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SUPPLEMENTARY INFORMATION

Controlling the anisotropic self-assembly of polybutadiene-grafted silica nanoparticles by tuning three-body interaction forces

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Characterization is crucial for synthesizing HNPs with specific molecular parameters, revealing their structures, understanding their behavior and properties, and using them in specific applications. The HNPs structures, behavior, and properties are mainly governed by molecular weights, dispersity, grafting density, polymer topology, size, and geometry of core NPs, etc. Accurate characterization of basic defining parameters and other aspects of HNPs require the use of a broad range of characterization techniques.

Here, we characterize the nanoparticles by means of TGA, SAXS, and TEM analyses.

TGA ANASISIS

The thermal degradation profile was obtained under the following conditions: constant airflow (50 $mLmin^{-1}$) and heating rate of $5^{o}Cmin^{-1}$ in the range 30-150ºC, constant airflow (50 mL min^{-1} at 150ºC for 10 min, constant airflow (50 $mLmin^{-1}$) and heating rate of $10^{o}C$ min^{-1} in the range 150-1000ºC.

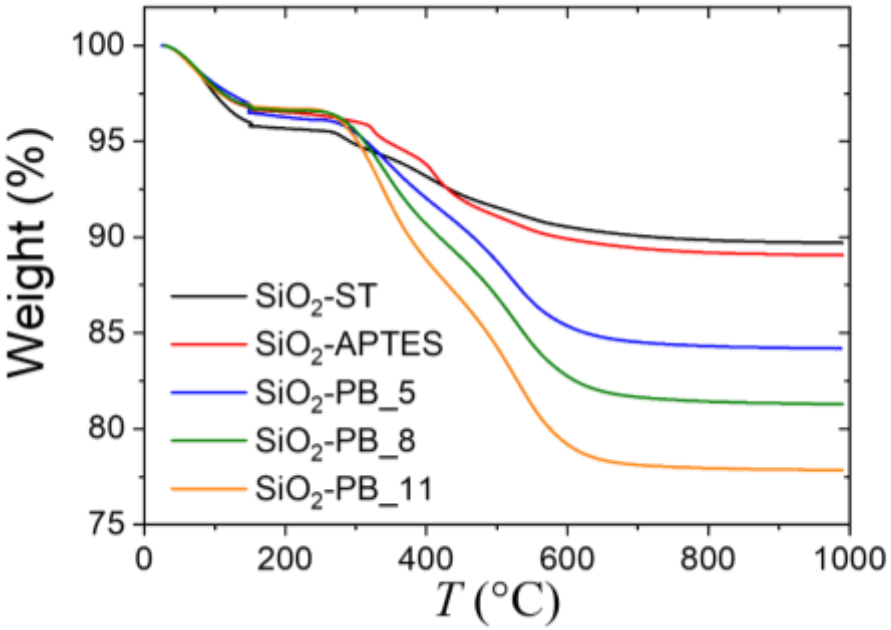

Figure S1: TGA weight loss curves of SiO_2-ST, SiO_2-APTES, and SiO_2-HNP_X.

SAXS ANALYSIS

SAXS measurements were conducted with an Incoatec™ X-ray source IμS with Quazar Montel optics at a wavelength of 0.154 nm. The focal spot size diameter at the sample was 700 μm. The sample to detector distance was 1.6 m with an evacuated flight tube installed, providing a maximum resolution (d-spacing) of 120 nm. A CCD-Detector Rayonix™ SX165 was employed for the detection of the 2D scattering patterns. The regular measurement time per sample accounted for 20 min. SPEC (ver. 5.32) by Certified Scientific Software, Cambridge, MA, USA was employed as control software. Dispersions of SiO_2-ST and SiO_2-HNP_X in THF for SAXS analysis were prepared by suspending 5 wt% of SiO_2 particles in THF by ultrasonication for 1 h.

