Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Surface-Initiated Polymerization-Induced Self-Assembly of Bimodal Polymer-grafted Silica Nanoparticles towards Hybrid Assemblies in One Step

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Experimental Section

Materials: 2-Hydroxyethyl methacrylate (Acros, 99%) and Benzyl methacrylate (Acros, 96%) were passed through basic aluminum column to remove inhibitors before use. 2.2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol and dissolved in methanol to make a 10mM solution. All other reagents were used as received.

Synthesis of PHEMA grafted silica nanoparticles. 4-Cyanopentanoic acid dithiobenzoate (CPDB) anchored 15nm silica nanoparticles were prepared according to the literature.[15] (Scheme S1) Graft density was determined by measuring the UV-vis peak at 304 nm, and calculated from CPDB calibration curve. A solution of 2-hydroxyethyl methacrylate (2.27 g), AIBN (263µl of 10mM solution in methanol), CPDB-anchored silica nanoparticles (0.76g, 23µmol/g) and DMF (5ml) was prepared in a Schlenk tube. The mixture was degassed by three freeze-pump-thaw cycles, backfilled with nitrogen, and then placed in an oil bath at 65°C for 5 hours. The polymerization solution was quenched in an ice bath and poured into diethyl ether to precipitate the SiO_2-g-PHEMA nanoparticles. The SiO_2-g-PHEMA nanoparticles were redispersed in DMF and precipitated in diethyl ether two more times to remove excess monomers and initiators.

Chain End Deactivation of SiO_2-g-PHEMA. Solid AIBN [58mg (20 eq)] was added to a solution of SiO_2-g-PHEMA in DMF and heated at 65°C for 1 hour. The resulting solution was poured into a large amount of diethyl ether and centrifuged at 5000rpm for 5 min. The recovered SiO_2-g-PHEMA completely lost its original pink color and appeared to be white in color.

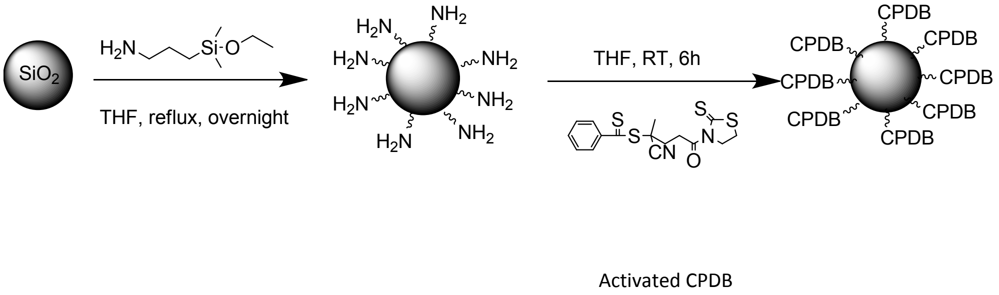
Second RAFT Agent attachment to SiO_2-g-PHEMA. SiO_2-g-PHEMA nanoparticles from the previous step were dispersed in ~15ml DMF, to which 17µl of 3-aminopropyl(dimethyl)ethoxysilane (APTES) was added to react with the remaining surface hydroxyl groups under N_2 for 1.5 hours. Excess AIBN was washed out by ether precipitation and activated CPDB (50 mg) was added to anchor a second population of RAFT agent to give SiO_2-g-(PHEMA, CPDB) nanoparticles. Graft density was determined by measuring the UV-vis peak at 304 nm, and calculated from the CPDB calibration curve. TGA results were used to adjust the calculation (55% weight percent silica in PHEMA grafted NPs)[1]. (It is worth noting that the added APTES will not react with hydroxyl groups on the PHEMA chains. In a control experiment, free PHEMA was synthesized, followed by RAFT agent cleavage, reaction with APTES and then activated CPDB using the same procedure. As a result, no RAFT agent was attached as detected by UV-vis absorption.)

