Photolabile well-defined polystyrene grafted on silica nanoparticle *via* Nitroxide-mediated polymerization (NMP)

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Abstract

We hereby describe the synthesis of a novel nitroxide-mediated polymerization (NMP) initiator bearing a photolabile *ortho*-nitrobenzyl (*o*NB) group allowing surface-initiated NMP preparation of well-defined photo-responsive polystyrene grafted to silica nanoparticles. The photocleavable and photo-responsive properties of the prepared materials were demonstrated using Small Angle X-ray Scattering (SAXS) characterization.

1. Introduction

Photo-responsive polymers have found widespread use in numerous applications such as controlled drug delivery, (bio)material applications and nanotechnology.^[1–3] There is naturally an interest in photo-responsive polymers that could change their chemical or physical properties in response to light stimulus. Especially if the light-regulation can be performed both for the total sample or at a specific section.^[4] Therefore, photo-responsive polymers have an advantage when compared to pH or thermal-responsive polymers. Nowadays, photo-responsive polymers are predominantly obtained by incorporating photochromic functional groups into their macromolecular structure.^[2] Among these chemical groups, the

photocleavable *ortho*-nitrobenzyl^[5,6] (*o*NB) group is considered as one of the most useful photochromic groups for synthesizing photo-responsive materials owing to its cleavability under mild light irradiation ($\lambda = 256$ nm or 365 nm).^[7,8] Depending on the application, the *o*NB functionality could be introduced along polymer side-chains by direct (co)polymerization of *o*NB vinyl monomers, or at the chain-end by using an initiator bearing *o*NB moieties. Owing to its photodegradable properties, *o*NB functionalized polymers are considered as “smart” photo-responsive materials that could be conjugated to biomolecules such as drugs and proteins/DNA and their liberation under ultraviolet (UV) irradiation performed for wide-range of applications.^[9–11] While *o*NB functionalized materials are mainly focused on hydrophilic (co)polymers for delivery applications, polymers bearing an *o*NB group have been successfully anchored on silicon wafer^[12] and gold nanoparticles^[13] to afford “smart” hybrid materials. Furthermore, due to the reinforcement of mechanical and physical properties for polymer grafted silica (SiO₂) nanoparticles in matrix polymers^[14], a photocleavable polymer-coated silica (SiO₂) nanoparticle could be an interesting candidate for the synthesis of “smart” nanocomposites. Nevertheless, there are few research reports on photo-responsive materials based on SiO₂ nanoparticles. For example, Khire et al.^[15] have reported the synthesis of *o*NB-functionalized polymer grafted SiO₂ using “thiol-ene” Michael addition step-growth polymerization of dithiol and diacrylate to SiO₂ functionalized with *o*NB modified acrylate. Besides, the photocleavability as well as the de-grafted polymers were both successfully demonstrated under UV irradiation. Notably, by defining the irradiated area, the de-grafting process could be performed for all of the sample or at specific sections to modulate the mechanical and physical properties of the material. For these reasons photocleavable polymer-grafted SiO₂ are significantly interesting materials for nanocomposite and “smart” hybrid applications.

Nevertheless, this approach only allowed for the grafting of copolymers based on dithiols and diacrylates monomers. On the other hand, the difficulty in controlling the molecular weight of the grafted polymer chains remained a major drawback. In order to prepare polymer-grafted nanoparticles two main strategies so-called grafting-from and grafting-to have been described. Due to the small size of the initiator, usually the grafting-from method allows higher grafting densities compared to the grafting-to method. Because well-defined polymer chains can be previously prepared under controlled manner, the grafting-to method could afford narrower polymer chains dispersity but a lower grafting density due to steric hindrance phenomena.^{[16–}

18]

Surface-initiated nitroxide-mediated polymerization (NMP)^[19] is considered as one of the most versatile method to synthesize well-defined polymer grafted SiO₂.^[16,17,20–22] In the NMP approach, the NMP initiator is attached early onto the SiO₂, then the graft polymer chains are grown on the modified surface during the polymerization. Hence, the grafting initiation over the SiO₂ is a crucial step for the surface-initiated polymerization process. Regrettably, none of the existing NMP initiators can be used for the synthesis of photocleavable well-defined polymer grafted SiO₂. Therefore, in this communication, a novel alkoxyamine bearing an *o*NB group has been designed as an NMP initiator and then used for synthesizing photocleavable well-defined *o*NB-functionalized polystyrene grafted SiO₂ (*o*NB-PS@SiO₂) nanoparticles. Moreover, the characterization of the resulting photo-responsive PS grafted SiO₂ and its response to UV irradiation was successfully performed by small angle X-ray scattering (SAXS) technique.