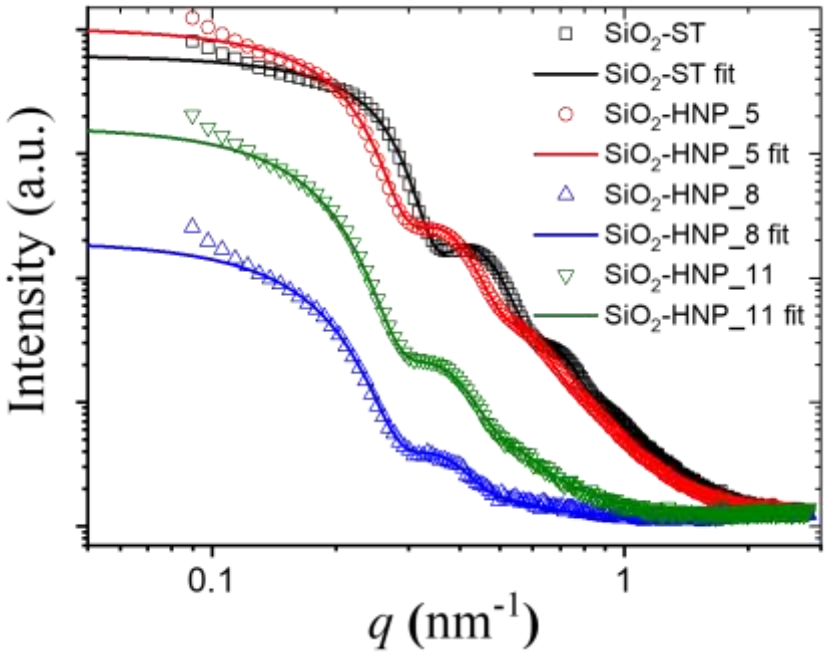

Figure S2: SAXS curves and fitting of bare SiO_2-ST and SiO_2-HNP_X, with X=5 8 and 11.

TEM ANALYSIS

Morphology of silica powders was investigated by TEM analysis, performed on a JEOL JEM 2100+ equipped with a LaB6 cathode. Images were taken at different magnifications with the TEM operated in bright-field parallel imaging mode at 200 keV.

We present below additional TEM micrographs that show the overall tendency of finding more string-like structures when increasing the concentration of grafted polymer. Some of the pictures were taken with one order of magnification larger to confirm the existence of these self-assembled structures. As observed below, uncovered silica NPs self-assemble into compact clusters. By increasing the concentration of grafted polymer, the formation of more anisotropic superstructures are detectable. For the largest polymer concentration studied in this work, we find that HNPs self-organize forming chains.

