

Supplementary Information

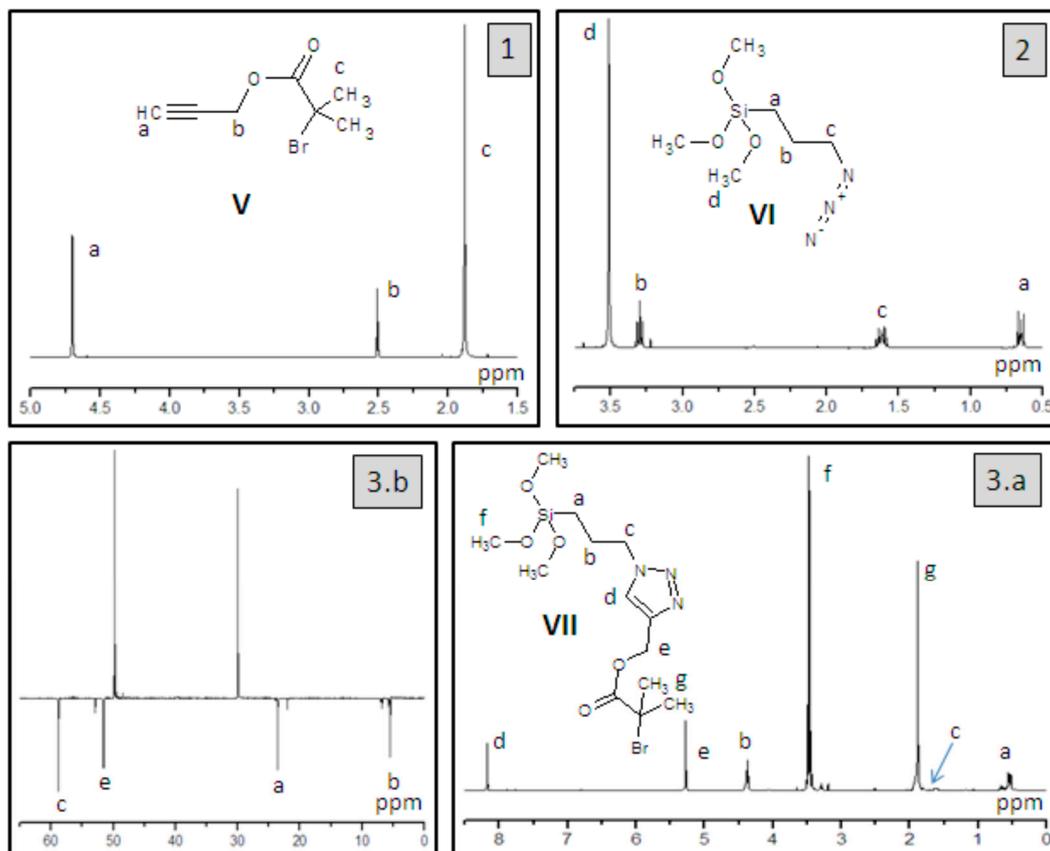


Figure S1. $^1\text{H}/^{13}\text{C}$ NMR spectra of the reaction intermediates and the final product in initiator synthesis. Spectra recorded at 400 MHz in DMSO- d_6 . **3.b.** distortionless enhancement of polarization transfer (DEPT) ^{13}C NMR of VII.