2. Results and Discussion

In order to obtain the photocleavable *o*NB-PS@SiO₂ by a surface-initiated NMP process, the synthesis of a novel alkoxyamine NMP initiator bearing the *o*NB group was successfully achieved in two steps following the synthetic pathway in **Scheme 1**. In the first step, the precursor (**1**) compound was obtained by the esterification of 5-hydroxy-2-nitrobenzyl alcohol with 2-bromopropanoyl bromide in the presence of triethylamine (TEA) in tetrahydrofuran (**Scheme 1**). Due to the relatively higher reactivity of the phenol compared to the alcohol moiety, the *ortho*-phenol esterification product (**1**) was the majority product with a good yield of 74.4% (*Figures S1-2 in ESI*). In the second step, compound (**1**) was then coupled with a stable radical nitroxide named SG1 in the presence of the Cu(0)/Cu(I)Br/PMDETA system in acetonitrile to obtain the target alkoxyamine (**2**) (*further synthesis detail provided in ESI*). After purification, the desired compound (**2**) was obtained as a mixture of two diastereoisomers (36 %: 64 %) by comparing the integration values of the signals at 3.30–3.47 ppm (labelled (i)) on the ¹H NMR spectrum (**Figure 1**), with a yield of 33 %. Additionally, **Figure 1** shows the presence of a characteristic signal at 7.12–8.10 ppm corresponding to the phenyl of the *o*NB group (labelled (b), (c) and (d)). Furthermore, the phosphorous moiety of (**2**) was also examined by ³¹P NMR spectroscopy with signals observed at 23.96 and 24.14 ppm. Finally, the successful synthesis of (**2**) was proven by HRMS analysis with a good consistency between the theoretical and experimental values of C₂₃H₃₉N₂O₉P. [M+ H⁺] at (m/z)_{exp}= 519.2463 Da and calculated value (m/z)_{cal}= 519.2466 Da.

Scheme 1: Synthetic pathway of photocleavable *o*NB-functionalized alkoxyamine as NMP initiator.

Figure 1: ^1H NMR (400 MHz) spectrum **(2)** in CDCl_3 .

Alkoxyamine **(2)** can be considered as a good initiator for NMP polymerization. To check its initiating and controlling efficiencies, the polymerization of styrene was carried out using **(2)** as an initiator in the presence of a stable radical nitroxide (SG1, 11% molar to **(2)**) in *N,N*-dimethylacetamide (DMAc) at 120 °C (*Scheme S1 in ESI*). The kinetic study of the polymerization (**Figure 2A**) showed a linear first-order plot indicating a constant concentration of propagating radicals. **Figure 2B** shows the linear evolution of the number-average molecular weight determined by SEC ($M_{n,\text{SEC}}$) with monomer conversion, as well as a good agreement between $M_{n,\text{SEC}}$ and their theoretical values ($M_{n,\text{th}}$). Additionally, the dispersities ($\bar{D}$) of the resulting polystyrenes (PS) were low ($\bar{D} < 1.30$) during the polymerization process which indicates that all polymer chains grew simultaneously, also indicating a well-defined structure

for the polymers. These results prove that alkoxyamine (**2**) is a good NMP initiator for controlling the polymerization of styrene. Encouraged by the successful controlled polymerization efficiencies of (**2**), we then attempted to immobilize (**2**) on SiO₂ nanoparticles to prepare photocleavable well-defined *o*NB-functionalized PS@SiO₂ by performing a surface-initiated polymerization.

Figure 2: NMP polymerization of styrene using (**2**) as alkoxyamine initiator with (A) $\ln([M]_0/[M]_t)$ versus time; (B) evolution of $M_{n,SEC}$ and dispersities ($\bar{D}$) with monomer conversion.

Scheme 2: Synthesis of photocleavable well-defined *o*NB-functionalized PS-grafted-SiO₂ nanoparticle (*o*NB-PS@SiO₂).

