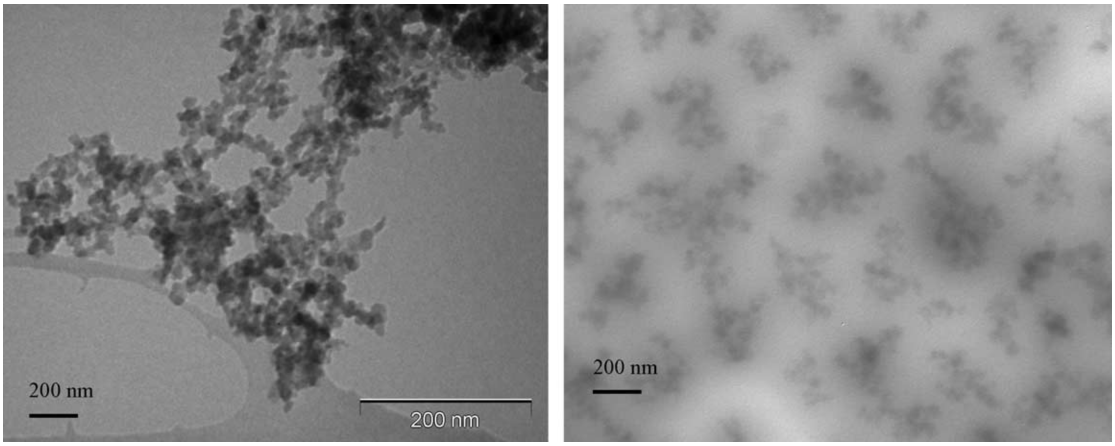


Fig. 4. TEM images of (a) bare silica and (b) PS-grafted silica cast from dilute toluene suspensions.

significantly improved after grafting. Fig. 4 shows the TEM images of the original silica and of the nanocomposite sample cast from dilute toluene suspensions. While the non-functionalized silica sample forms stringy-shaped aggregates, these agglomerates are partly destroyed after polymerization, and the silica particles appear randomly distributed within patchy domains of silica/polystyrene aggregates. It is worthwhile to notice that the size of these domains is close to the hydrodynamic diameter of the PS-grafted silica samples determined by DLS measurements. Our grafting procedure thus appears particularly well suited if one aim to incorporate these naturally aggregated fumed silica particles into a polymer matrix and control the size of the silica aggregates. The effects of the polymer chain length and polymer grafting density on the viscoelastic and structural properties of such nanocomposite materials will be examined in a forthcoming paper [22].

5. Conclusion

We have described in this work the grafting of polystyrene chains from the surface of fumed silica using the NMP technique. Two routes were investigated in order to attach the control agent on the inorganic surface. The first route involves the grafting of a preformed triethoxysilyl-terminated alkoxyamine while in the second route, the alkoxyamine is produced in situ by the simultaneous reaction of APTMS, DEPN and AIBN in the presence of silica. The two routes allow the grafting of moderate amounts of alkoxyamine initiator which surface concentration is mainly limited by steric hindrance. Although the second route gave slightly lower grafting densities in comparison to the first route, presumably because of competitive reactions occurring during in situ formation of the alkoxyamine initiator, it is to our opinion a better method since it allows alkoxyamine grafting in only one reaction step. In both cases, a maximum polymer grafting density of around 0.35 μmol/m^2 was achieved which suggests that some alkoxyamine initiator molecules might have desorbed during the grafting reaction. As far as we are aware, this is the first time that such a hypothesis is formulated in the literature. However, previous works in this field clearly indicate that similar results have been obtained [20]. In order to assess the living character of the grafted polystyrene, a chain growth experiment was carried out that indicated successful chain extension without significant termination. This experiment is promising as it opens the route to the elaboration of block copolymer architectures from the silica particles surface. Finally, DLS measurements and TEM observations showed that the dispersability of silica in toluene was significantly improved when the molecular weight of the grafted PS chains was larger than around 20,000 g/mol. Future work will examine in more details the influence of the polymer molecular weight and grafting density on the conformation of the grafted polymer chains using small angle X-ray scattering and viscoelastic measurements performed on nanocomposite materials made of PS-grafted silica particles dispersed in a polystyrene matrix.

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