Electronic Supplementary Material (ESI) for Polymer Chemistry.

# Supporting Information

# One-pot Synthesis of Inorganic Nanoparticle Vesicles via Surface-initiated Polymerization-induced Self-assembly

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## Experimental Section

**Materials:** 2-Hydroxypropyl methacrylate (Mixture of hydroxypropyl and hydroxyisopropyl methacrylates) (TCI, 97%) 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 ethanol to make 10mM solution. All other reagents were used as received.

**Synthesis of PHPMA grafted silica nanoparticles.** 4-Cyanopentanoic acid dithiobenzoate (CPDB) anchored 15nm silica nanoparticles were prepared according to literature.[1] A solution of 2-Hydroxypropyl methacrylate (3.8 g), AIBN (266µl of 10mM solution in methanol), CPDB-anchored silica nanoparticles (1g, 23µmol/g) and DMF (8ml) 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 3 hours. The polymerization solution was quenched in an ice bath and poured into 1:1 mixture of diethyl ether and petroleum ether to precipitate the $SiO_2$-g-PHPMA nanoparticles. The $SiO_2$-g-PHPMA nanoparticles were redispersed in DMF and precipitated two more times to remove excess monomers and initiators.

**Chain End Deactivation of $SiO_2$-g-PHPMA.** 80mg (20 eq) solid AIBN was added to a solution of $SiO_2$-g-PHPMA in DMF and heated at 65°C for 1 hour. The resulting solution was poured into large amount of 1:1 mixture of diethyl ether and petroleum ether and centrifuged at 5000rpm for 5 min. The recovered $SiO_2$-g-PHPMA completely lost its original pink color and appeared to be white in color.

**Second RAFT Agent attachment to $SiO_2$-g-PHPMA.** $SiO_2$-g-PHPMA nanoparticles from the previous step were dispersed in ~15ml DMF, to which 20 µl of 3-aminopropyl(dimethyl)ethoxysilane 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-(PHPMA, CPDB) nanoparticles, which regained the characteristic pink color of the RAFT agent. Graft density was determined by measuring the UV-vis peak at 304 nm, and calculated from CPDB calibration curve. The TGA result was used to adjust calculation (60% weight percent silica in PHPMA grafted NPs). (It is worth noting that the added APTES will not react with hydroxyl groups on PHPMA chains. In a control experiment, free PHPMA 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-(PHPMA, CPDB) as macro chain transfer agent and stabilizer.** $SiO_2$-g-(PHPMA, CPDB) nanoparticles (0.143g, 70wt% silica), BzMA (0.42 g), ACVA (36µl of 10mM solution in ethanol) and ethanol (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 70°C. Aliquots of the reaction solution were withdrawn from the flask periodically since the beginning of polymerization. Grafted polymer chains were cleaved off from silica nanoparticles by reacting with excess amount of HF. Toluene was then used to selectively dissolve PBzMA for GPC analysis.

**Synthesis of PHPMA grafted silica nanoparticles.** A solution of methacrylic acid (2.6 g), AIBN (300µl of 10mM solution in methanol), CPDB-anchored silica nanoparticles (1g, 23µmol/g) and DMF (6ml) 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 2.5 hours. The polymerization solution was quenched in an ice bath and poured into diethyl ether to precipitate the $SiO_2$-g-PMAA nanoparticles. The $SiO_2$-g-PHPMA nanoparticles were redispersed in DMF and precipitated two more times to remove excess monomers and initiators.

**Surface-initiated RAFT polymerization of BzMA using $SiO_2$-g-(PMAA, CPDB) as macro chain transfer agent and stabilizer.** $SiO_2$-g-(PMAA, CPDB) nanoparticles (0.16g), BzMA (1.5 g), ACVA (86µl of 10mM solution in ethanol) and ethanol (20ml) 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 70°C. Aliquots of the reaction solution were withdrawn from the flask periodically since the beginning of polymerization. Grafted polymer chains were cleaved off from silica nanoparticles by reacting with excess amount of HF. Toluene was then used to selectively dissolve PBzMA for GPC analysis.

**Characterization.**

$^1H$ 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 consist 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. Infrared spectra were obtained using a BioRad Excalibur FTS3000 spectrometer. 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. Scanning electron microscopy (SEM) was performed by drop-casting 10 µl of diluted nanoparticle solution on copper grids with carbon film.