To covalently attach (**2**) to SiO₂ nanoparticles, the hydroxyl moiety of (**2**) was firstly activated by reacting it with *N,N*-disuccinimidyl carbonate (DSC) in the presence of triethylamine as a catalyst in acetonitrile to provide the NHS-carbonate functionalized (**2**) (**Scheme 2**). The successful activation reaction was confirmed by ¹H NMR analysis as the methylene group (-CH₂O-) moved from 4.93–4.97 ppm to 5.78–5.80 ppm (*Figure S3 in ESI*).

Due to the high reactivity of the NHS-carbonate functionality towards amine groups, the NHS-carbonate (**2**) was readily coupled with an amine-functionalized SiO₂^[21] (NH₂@SiO₂) to afford the (**2**)-grafted SiO₂ ((**2**)@SiO₂, **Scheme 2**). After purification, the (**2**)@SiO₂ solution then served to initiate the polymerization of styrene in DMAc at 120 °C in the presence of “free” MAMASG1 as a sacrificial initiator to target the photocleavable *o*NB-functionalized PS-grafted SiO₂ (*o*NB-PS@SiO₂, **Scheme 2**). The addition of free initiator was performed to improve the controlled polymerization process.^[16,23] Besides, the free polymer initiated by the sacrificial initiator could prevent the aggregation of nanoparticles during the polymerization and is also used to estimate the M_n and $\bar{D}$ of the grafted polymers on the SiO₂ surface.^[16,17,20]

Table 1 shows that the free PS polymers have a well-defined structure with low dispersity values ($\bar{D} \leq 1.30$). Because of the good correlation of M_n and $\bar{D}$ values between the free and grafted chains^[20–22], this result indicates that the graft polymers on the SiO₂ surface also have a well-defined structure. Furthermore, to confirm the successful polymerization without formation of aggregation, the small angle X-ray scattering (SAXS) analysis of *o*NB-PS@SiO₂ was performed (Entry 1, **Table 1**). **Figure 3** shows the SAXS signal (open circles) of the solution of grafted particles at a volume fraction of particles of 1%. The red curve represents the fit using a form factor of spherical particles of mean radius ($r=12.5\text{nm}$) with a log normal poly-dispersity equal to $\sigma=0.12$ and a scattering contrast ($\Delta\rho^2=3\ 1010\ \text{cm}^{-2}$) representing the difference between the scattering length density of the silica particles and the scattering length density of the solvent. In the inset, the corresponding structure factor ($S(q)$, full circles) calculated by dividing the experimental curve by the fitted form factor. The green curve corresponds to modelling the interactions using a Percus-Yevick function with a mean distance between the particles ($r_0=42\ \text{nm}$) and an apparent volume fraction ($\Phi=0.26$) (**Figure 3**). The detail of the modelling can be found in the previous work.^[24] The presence of the repulsive peak illustrates the well dispersion of the particles, namely the absence of aggregation or clustering. Moreover, the formation of grafted PS was also confirmed by thermogravimetry analysis (TGA), comparing the weight loss due to the degradation of the grafted polymer chains to that of the amine and (**2**) coated SiO₂, respectively (*Figure S4 in ESI*). In addition, the polymer grafting density was calculated to be 0.024 chains per nm² (**Table 1**). The low grafting density value could be explained due to steric hindrance of the alkoxyamine (**2**) on the SiO₂ surface which limits contact of the propagating radical with monomers during polymerization. All these results indicate the presence of a PS corona surrounding the SiO₂ nanoparticles together with a successful NMP process for the synthesis of well-defined *o*NB-PS@SiO₂. Indeed, as the *o*NB group was introduced as a linker between the SiO₂ nanoparticles and its

polymer corona, the UV irradiation of photolabile *o*NB group could directly lead to the cleavage of the grafted PS chains attached to the SiO₂. Therefore, the photocleavable grafted chains and the response behaviour of *o*NB-PS@SiO₂ upon UV irradiation ($\lambda=365$ nm) was studied.

