

## Supplementary Information

# Silica hairy nanoparticles: a promising material for self-assembling processes

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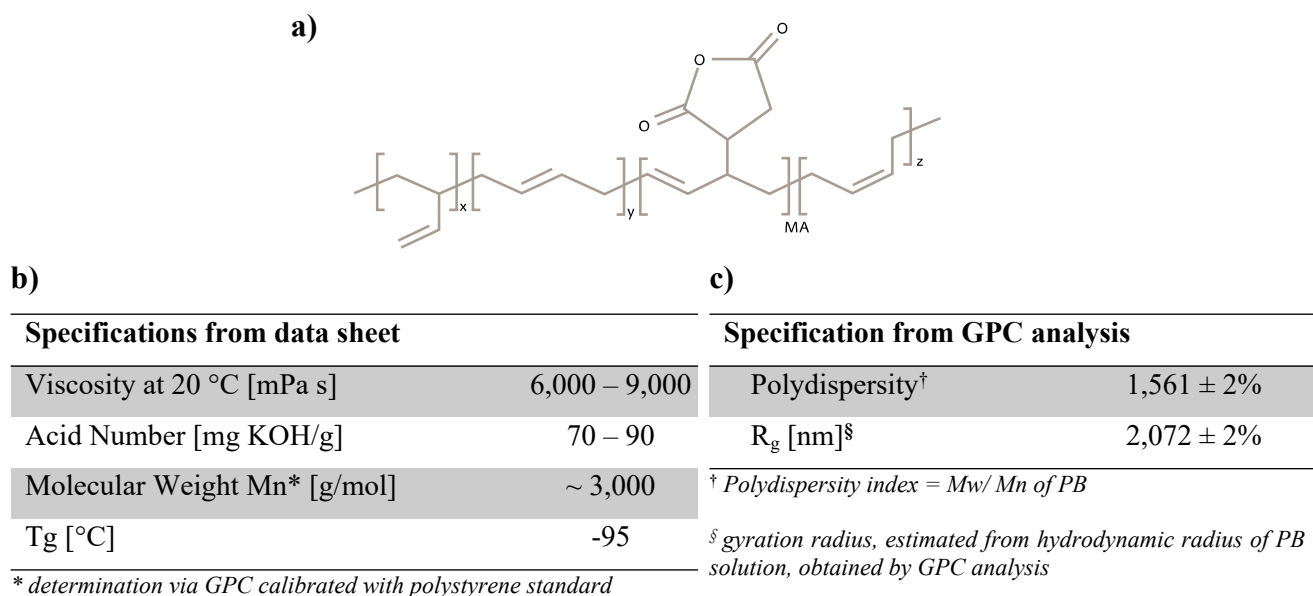
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## 1 Polyvest MA 75

Polyvest MA 75, namely PB, is a commercial maleic anhydride functionalized adduct of a low molecular weight 1,4-cis liquid polybutadiene, which has succinic anhydride groups randomly distributed along the polymer chains (Figure S1a). This makes the originally apolar polybutadiene more polar and exploitable in various chemical reactions. Chemical-physical characteristics of PB from Evonik data sheet are reported in Figure S1b. To further complete the characterization of the oligomer, polydispersity index and gyration radius ( $R_g$ ) values were determined by Gel Permeation Chromatography (GPC) and reported in Fig. S1c. The analysis was carried out using a WATER 1515 isocratic HPLC Pump, a WATER 2414 refractive index detector, four Styragel columns (HR2, HR3, HR4, HR5). PB was dissolved in THF and its chromatograms recorded with a flow of 1.0 mL/min at 35°C. A calibration with polystyrene standard (Merck).