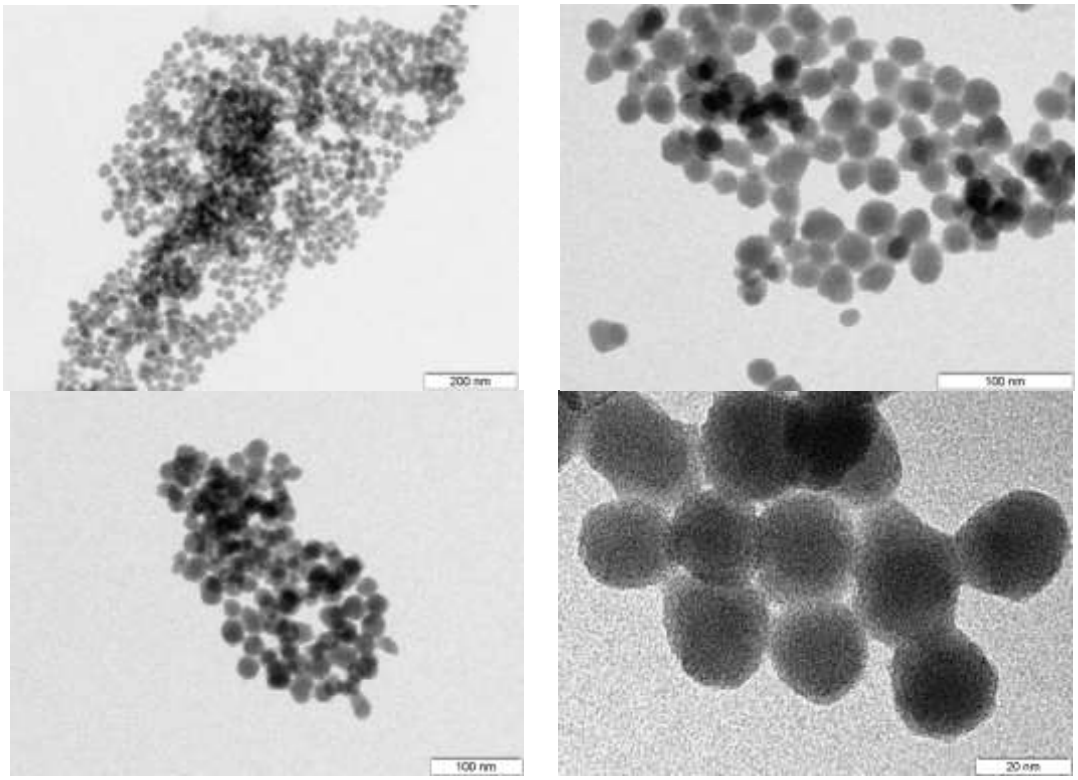

Figure S3: TEM images of SiO_2-ST sample.

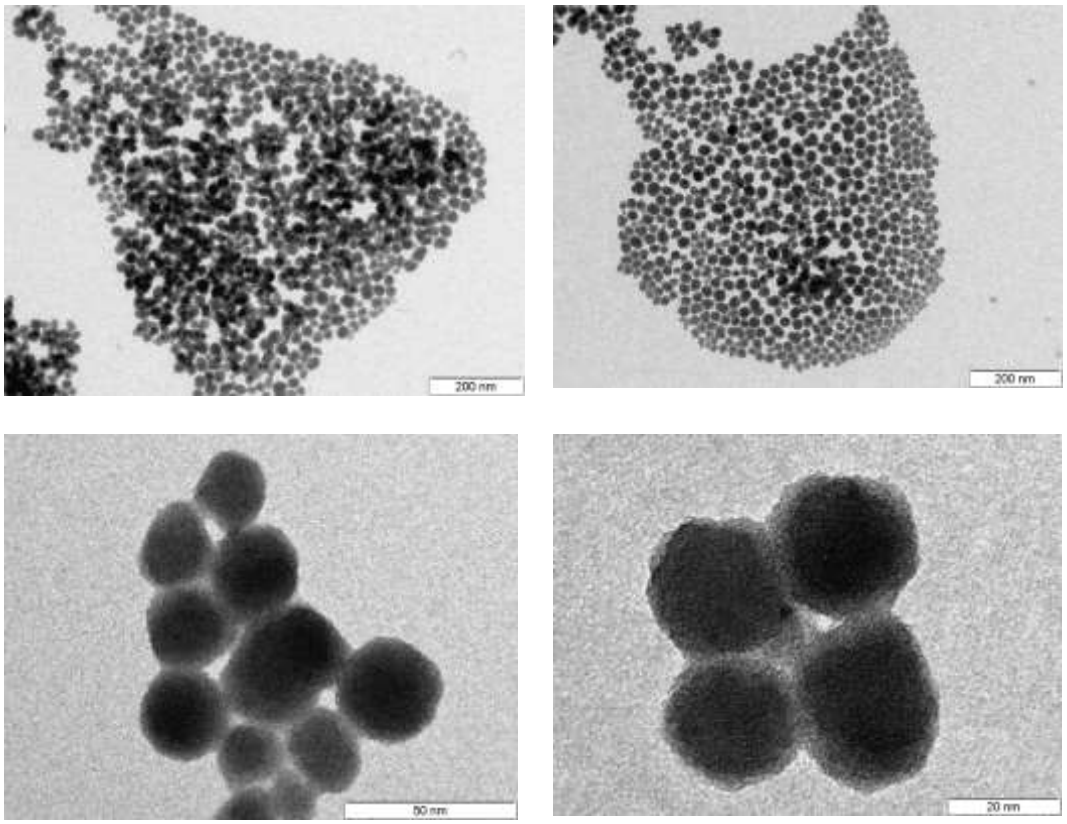

Figure S4: TEM images of SiO_2-APTES sample.