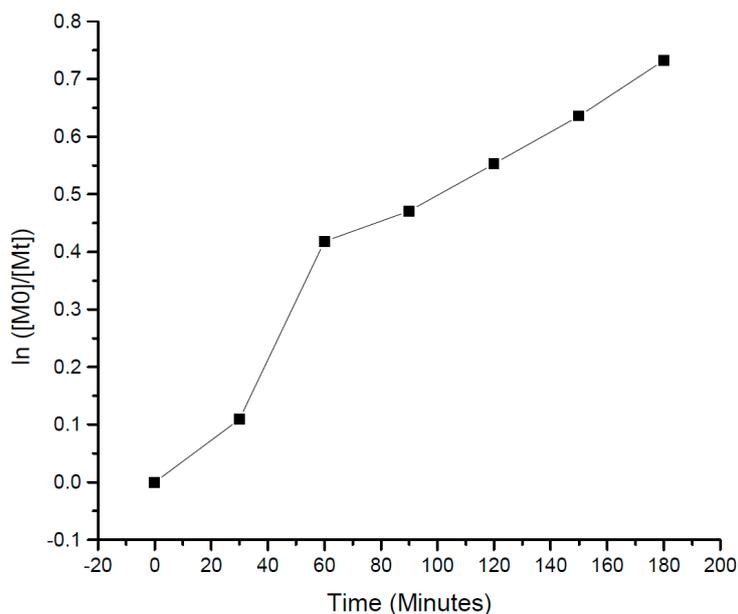


Figure S2. Kinetic plot of the *t*-BMA conversion in the surface polymerization from ATRP initiator decorated Si-NP in the presence of sacrificial initiator.

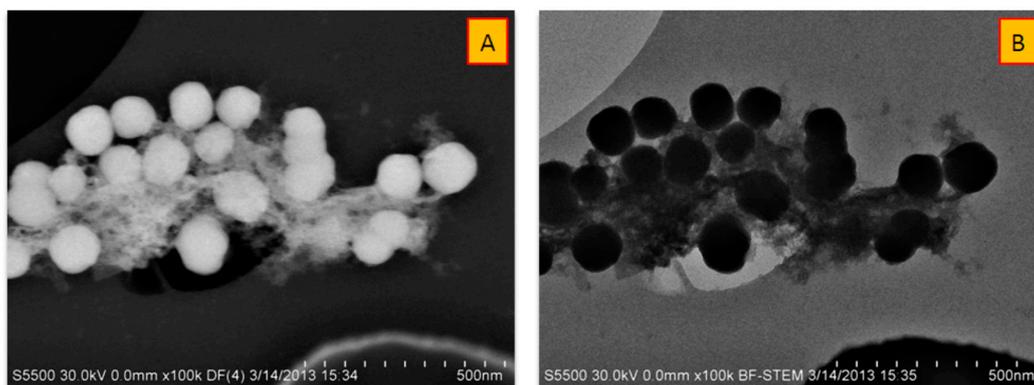


Figure S3. Brush PBMA Si-NP (200 nm) after a 24 h deprotection with aqueous phosphoric acid. (A) Dark Field secondary electron mode; (B) Bright Field standard emission. The presence of the degrafted brush surrounding the Si-NP can be seen. Moreover, diameter reduction from 200 nm to 150 nm is evident as well as a less regular shape of the nano-particles compared to the bare Si-NPs due to the hydrolysis of the brush and of a partial silica re-dissolution.

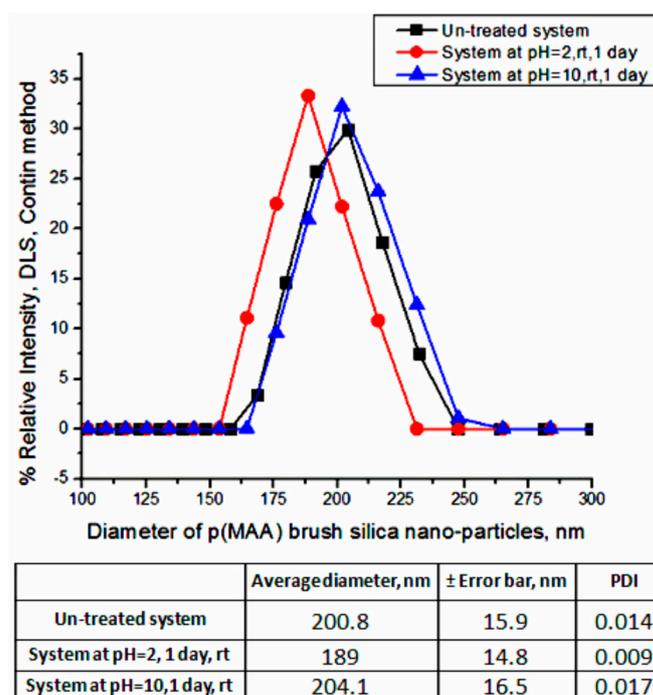


Figure S4. DLS results of three water suspensions of brush PMAA Si-NPs (polymerization time 180 min) at 5 mg/mL. One sample was treated at pH = 2 (by HCl) at room temperature for 1 day, then centrifuged and re-suspended in water up to neutrality of the supernatant. Another system was treated at pH = 10.0 (by NaOH) under the same conditions. The three systems were then analysed by DLS using the Contin method.