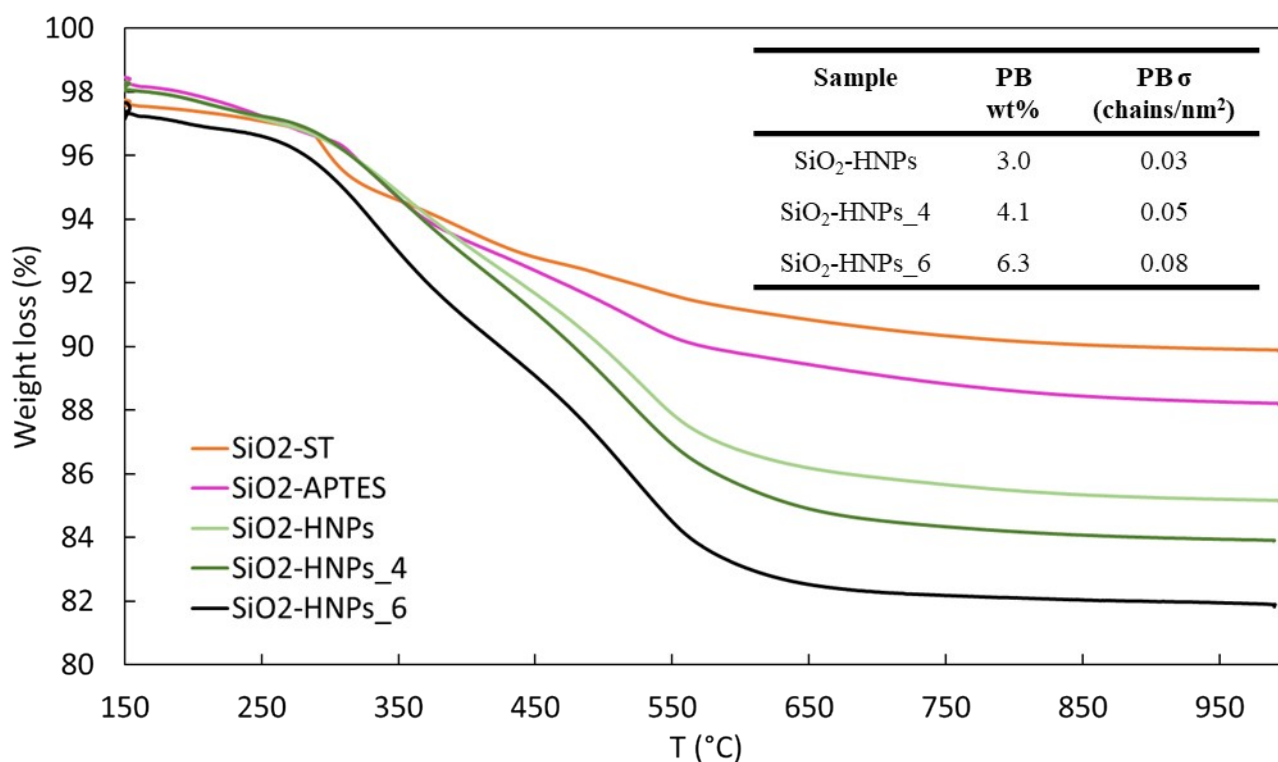


**Fig. S1** Chemical structure (a); chemical-physical characteristics of PB from Evonik data sheet (b); polydispersity index  $R_g$  values derived from GPC analysis of pristine PB (c).