Table S1. Summary of reaction time, monomer conversions, GPC data, DLS data, and visual appearance obtained for a series of $SiO_2$-g-(PHPMA, PBzMA) nanoparticles.

| **Entry No.** | **Reaction Time (min)** | **BzMA Conversion (%)[a]** | **Bimodal polymer composition[b]** | **Mn of PBzMA (g/mol) [c]** | **Mw/Mn [d]** | **Hydrodynamic radius (nm)[e]** | **Visual appearance** |
|---|---|---|---|---|---|---|---|
| **180-0** | 0 | 0 | $PHPMA_{111}$ | N/A | N/A | 45.12 | Clear |
| **180-1** | 60 | 0.3 | $PHPMA_{111}$<br>$PBzMA_3$ | N/A | N/A | 51.46 | Clear |
| **180-2** | 90 | 1.1 | $PHPMA_{111}$<br>$PBzMA_{11}$ | 6500 | 1.07 | 54.15 | Clear |
| **180-3** | 120 | 2.2 | $PHPMA_{111}$<br>$PBzMA_{22}$ | 9100 | 1.09 | 171.3 | Slight Cloudy |
| **180-4** | 150 | 5.0 | $PHPMA_{111}$<br>$PBzMA_{50}$ | 11900 | 1.09 | 343.6 | Cloudy |
| **180-5** | 180 | 7.8 | $PHPMA_{111}$<br>$PBzMA_{78}$ | 14600 | 1.06 | 1740 | Cloudy |
| **180-6** | 210 | 9.2 | $PHPMA_{111}$<br>$PBzMA_{92}$ | 16900 | 1.09 | 2952 | Milky/Phase Separate |
| **180-7** | 280 | 10.6 | $PHPMA_{111}$<br>$PBzMA_{106}$ | 19500 | 1.13 | 2960 | Milky/Phase separate |

[a] Determined by $^1H$ NMR spectroscopy. [b] Determined by $^1H$ NMR spectroscopy. Assuming 100% RAFT agent efficiency. [c] Determined by size exclusion chromatography using PMMA as standard. [d] Determined by size exclusion chromatography. [e] Determined by dynamic light scattering. Z-average size reported for all samples.

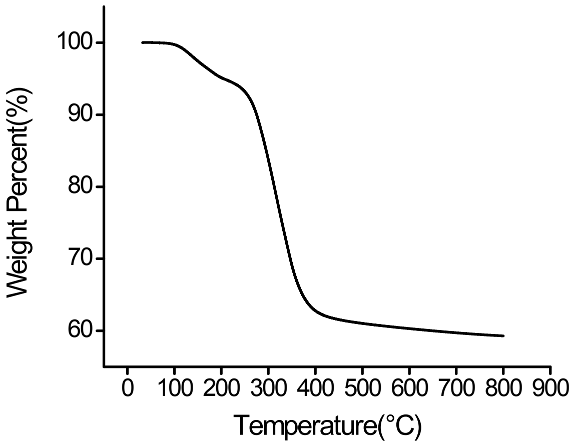
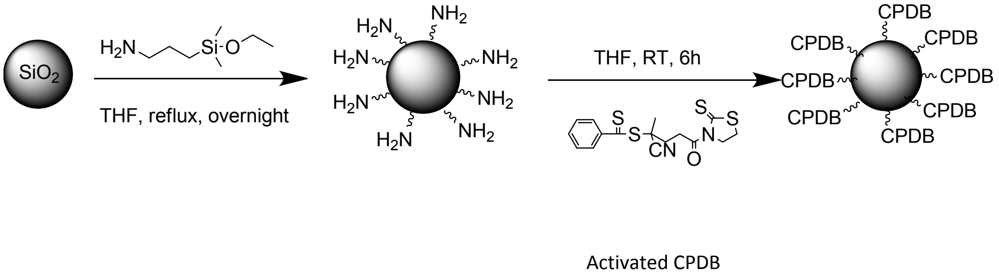


Figure S1. Thermal gravimetric analysis of $SiO_2$-g-(PHPMA, CPDB) NPs.

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



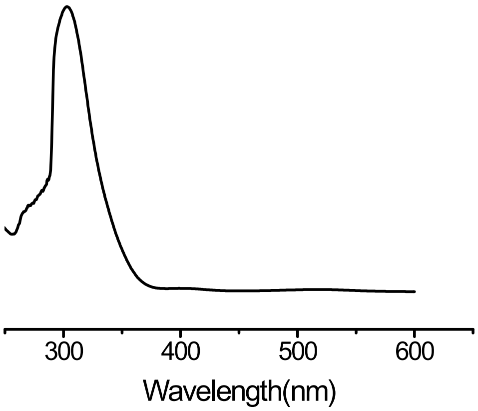


Figure S2. UV-vis analysis of $SiO_2$-g-[PHPMA, CPDB]