Table 1: Synthesis conditions and characterization of well-defined *o*NB-PS@SiO₂

Entry	[styrene] ₀ : [MAMASG1] ₀ [(2)@SiO ₂] ₀ :	Time (min)	Conv. (%) ^{a)}	$M_{n,SEC}$ (g.mol ⁻¹) ^{b)}	$\bar{D}$ ^{b)}	Grafting density (σ_G) (chain.nm ⁻²) ^{c)}
1	1069 : 1 : 0.18	180	21	27000	1.26	0.024
2	1456 : 1 : 0.18	180	20	34000	1.30	0.024

^{a)} Determined by ¹H NMR. ^{b)} Determined by using SEC chromatography in THF with polystyrene standard calibrated. ^{c)} Determined by using TGA analysis.

Figure 3: SAXS analysis of *o*NB-functionalized PS@SiO₂ (Entry 1, Table 1).

Scheme 3: Response of the well-defined *o*NB-functionalized PS@SiO₂ solution to UV irradiation.

To optimize the degradation time of the *o*NB, the purified *o*NB-PS@SiO₂ solution (Entry 1, **Table 1**) was diluted with DMAc and then irradiated with a UV lamp ($\lambda=365 \text{ nm}$) (**Scheme 3**). The UV spectra of the *o*NB-PS@SiO₂ solution at different irradiation times (**Figure 4**) shows a decreasing absorbance intensity at 396 nm and a slight increase in intensity at 450–500 nm. These phenomena were due to the degeneration of the *o*NB group and the release of nitrosobenzaldehyde under UV irradiation.^[25,26] Additionally, the degradation of *o*NB was completely reached after 20 min of irradiation at minimum intensity.

Figure 4: UV spectra of the well-defined *o*NB-PS@SiO₂ (Entry 1, **Table 1**) with concentration of SiO₂ to be 0.1 % (v/v) in DMAc in response to UV irradiation ($\lambda=365 \text{ nm}$).

After optimizing the irradiation time, the well-defined *o*NB-PS@SiO₂ (Entry 1, **Table 1**) was irradiated and characterized using SAXS analysis to demonstrate the photocleavable property of the PS corona. **Figure 5A** shows the decreased intensity of the peak of the *o*NB-PS@SiO₂ structure at low *q* value due to reducing interaction numbers between particles.

Besides, the displacement of the maximum peak to a higher q value indicates the decrease of the average interparticle distance ($r_0=2\pi/q_{\text{Max}}$). Therefore, the calculated average distance value between nanoparticles rapidly dropped-off in response to higher UV irradiation time (**Figure 5B**). All these results prove that the de-grafting of the polymer chains surrounding the SiO_2 under UV irradiation.

Finally, in an effort to isolate the cleaved chain, the $o\text{NB-PS@SiO}_2$ (Entry 2, **Table 1**) was also exposed to UV light to recover the de-grafted polymers. The SEC analysis result confirmed a good agreement of the grafted polystyrene on the SiO_2 surface and the free PS chain (Figure S5 in ESI). The presence of a broad higher molecular weight on the cleaved polymer SEC trace could be assigned to the radical coupling of two polymer chains generated during the photo-cleavage process.

Figure 5: SAXS analysis of the photocleavable $o\text{NB}$ -functionalized PS@SiO_2 (Entry1, Table 1): (A) structure factor ($S(q)$) versus scattering vector (q); (B) inter-particle distance between nanoparticles with irradiation time.

3. Conclusion

In conclusion, a novel alkoxyamine initiator bearing a photocleavable $o\text{NB}$ group was successfully synthesized and used as an NMP initiator for the controlled polymerization of styrene. Furthermore, the $o\text{NB}$ -functionalized alkoxyamine was immobilized on SiO_2 nanoparticles to synthesize an unprecedented photocleavable well-defined PS grafted SiO_2 via a surface-initiated NMP process. Additionally, the photocleavable property as well as the photo-responsive behaviour of the graft PS polymer on the SiO_2 was demonstrated using SAXS analysis and UV spectroscopy. Owing to the cleavable grafted corona polymers, such photocleavable polymer grafted SiO_2 could be an important material for nanocomposite research, in which the mechanical and physical properties of nanocomposites could

modulated by switching the SiO₂ coated with polymers into uncoated nanoparticles upon UV irradiation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Title

Photolabile well-defined polystyrene grafted on silica nanoparticle via Nitroxide-mediated polymerization (NMP)