## 2 Synthesis of SiO<sub>2</sub>-HNPs with different grafting density

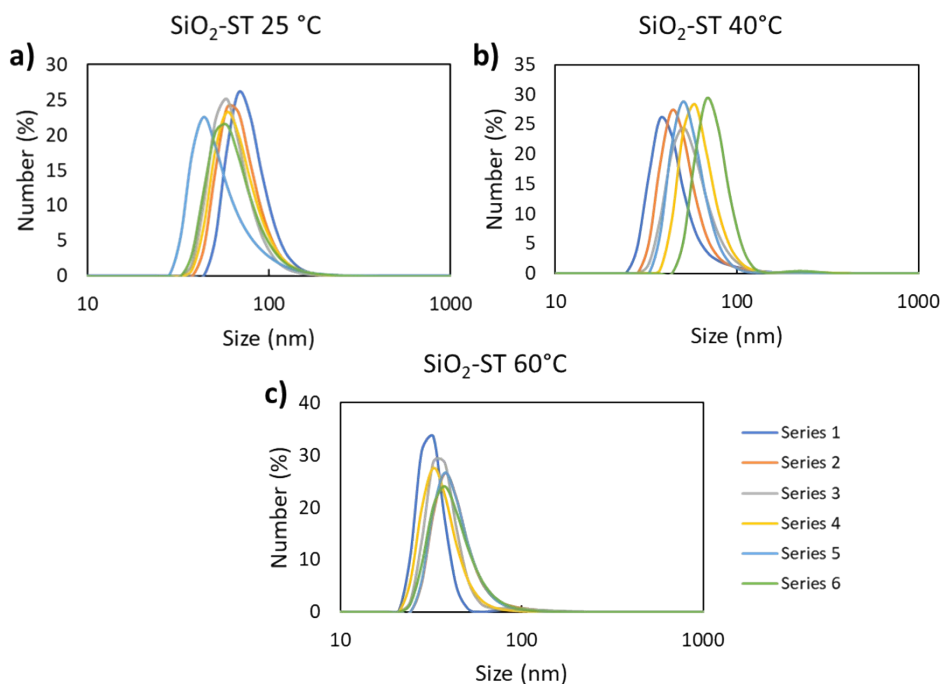
To validate the synthetic approach the synthesis of HNPs was performed by changing the amount of PB to increase the grafting density of polymer shell.

By doubling and quadrupling the amount of PB added to the SiO<sub>2</sub>-APTES solution, SiO<sub>2</sub>-HNPs with increased grafting density were prepared. In detail, a degree of functionalization of 4.1 wt % (SiO<sub>2</sub>-HNPs\_4) and 6.3 wt% (SiO<sub>2</sub>-HNPs\_6) was achieved, which corresponds to 0.05 and 0.08 chains/nm<sup>2</sup> respectively. This indicates that our method can be successfully extended to a range of different grafting densities. The weight percentage and grafting density of PB for each sample and the weight loss curves from TGA are reported in Figure S2.

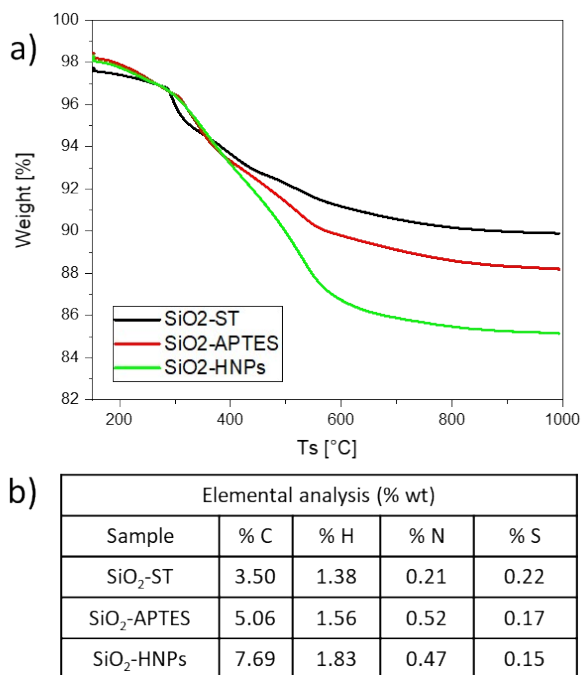


**Fig. S2** TGA analysis of SiO<sub>2</sub>-HNPs\_4 and SiO<sub>2</sub>-HNPs\_6, in comparison with HNPs having a functionalization degree of 3 wt%, reported in the manuscript.

### 3 Surface chemistry and the functionalization degree of NPs samples

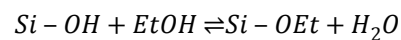


**Fig. S3** DLS graphs show the six subsequent analysis repetitions of SiO<sub>2</sub>-ST at different reaction temperatures: a) 25 °C; b) 40 °C; c) 60 °C.