Example for TGA calculation:

(1) From Figure 1, see curves C and B: $-(61.51\% - 83.79\%) = 22.28\%$. So, in a 100 g sample of brush PBMA decorated silica nano-particles 22.28 g is the weight of the grafted PBMA brush.

(2) $22.28 \text{ g} / 142.20 \text{ g/mol} = 0.01567 \text{ mol}$ are the mol of *tert*-BMA monomer in the grafted PBMA in a 100 g sample of silica nano-particles (Note: Molecular Weight (MW) of *tert*-BMA: 142.20 g/mol).

(3) As a consequence, 0.01567 mol of $-\text{C}(\text{CH}_3)_3$ would be eliminated in the ideal case of a quantitative de-protection. Corresponding to $0.01567 \text{ mol} \times 58.1414 \text{ g/mol} = 9.1108 \text{ g}$ (Note: MW of the $-\text{C}(\text{CH}_3)_3$ group is 58.1414 g/mol).

(4) From Figure 1, curves D and B: $-(67.07\% - 83.79\%) = 16.72\%$ corresponding to $22.28 \text{ g} - 16.72 \text{ g} = 5.56 \text{ g}$ as the effective mass loss after deprotection (Note: 22.28 g is the brush mass before de-protection and 16.72 g is the brush mass after de-protection).

(5) In this way it is possible to conclude that, for the specific de-protection process the measured mass loss (5.56 g) is around the half (50%) of max possible de-protection yields (9.1108 g).

Note on TGA determination of the initiator on the Si-NP: In Figure S5 the TGA of the free initiator is shown. This Figure demonstrates that the major point of mass loss for the initiator is a 202.96 °C (minor mass losses are located at 282.42, 440.09 and 543.52 °C). For the mass loss calculation the comparison at 800 °C must be considered for the following reasons. As the Zhuravlev model demonstrated, at ~ 200 °C there is the major mass loss of the physisorbed water (and alcohols) from the inside and from the surface of the silica nano-particles. The ability to trap (and to release) physisorbed water is clearly different between bare silica nano-particles and initiator coated silica nano-particles [37]. An analytical evidence of this the fact that the TGA curve of the initiator decorated silica nano-particles (see curve b in Figure 1) is systematically higher than the TGA curve of the bare silica nano-particles (see curve a in Figure 1). The temperature of 350 °C is only the point where these effects are more evident. This is due to the influence of the initiator “skin” on the surface of the nano-particles (at $t < 203$ °C) and so the progressive water release is more difficult (to be noted, all the TGA samples of Figure 1 are from a rigorous washing and drying procedure and all the samples are dried under the same conditions). Above 800 °C, the relative mass loss difference between curve a and b is stable up to 1200 °C and for this reason, 800 °C is the minimum temperature to consider for reliable results.

The following theoretical calculation can be done: From the comparison of the residual masses at 800 °C of the bare Si-NP (87.3%) and the initiator decorated Si-NP (83.8%) a total mass increase of 3.5% upon the reaction was calculated. Considering the surface area of 1 g of 200 nm NPs of 11.34 m² (density 2.648 g/cm³), this corresponds to an initiator concentration of 3.06 mg/m². Assuming a fully hydrated surface of 4.5 silanol groups per nm², it equals to 7.47×10^{-6} mol of silanols on 1 m² [37]. This value, multiplied by the initiator molar mass, is a rough estimation of the expected mass of initiator molecules per m², in this case 3.07 mg/m². This is in very good agreement with the measured value and suggests a monolayer decoration of initiator molecules on the NP surface, which would need to be confirmed by other analytical methods. It has to be noted that careful drying of the NP prior to the decoration is crucial to achieve a monolayer.