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Supporting Information

Photolabile well-defined polystyrene grafted on silica nanoparticle via Nitroxide-mediated polymerization (NMP)

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Materials

5-hydroxy-2-nitrobenzyl alcohol (97%), Triethylamine (TEA, 99%), 2-bromopropanoyl bromide (97%), styrene (S, 99%), *N,N'*-disuccinidyl carbonate (DSC, 95%), LUDOX® TM-40 colloidal silica (40 wt.% suspension in H₂O), (3-aminopropyl)triethoxysilane (APTS, ≥98%), *N,N*-dimethylacetamide (DMAc, ≥99.8%) anhydrous sodium sulfate (Na₂SO₄), sodium bicarbonate (NaHCO₃), sodium chloride (NaCl), tetrahydrofuran (THF, 99%), methanol (CH₃OH, 99.6%), ethyl acetate, *n*-pentane, diethyl ether, copper (I) bromide (Cu(I)Br, 99.99%), powdered copper (Cu(0), 99.99%), anhydrous acetonitrile (CH₃CN, 99.8%), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 99%), butylated hydroxytoluene (BHT, ≥ 99%) were purchased from Sigma-Aldrich. The stable radical *N*-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (SG1, 85%) and Blocbuilder (MAMASG1) were received from Arkema. The styrene was passed over a short plug of neutral aluminum oxide prior to use. Regenerated cellulose membrane (MW: 30KDa and 100KDa) was purchased from Merck. The amine-functionalized SiO₂ nanoparticle

(NH₂@SiO₂), and ultrafiltration process were performed following a previously described procedure in the literature.¹

Characterizations

High resolution mass spectrometry (HRMS): all experiments were performed with a Synapt G2 HDMS quadrupole/time-of-flight (Manchester, UK) and subcontracted by Spectropole, an analytical platform of Aix-Marseille University.

Typically, samples were introduced at 10 μl min⁻¹ flow rate (capillary voltage +2.8kV, sampling cone voltage varied between +20V and +60V) under a desolvation gas (N₂) flow of 100 L h⁻¹ heated at 35°C. Accurate mass experiments were performed using reference ions from PPG, PEG or CH₃COONa internal standard. All the samples were dissolved in methanol doped with 3mM ammonium acetate prior to analysis. Data analyses were conducted using MassLynx 4.1 programs provided by Waters.

Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer thermogravimetric analyzer (TGA 800) with a heating rate of 10 °C/min from 30 °C to 800 °C under a nitrogen atmosphere. The temperature was then raised to 1000 °C at a heating rate of 20 °C/min under an oxygen atmosphere to pyrolyze all organic residues.

The grafting density (σ_G) was determined according to the following formula.²

$$\sigma_G = \frac{\frac{W_{after}}{100 - W_{after}} - \frac{W_{before}}{100 - W_{before}}}{M \times S_{specific}} \times N_{Avg}$$

With σ_G: grafting density (molecule per nm²), W_{after}, W_{before} (%): the weight loss after and before grafting reaction determined by TGA. S_{specific}: specific surface of the silica nanoparticle given by the manufacturer (140 nm².g⁻¹), N_{Avg}: Avogadro number

Nuclear magnetic resonance (NMR): spectra of different nucleus were recorded by using Bruker AC 400 MHz.

Size exclusion chromatography (SEC analysis) were performed on an EcoSEC apparatus from PSS, equipped with a dual flow cell refractive index detector. Eluent was THF at a flow rate of 0.3 mL.min⁻¹ for the sample pump and 0.15 mL.min⁻¹ for the reference pump. The stationary phase was a combination of one PL Resipore (50x4.6) mm guard column and two PL Resipore (250x4.6) mm columns thermostated at 40°C. Samples were prepared at

concentration of 0.25 wt.% in THF containing 0.25 vol.% of toluene, as a flowmarker. Injection volume was set to 20 μL . Polystyrene equivalent number-average and weight-average molar masses (M_n and M_w) and dispersities $\bar{D}$ were calculated by means of PS calibration curve using PS-M Easivial standards (Agilent, USA).

UV irradiation: irradiation was carried out at a distance of 1 cm for various times using a UV spot light (4500 mW.cm^{-2} , Hamamatsu LC8 UV) operated at 365 nm.

UV-Vis spectroscopy characterization: UV-Vis spectra were recorded on a Varian Cary 50 Scan spectrometer.