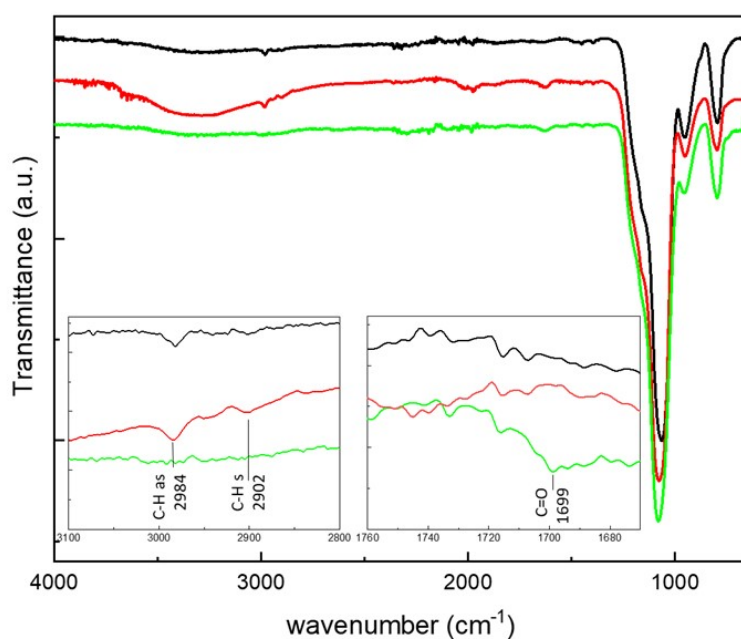


**Fig. S4** a) TGA and b) CHNS elemental analyses of SiO<sub>2</sub>-ST, SiO<sub>2</sub>-APTES and SiO<sub>2</sub>-HNPs. Traces of N and S can be ascribed to residuals of reagents during the silica synthesis.

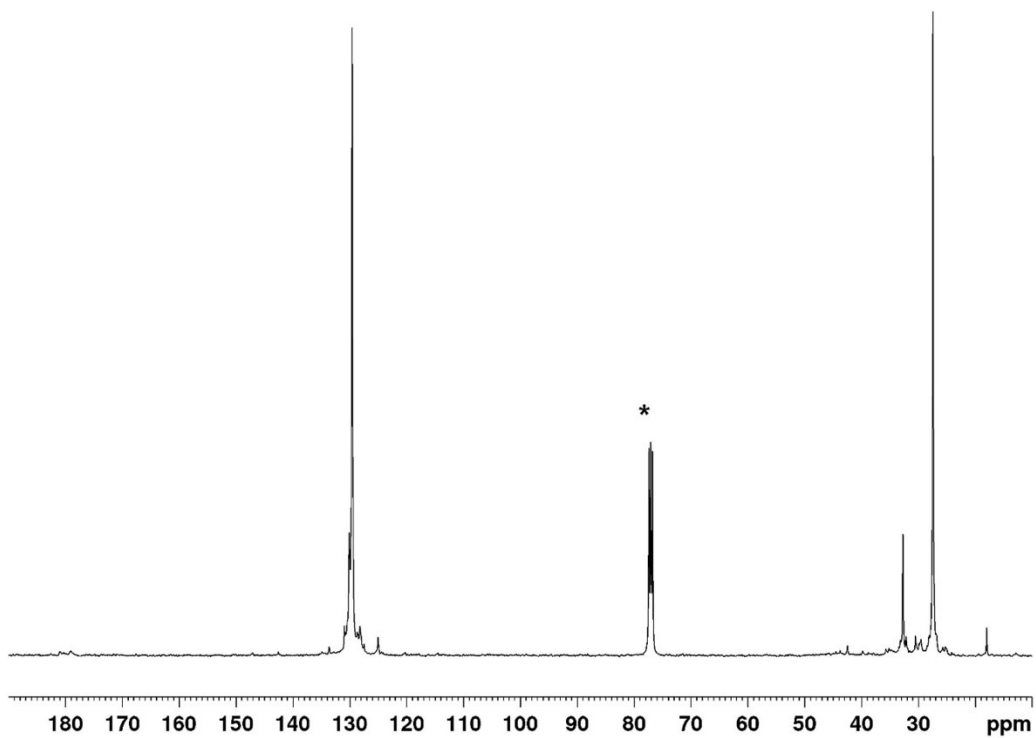
The weight percentage of ethoxy-groups in SiO<sub>2</sub>-ST, estimated on the basis of carbon content by CHNS elemental analysis (Fig S4b), is of 6.56 wt %. In fact, the surface chemistry of the SiO<sub>2</sub> NPs is determined by the following hydrolysis equilibrium:



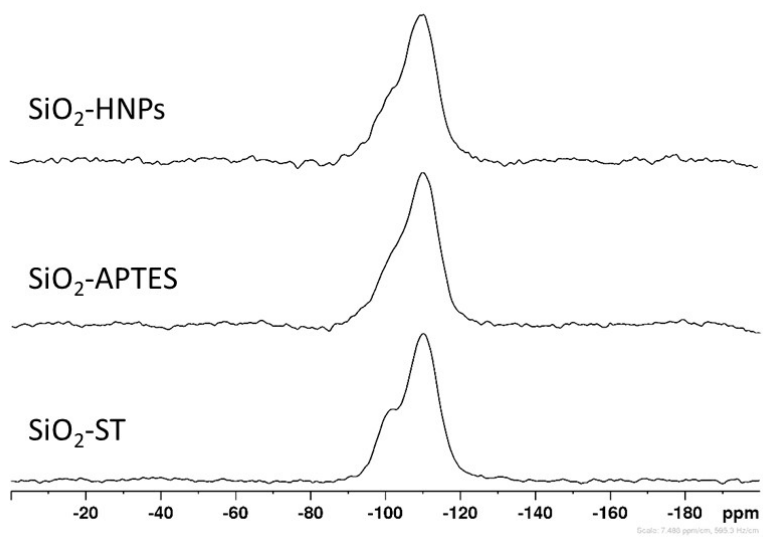
Because of the high EtOH/H<sub>2</sub>O ratio used during the synthesis, the reaction equilibrium is shifted to the right. For instance, Suratwala *et al.*<sup>1</sup> found that colloidal silica sols prepared by the Stöber method with increasing ethanol concentrations showed a decreasing concentration of surface silanols and an increasing concentration of residual ethoxy groups. Upon functionalization of the silica sols with ethoxytrimethylsilane, it was found that that a high density of residual ethoxy groups could hinder the surface functionalization of SiO<sub>2</sub> NPs.



**Fig. S5** FTIR spectra of SiO<sub>2</sub>-ST, SiO<sub>2</sub>-APTES and SiO<sub>2</sub>-HNPs.



**Fig. S6**  $^{13}\text{C}$  NMR spectrum of pristine Polyvest MA75 in  $\text{CDCl}_3$ . Solvent peaks are marked with \*.



**Fig. S7**  $^{29}\text{Si}$  proton decoupled MAS NMR spectra of the three samples.

**Table S1** Chemical shifts and relative amounts of Q<sup>n</sup> structural units in the three samples obtained through profile-fitting analysis. Confidence level > 97%.

<b>structural unit</b>	<b>Q<sup>2</sup></b>	<b>Q<sup>3</sup></b>	<b>Q<sup>4</sup></b>
<i>δ (ppm)</i>	-92.7	-100.5	-109.5
<b>SiO<sub>2</sub>-ST</b>	3.8	23.4	72.8
<b>SiO<sub>2</sub>-APTES</b>	4.6	21.7	73.7
<b>SiO<sub>2</sub>-HNPs</b>	1.5	22.4	76.1

#### *4 Comparison of SiO<sub>2</sub>-ST with commercial colloidal silica*

In the field of HNPs synthesis, most papers report the use of commercial SiO<sub>2</sub> NPs purchased from Nissan Chemicals. For this, here we reported a brief comparison between our colloidal SiO<sub>2</sub>-ST with the parameters of Nissan NPs, as reported in the literature.