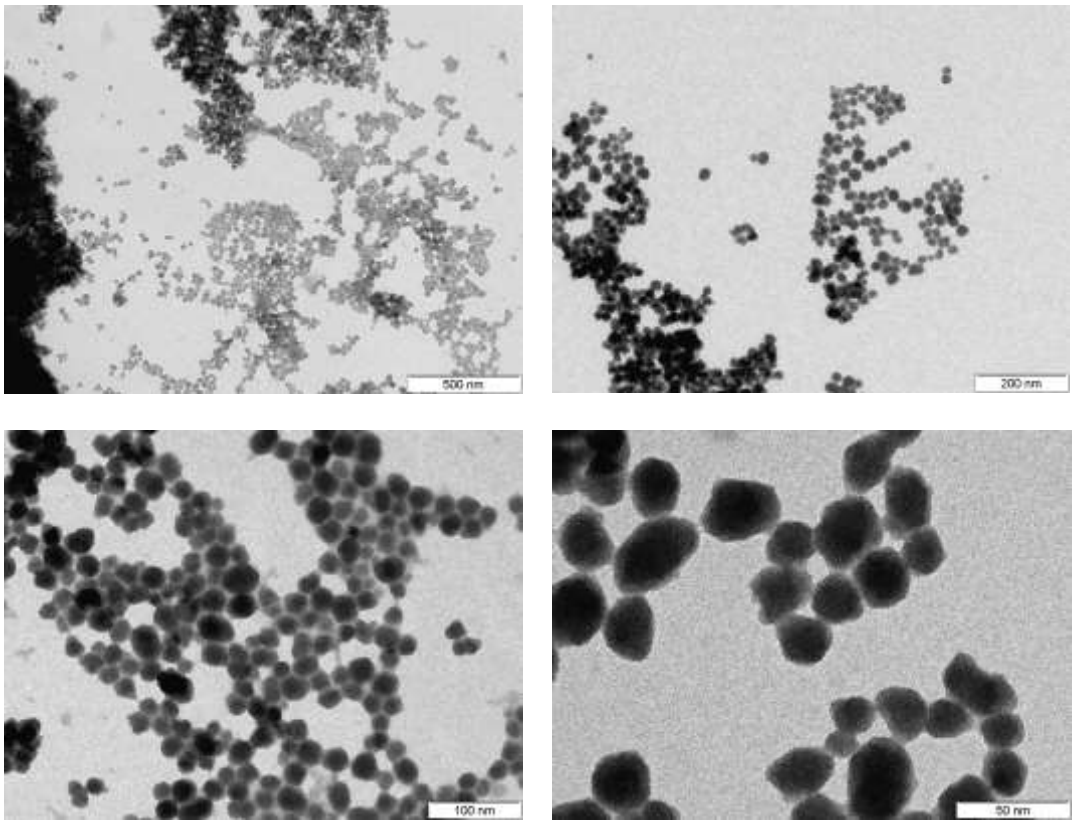

Figure S5: TEM images of SiO_2-HNP_5 sample.