Surface-initiated RAFT polymerization of BzMA using SiO_2-g-(PHEMA, CPDB) as a macro chain transfer agent and stabilizer. SiO_2-g-(PHEMA, CPDB) nanoparticles (0.22g, 45wt% silica), BzMA (0.76 g), AIBN (56µl of 10mM solution in methanol) and methanol (8ml) were mixed together and added to a Schlenk flask with rubber stopper. The mixture was degassed by three freeze-pump-thaw cycles, backfilled with nitrogen and then placed in an oil bath of 80°C. In a sealed tube environment, the tube is under slight pressure and the internal measured temperature was consistent with the bath temperature. Aliquots of the reaction solution were withdrawn from the flask at 1h, 1.5h, 2h, 2.5h, 3.5h, 4.5h respectively.

Characterization.

^{1}H NMR (Bruker ARX 300/ARX 400) was conducted using CD_3OD as the solvent. Molecular weights and dispersity were determined using a gel permeation chromatography (GPC) with a 515 HPLC pump, a 2410 refractive index detector, and three Styragel columns. The columns consists of HR1, HR3 and HR4 in the effective molecular weight ranges of 100-5000, 500-30000, and 5000-500000, respectively. THF was used as eluent at 30°C and flow rate was adjusted to 1.0mL/min. Molecular weights were calibrated with poly(methyl methacrylate) standards obtained from Polymer Laboratories. Dynamic Light Scattering characterizations were conducted using Zetasizer Nano ZS90 from Malvern. Each samples was diluted with methanol to ~1mg/ml prior to DLS analysis. The transmission electron microscopy (TEM) was performed on a Hitachi H8000 TEM at an accelerating voltage of 200 KV. The samples were prepared by depositing a drop of the diluted nanoparticle solution in methanol on copper grids.

Scheme S1. Synthesis Procedures of 4-Cyanopentanoic Acid Dithiobenzoate (CPDB) Anchored onto Silica Nanoparticles