Small angle X-ray scattering (SAXS): SAXS experiments were carried out on a Xeuss 2.0 apparatus (Xenocs, France) at the Laboratory Léon Brillouin (LLB CEA Saclay). The instrument uses a micro-focused Cu k-alpha source with a wavelength of $1.54 \text{ \AA}$ and a Pilatus3 detector (Dectris, Switzerland). The experiments were performed with a collimated beam size of $0.3 \times 0.25 \text{ mm}$. The sample-to-detector distance was chosen to be 2540 mm to achieve a Q range of $0.004\text{--}0.2 \text{ \AA}^{-1}$. The sample solutions were contained in glass capillaries of 1.5 mm external diameter with a wall thickness of 0.01 mm. The scattering from solvent, empty capillary, empty beam and dark field were measured independently and subtracted using standard protocols. The data were normalized to absolute units. The modelling and fitting were performed with the SASFIT software.

Experimental

1. Synthesis of 3-(hydroxymethyl)-4-nitrophenyl 2-bromopropanoate (1)

Under argon atmosphere, 5-hydroxy-2-nitrobenzyl alcohol (1.00 g, $5.92 \times 10^{-3} \text{ mol}$) and anhydrous tetrahydrofuran (THF, 8.0 mL) were added in a round bottom flask. The solution was then stirred at 0°C under argon for 10 min. Triethylamine (TEA, 0.70 mL, $5.03 \times 10^{-3} \text{ mol}$) was then added into the reaction flask. The resulting solution was continuously stirred for 30 min at 0°C under argon in the dark. To this solution, 2-bromopropanoyl bromide (0.58 mL, $5.53 \times 10^{-3} \text{ mol}$) was slowly added over 35 min under argon at 0°C . After, the mixture reaction was continuously stirred at 0°C for 3 h and 18 h at room temperature under argon. The reaction mixture was filtered and the solid was washed with THF. The filtrate was concentrated under vacuum to obtain a brown oil. The resulting residue was then dissolved with ethyl acetate and washed twice with a saturated solution of NaHCO_3 and finally brine.

The organic phase was dried over Na_2SO_4 , filtered and evaporated under reduced pressure. The crude product was purified by column chromatography with mixture of ethyl acetate/ n-pentane (20/80%: v/v) to give final product as viscous yellow oil (1.25 g). Yield: 74.4%. HR-MS analysis of $\text{C}_{10}\text{H}_{10}\text{NO}_5\text{Br}$: detected ion $[\text{M}+\text{Na}]^+$, calculated value $m/z_{\text{calc}} = 325.9635$ Da and experimental value $m/z_{\text{exp}} = 325.9633$ Da.

^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.14 (d, $J = 8.9$ Hz, 1H), 7.55 (d, $J = 2.6$ Hz, 1H), 7.19 (dd, 1H), 4.98 (s, 2H), 4.54 (q, $J = 6.9$ Hz, 1H), 1.89 (d, $J = 6.9$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 168.00, 154.49, 144.52, 139.93, 126.98, 121.83, 120.90, 62.06, 38.98, 21.27.

Figure S1: ^1H NMR (400 MHz) spectrum of **(1)** in CDCl_3 .

Figure S2: ^{13}C NMR (101 MHz) spectrum of **(1)** in CDCl_3 .

2. Synthesis of *o*NB functionalized alkoxyamine (**2**)

Under an argon atmosphere, 3-(hydroxymethyl)-4-nitrophenyl 2-bromopropanoate (0.91 g, 2.99×10^{-3} mol), copper powder (0.20 g, 3.13×10^{-3} mol), copper (I) bromide (CuBr, 2.99×10^{-3}), radical nitroxide SG1 (85%, 1.04 g, 3.01×10^{-3} mol) and anhydrous acetonitrile (8.0 mL) were added in a round bottom flask. The solution was then stirred and deoxygenated at 0 °C by bubbling argon for 30 min. Then, the deoxygenated PMDETA (1.20 mL, 5.03×10^{-3} mol) was injected into the reaction flask. The resulted solution was continuously stirred at 0 °C for 2 h and room temperature under argon for 24 h in the dark. After, the crude reaction was rapidly filtrated over silica gel column with THF as the eluent and then concentrated under vacuum at room temperature (22 °C). The crude product was dissolved in diethyl ether, filtered over a silica gel pad and concentrated under reduced pressure until dryness. The residual sticky yellow solid was dispersed in *n*-pentane and kept at -30 °C for 3 h. After, the *n*-pentane was removed and dried under vacuum at room temperature in the dark to give the final solid product (0.52 g). Yield: 33.5%. HRMS analysis ($C_{23}H_{39}N_2O_9P$): detected ion $[M+H]^+$, calculated value $m/z_{calc} = 519.2466$ Da, $m/z_{exp} = 519.2463$ Da.