Madathingal *et al.*<sup>2</sup> measured the density of surface silanols of Nissan SiO<sub>2</sub> NPs with different primary particle sizes and reported that a surface silanol density of Nissan's SiO<sub>2</sub> NPs in isopropanol is in the range of 1.7 – 7.8 SiOH/nm<sup>2</sup>. In comparison, the density of surface silanols of our colloidal SiO<sub>2</sub>-ST is 52.8 OH/nm<sup>2</sup>, indicating a significantly larger number of available sites for functionalization. Similarly, Barabanova *et al.*<sup>3</sup> evaluated the the density of surface silanols for Nissan SiO<sub>2</sub> NPs (having diameter of about 10-15 nm) in methyl ethyl ketone by using several volumetric and titration methods, establishing the density value of surface silanols between 0.210 and 0.500 mmol OH/g SiO<sub>2</sub>, which is significantly lower than 2.39 mmol OH/g SiO<sub>2</sub> calculated for our colloidal SiO<sub>2</sub>-ST

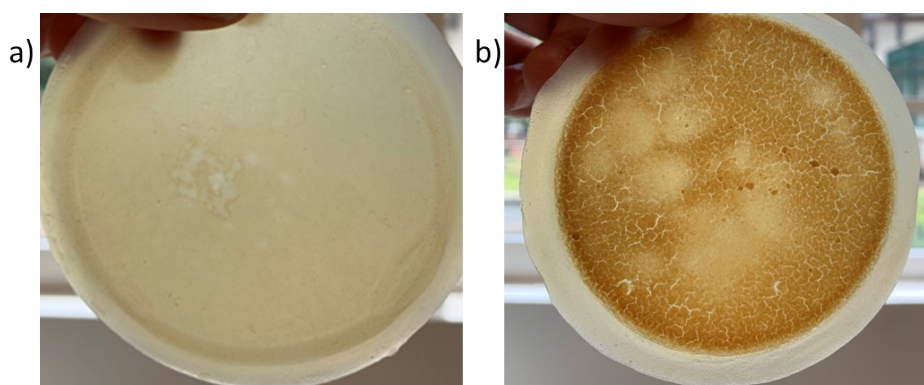
Overall, this suggests that colloidal silica NPs, here reported, have the advantage of offering a much greater amount of functionalization sites compared to commercial colloidal silica.



### 5 Test on HNPs aggregation in cis-PB

By dispersing SiO<sub>2</sub>-HNPs in cis-PB matrices at different loadings, we found the percolation threshold to be between 20 wt% and 25 wt% with respect to the cis-PB matrix, as shown in Figure S8.

At 20 wt%, SiO<sub>2</sub>-HNPs begin to aggregate and phase separation arises between the filler and the polymer matrix



**Fig. S8** Cis-PB films containing a) 20 wt% and b) 25 wt% of SiO<sub>2</sub>-HNPs, showing the loading at which HNPs aggregation begins.

**Table S2** Flocculation experiments on the HNPS aggregation on cis-PB NC

Sample	SiO <sub>2</sub> -HNP wt%	Experimental observation
SiO <sub>2</sub> /cis-PB_5	5	No percolation
SiO <sub>2</sub> /cis-PB_10	10	No percolation
SiO <sub>2</sub> /cis-PB_15	15	No percolation
SiO <sub>2</sub> /cis-PB_20	20	No percolation
SiO <sub>2</sub> /cis-PB_25	25	Percolation
SiO <sub>2</sub> /cis-PB_30	30	Percolation

### References

- 1 T. I. Suratwala, M. L. Hanna, E. L. Miller, P. K. Whitman, I. M. Thomas, P. R. Ehrmann, R. S. Maxwell and A. K. Burnham, *J. Non. Cryst. Solids*, 2003, **316**, 349–363.

- 2 R. R. Madathingal and S. L. Wunder, *Thermochim. Acta*, 2011, **526**, 83–89.
- 3 A. I. Barabanova, T. A. Pryakhina, E. S. Afanas'Ev, B. G. Zavin, Y. S. Vygodskii, A. A. Askadskii, O. E. Philippova and A. R. Khokhlov, *Appl. Surf. Sci.*, 2012, **258**, 3168–3172.