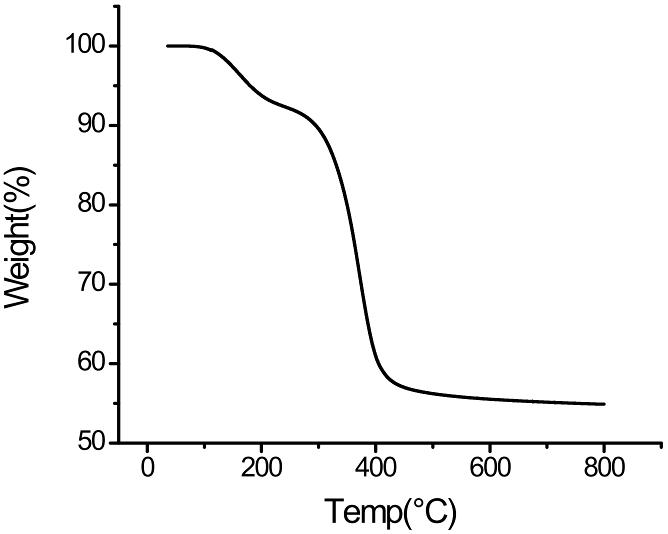


Figure S1. TGA analysis of SiO_2-g-PHEMA

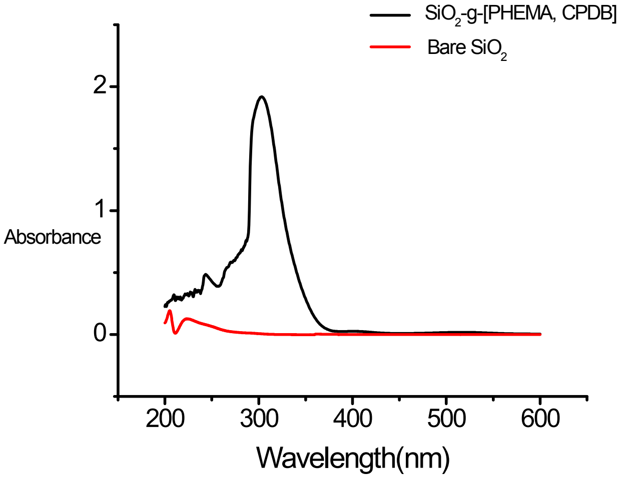


Figure S2. UV-vis analysis of SiO_2-g-[PHEMA, CPDB] and bare SiO_2

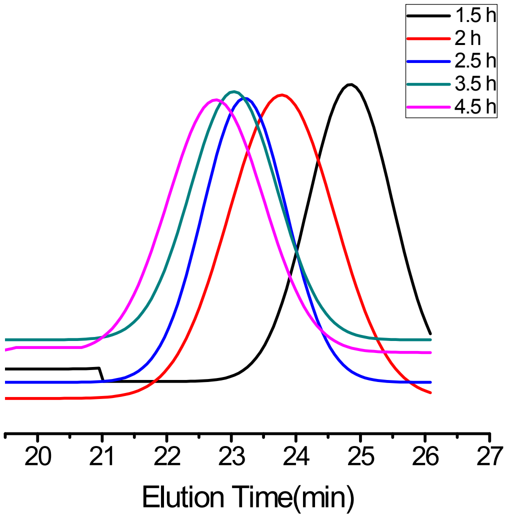


Figure S3. GPC traces of BzMA chains cleaved from silica nanoparticle surfaces.

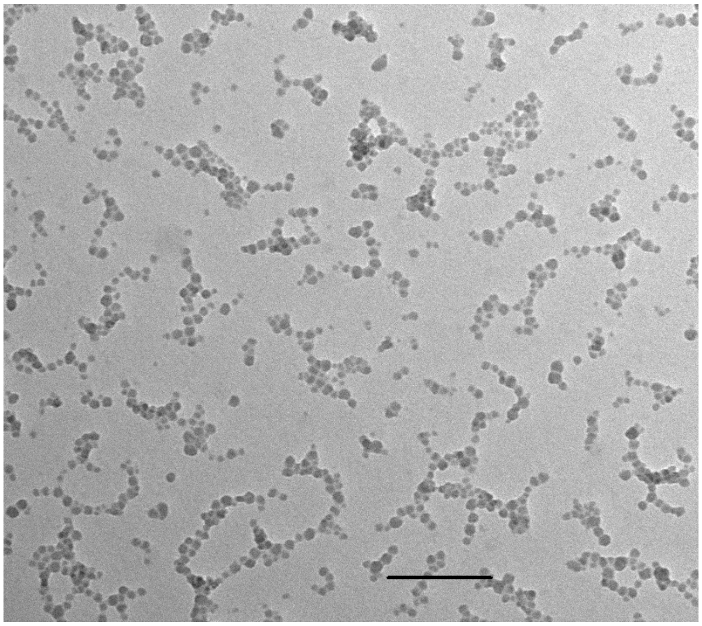


Figure S4. TEM of polymerization sample at 1.5h. Scale bar 200nm.