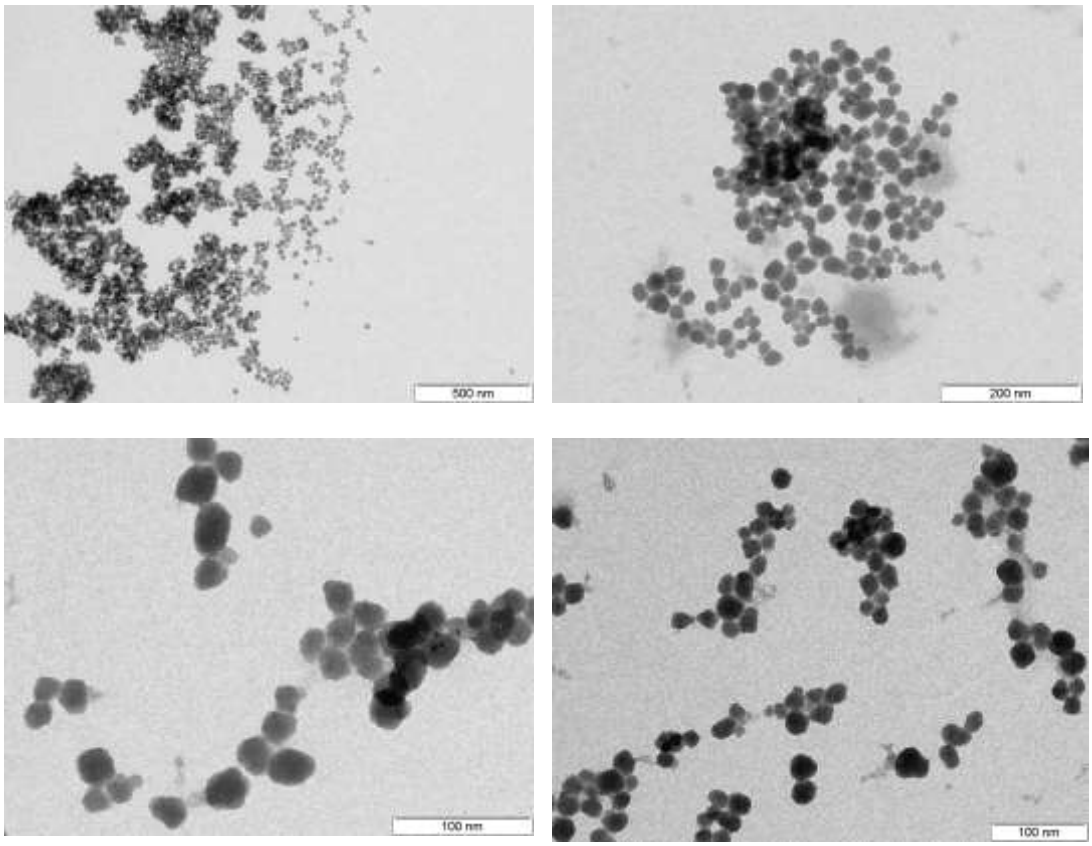

Figure S6: TEM images of SiO_2-HNP_8 sample.

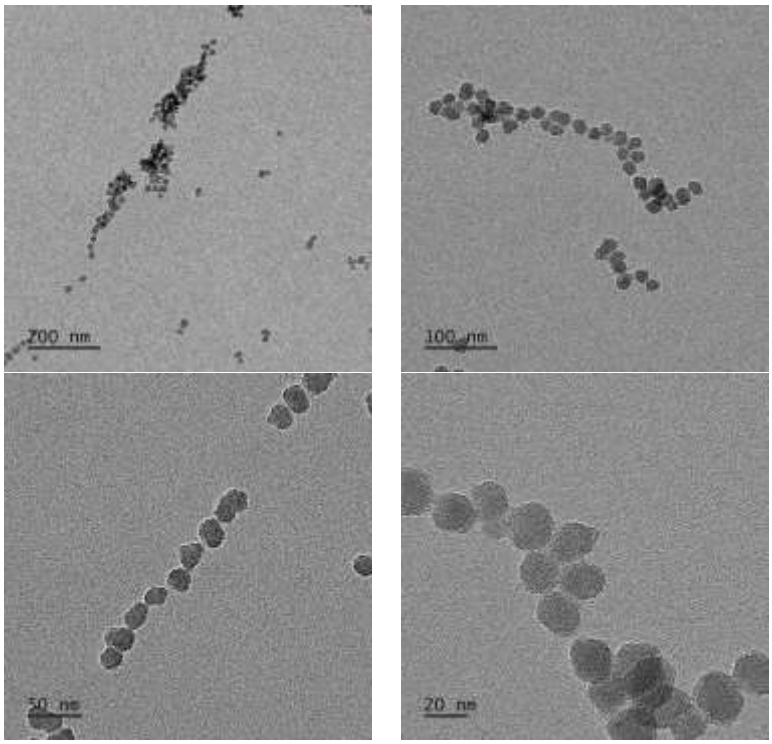

Figure S7: TEM images of SiO_2-HNP_11 sample.