1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.10 (dd, $J = 17.8, 8.9$ Hz, 1H), 7.53 (dd, $J = 29.3, 2.2$ Hz, 1H), 7.25-7.12(1H), 4.97–4.93 (2H), 4.78 (1H), 4.28-3.82 (m, 4H), 3.40-3.23 (1H), 1.59–0.90 (m).

^{31}P NMR (376 MHz, $CDCl_3$) δ (ppm): 24.14 and 23.96.

3. Polymerization of styrene using *o*NB functionalized alkoxyamine (2) as NMP initiator

Scheme S1: Polymerization of styrene using (2) alkoxyamine as NMP initiator with [styrene]₀:(2):[SG1]=543:1:0.11 in DMAc at 120 °C.

Typical procedure for polymerization of styrene, styrene (2.40 g, 2.31×10^{-2} mol) and (2) (0.022 g, 4.25×10^{-5} mol), stable radical nitroxide SG1 (85%, 1.6 mg, 4.63×10^{-6} mol) and DMAc (1.0 mL) were charged to a round bottom flask equipped with a magnetic stir bar. The mixture was deoxygenated by bubbling argon for 40 min with an ice bath. The solution was then immersed in an oil bath thermostated at 120 °C to allow the polymerization to occur.

Samples were periodically taken *via* a degassed syringe to perform the SEC and ^1H NMR analysis. The polymerization was quenched by rapid cooling and exposure of the polymerization solution to air. The resulting product was then dissolved in dichloromethane and precipitated in methanol, filtered and dried under vacuum to obtain the final polymer as a solid.

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.34-6.28 ($(\text{C}_6\text{H}_5)_n$), 1.22-2.14 ($(\text{CH}_2\text{-CH})_n$).

Table S1: Nitroxide-mediated polymerization of styrene with **(2)** in DMAc at 120 °C

[styrene] ₀ : [(2)] ₀ : [SG1] ₀	Time (min)	Conv. ^a (%)	$M_{n,\text{th}}$ ^b (g.mol ⁻¹)	$M_{n,\text{SEC}}$ ^d (g.mol ⁻¹)	$\bar{D}$ ^d
543:1:0.11	0	0	518	-	-
	30	9	5 600	6 700	1.25
	60	13	7 859	10 600	1.19
	90	20	11 812	13 800	1.16
	120	23	13 507	16 800	1.16
	150	29	16 895	20 200	1.17
	180	33	19 154	23 200	1.21

^aDetermined by ^1H NMR; ^b $M_{n,\text{th}} = 518 + (104 \cdot (\text{DP}_{n,\text{th}} \cdot \text{Conv.})/100)$. ^c Determined by using SEC chromatography in THF with polystyrene standard calibrated.

4. Grafting photocleavable *o*NB-functionalized alkoxyamine (**2**) on the surface of SiO_2 nanoparticles

Under an argon atmosphere and avoiding any contact with sunlight, the **(2)** compound (0.052 g, 1.00×10^{-4} mol) and anhydrous acetonitrile (5.0 mL) were added into a round bottom flask. The solution was then stirred at 0 °C under argon for 10 min. Then, *N,N'*-disuccimidylcarbonate (DSC, 0.032 g, 1.25×10^{-4} mol) was added into the reaction flask. After 20 min, anhydrous triethylamine (0.05 mL, 3.59×10^{-4} mol) was then slowly added. The resulted solution was continuously stirred at 0 °C under argon for 4 h in the dark. After, the acetonitrile and triethylamine were removed under vacuum to obtain the NHS-carbonated activated **(2)** as a brownish gummy solid.