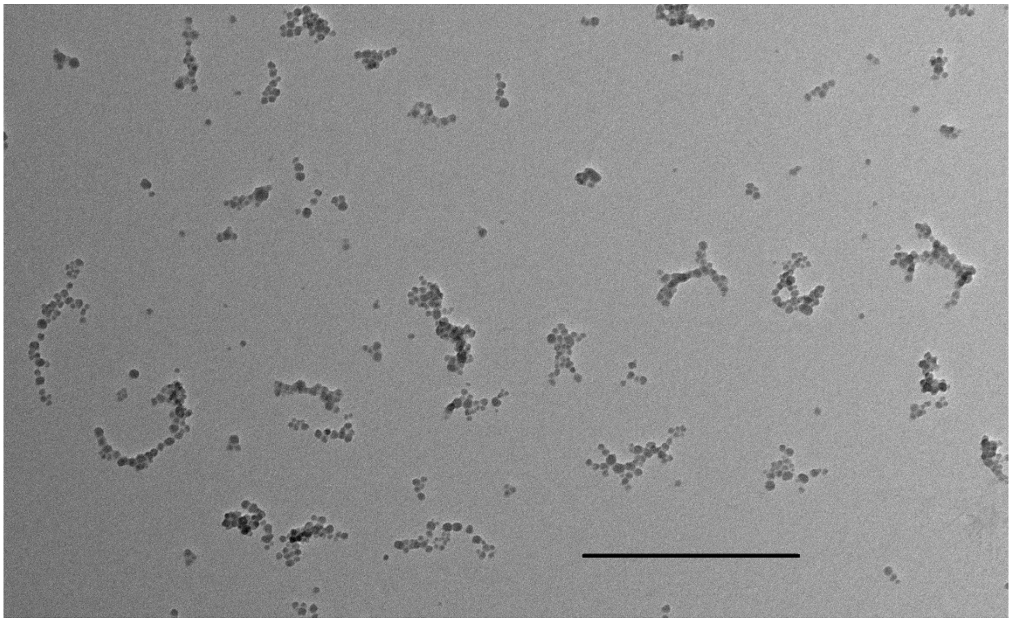


Figure S5. TEM of polymerization sample at 2h. Scale bar 500nm.

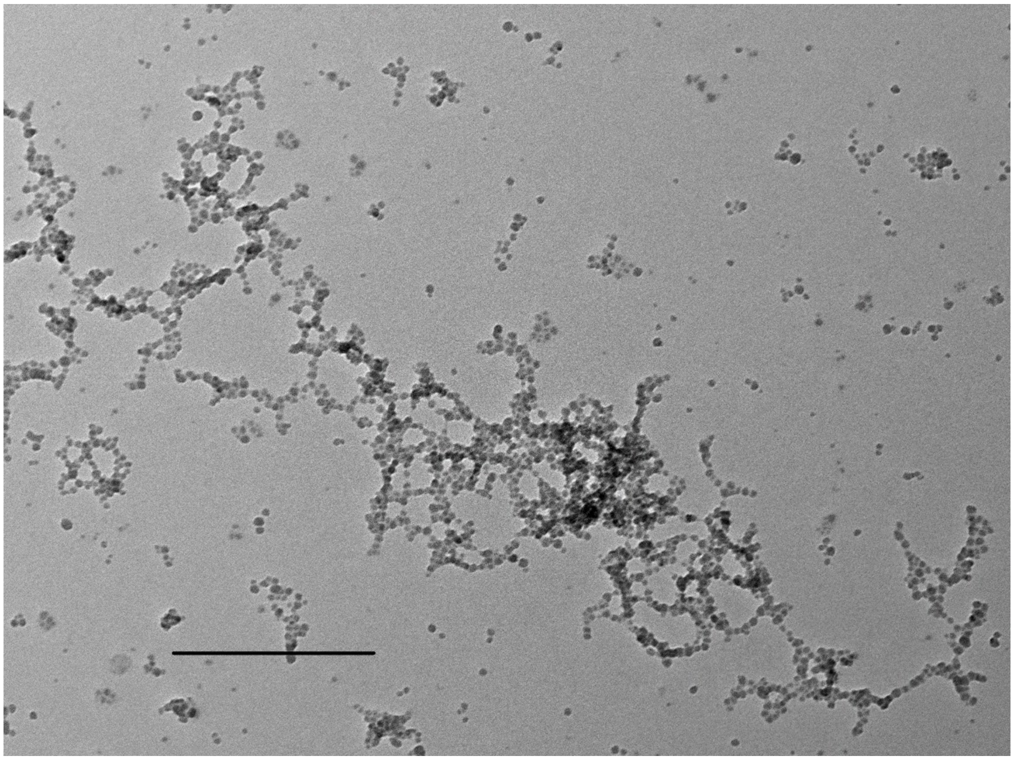


Figure S6. TEM of polymerization sample at 4.5h. Scale bar 500nm.