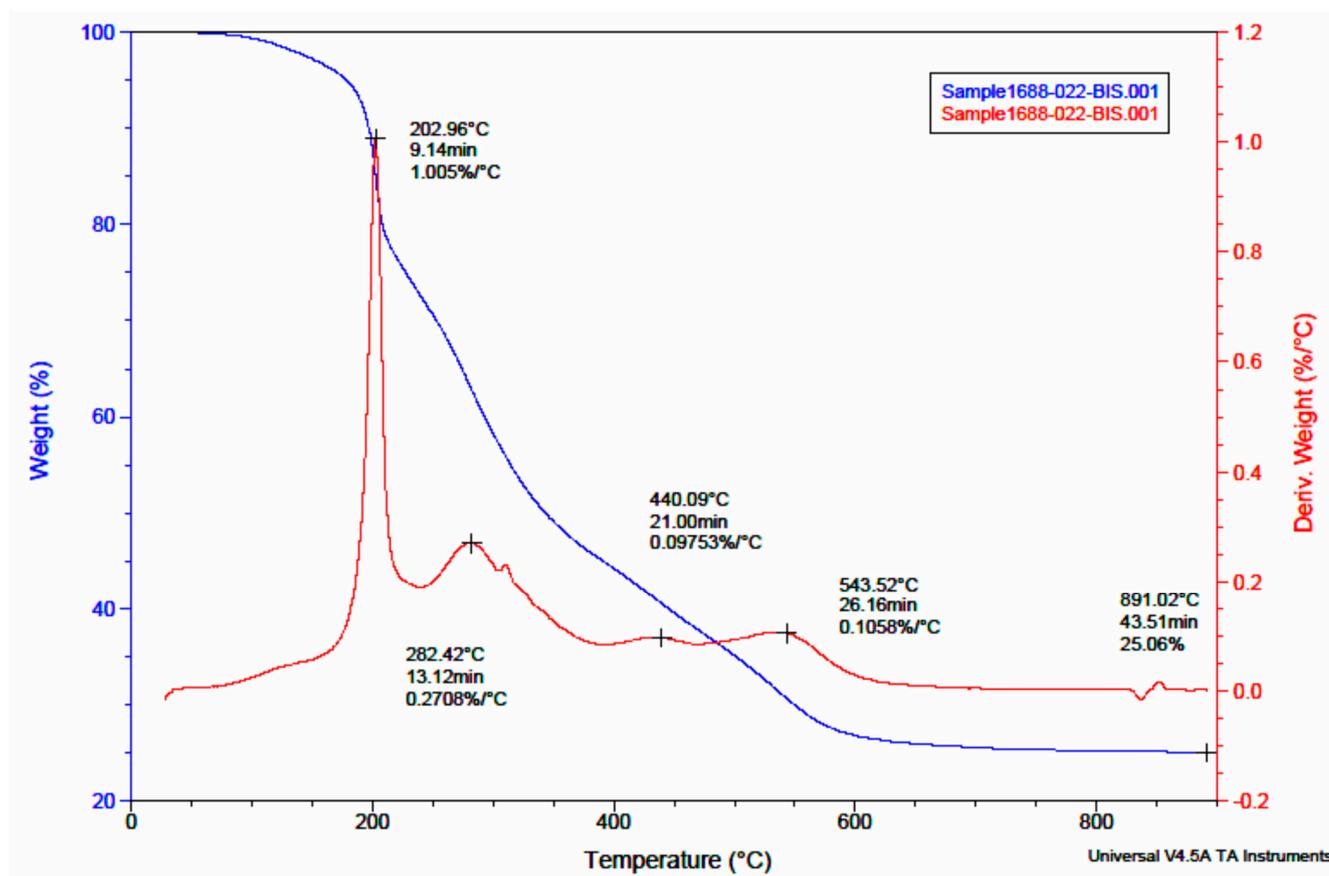


Figure S5. Thermo-gravimetric analysis (TGA) results of initiator VII. The curve in blue shows the TGA of the free initiator, the red curve being the first derivative.

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