This product was then dissolved in DMAc (5.0 mL) and added dropwise into the previously prepared solution of $\text{NH}_2@\text{SiO}_2$ in DMAc (10.0 g, $\sigma_{\text{G}} = 0.18$ amine per nm^2) with the concentration of SiO_2 to be 4.2 % (w/w) at 0 °C under argon. The solution was continuously

stirred at 0 °C and room temperature under argon for 16 h. The **(2)**-grafted SiO₂ solution was then purified using an ultra-filtration with membrane (M_w = 30 KDa) until a colorless filtrate was observed. The final **(2)**-grafted SiO₂ solution was a clear yellow solution prior to use for the polymerization. To determine grafting density as well as the amount of grafted initiator on SiO₂, a small quantity of the final solution (2.00 g) was dried in an oven at 130 °C for TGA analysis. The grafting density of **(2)** over SiO₂ was determined to be 0.14 molecules per nm².

Figure S3: ¹H NMR (400 MHz) spectra of **(2)** before (bottom) and after (above) activation reaction in CDCl₃.

5. Synthesis of photocleavable well-defined *o*NB-functionalized polystyrene grafted silica nanoparticle (*o*NB-PS@SiO₂)

Typical procedure, in a round bottom flask equipped with a magnetic stir bar, 7.00 g of **(2)**-grafted SiO₂ (2.8 wt.% of SiO₂ in DMAc) with molar number of the graft **(2)** to be 0.64×10^{-5} (mol), was diluted with a solution of free MAMASG1 (13.7 mg, 3.60×10^{-5} mol) in DMAc (7.00 mL). Styrene (4.00 g, 3.85×10^{-2} mol) was then slowly added under vigorous stirring. The resulting mixture was then deoxygenated by bubbling argon for 40 min and immersed in an oil bath thermostated at 120 °C under argon to allow the polymerization to occur. The polymerization was quenched after 180 min by rapid cooling and exposure of the polymerization solution to air. The *o*NB functionalized PS-grafted SiO₂ nanoparticle was purified using an ultra-filtration apparatus with regenerated cellulose membrane (M_w = 100 KDa) under nitrogen pressure to remove the styrene and free polystyrene in solution. Each time, the solution was diluted with 50.0 mL of DMAc and concentrated to the initial concentration. This filtration process was performed until the complete removal of the free

polystyrene. The separated free PS was recovered by precipitation in methanol to determine the number average molecular weight and dispersities using SEC analysis.

Figure S4: TGA thermographs of amine-grafted SiO₂, (2)-grafted SiO₂ and well-defined oNB-PS grafted SiO₂ (oNB-PS@SiO₂).

6. Irradiation studies of well-defined oNB-functionalized PS@SiO₂

Irradiation and UV characterization:

The purified oNB-functionalized PS@SiO₂ was diluted in DMAc until the concentration of SiO₂ was 0.1% (v/v). The diluted oNB-PS@SiO₂ (2.0 mL) was then charged into a headspace vial and irradiated with a UV lamp ($\lambda=365$ nm). The irradiated solution was measured by a UV photo-spectrometer.

Irradiation and SAXS characterization:

In a headspace vial, the purified oNB-PS@SiO₂ solution (0.7 mL) with a 1% (v/v) concentration of SiO₂ was irradiated with a UV lamp. Small samples were periodically taken *via* a syringe to perform the SAXS analysis.

7. De-grafting polystyrene from oNB-functionalized PS@SiO₂

The oNB-functionalized PS@SiO₂ solution (2.0 mL) was added to the cooled methanol and kept in a refrigerator (-20 °C) for 2h. The suspended solid was then recuperated using centrifugation and dried under vacuum at 40 °C. The precipitated oNB-PS@SiO₂ (50.0 mg) and a solution BHT (2.2 mg) in THF (1.0 mL) were then added into a headspace vial with a magnetic stirrer. The mixture was dissolved under vigorous stirring and the aid of ultrasonic. The solution was then irradiated with UV ($\lambda=365$ nm) for 30 min. and centrifugated for 20 min with 11500 rpm at 10 °C. The supernatant was collected and concentrated until dryness.

The final solid was characterized with SEC analysis to determine the grafted chain length distribution.

Figure S5: SEC chromatographs of free PS chain due to sacrificial initiator and cleaved PS.

Reference:

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