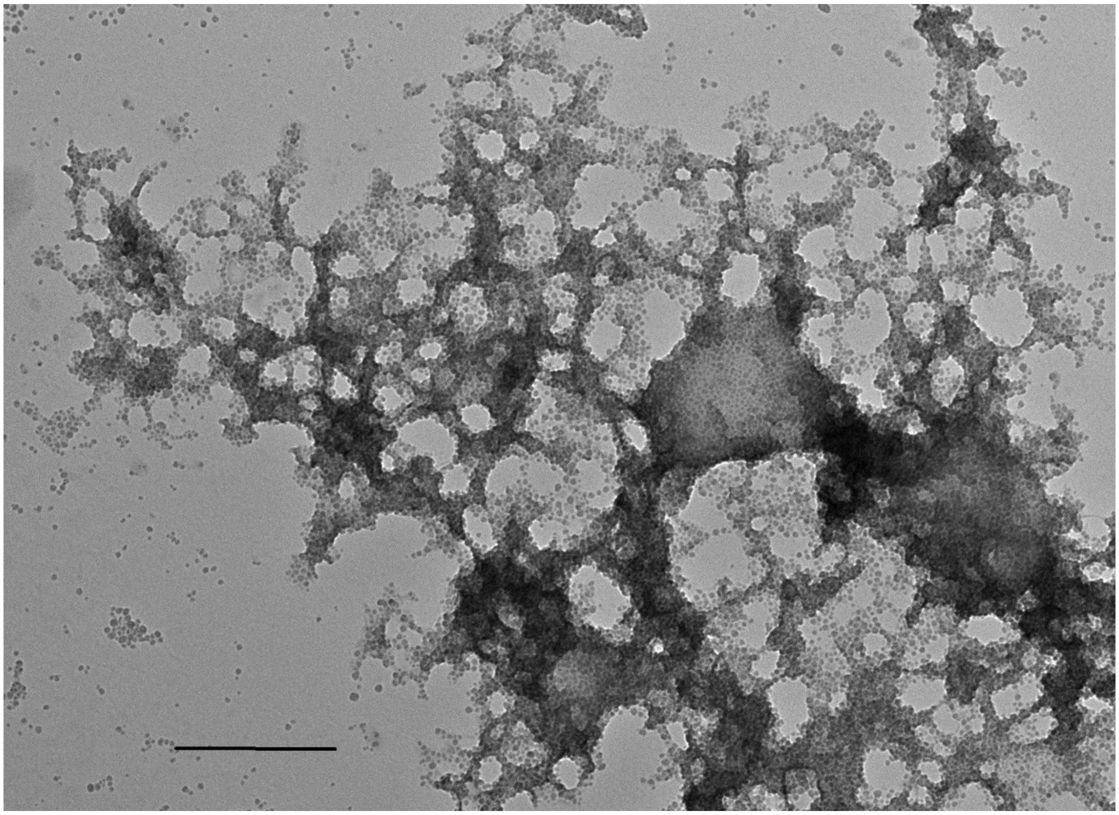


Figure S7. TEM of polymerization sample after 5h. Scale bar 500nm.

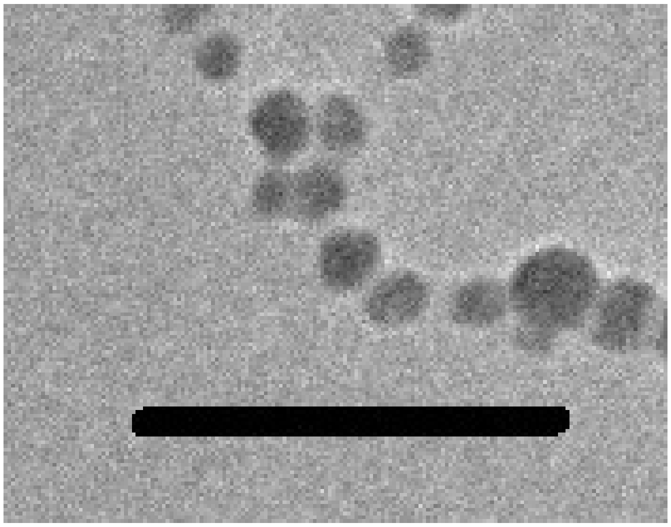


Figure S8. High magnification TEM nanoparticle strings. Scale bar 100nm.

References

1. A. Rungta, B. Natarajan, T. Neely, D. Dukes, L. S. Schadler and B. C. Benicewicz, *Macromolecules*, 2012, **45**, 9303-9311.