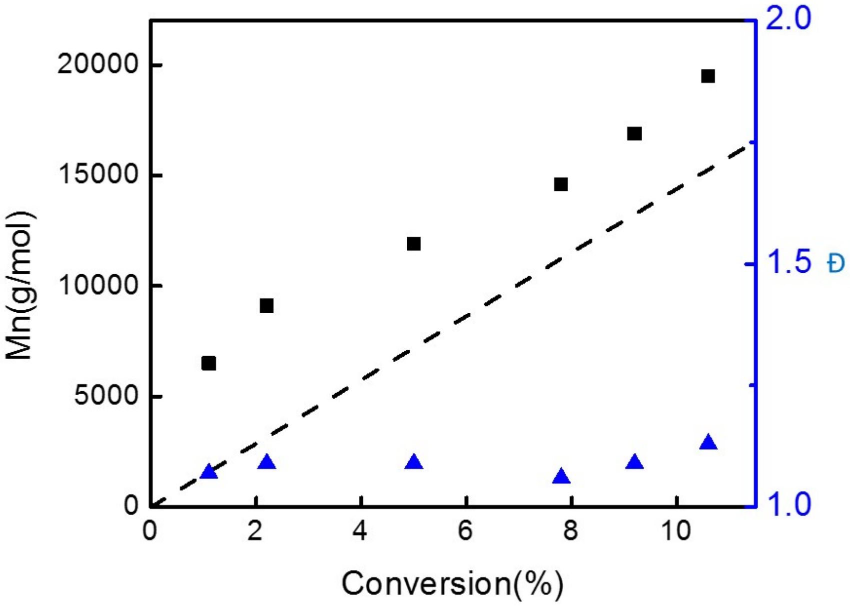


Figure S3. Molecular weight versus conversion and polydispersity for surface-initiated polymerization of BzMA from $SiO_2$-g-(PHPMA, CPDB) NPs at 70°C in ethanol.

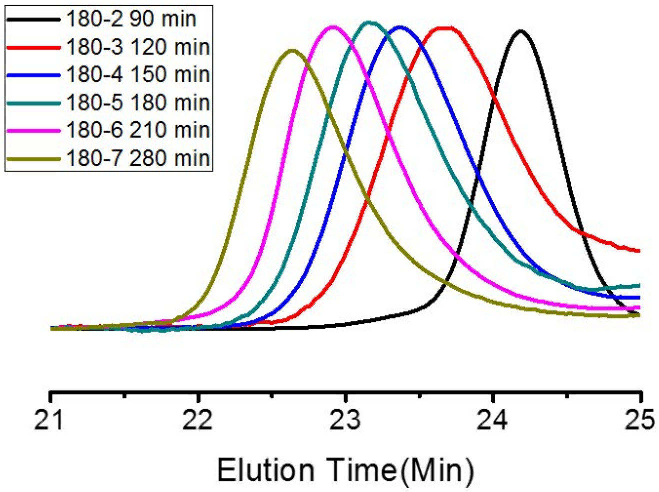
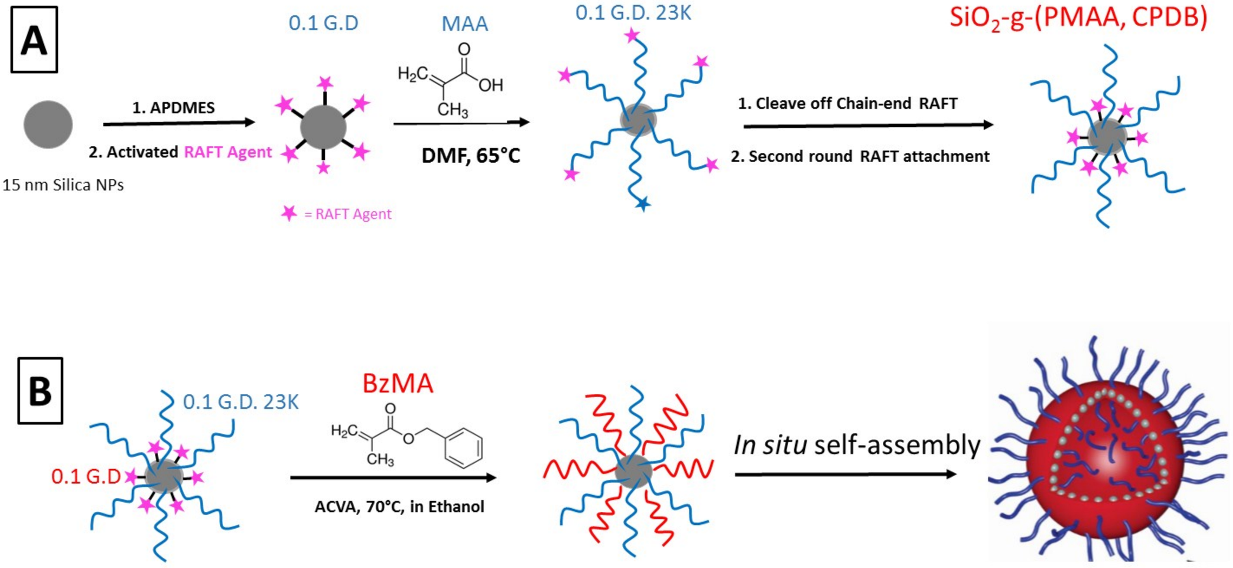


Figure S4. THF gel permeation chromatograms (vs poly (methyl methacrylate) standards) obtained from PBzMA chains cleaved-off from $SiO_2$-g-(PHPMA, PBzMA) NPs.

Scheme S2. (A) Synthesis of $SiO_2$-g-(PMAA, CPDB). (B) One-pot surface-initiated RAFT polymerization-induced self-assembly of grafted NPs into vesicles.



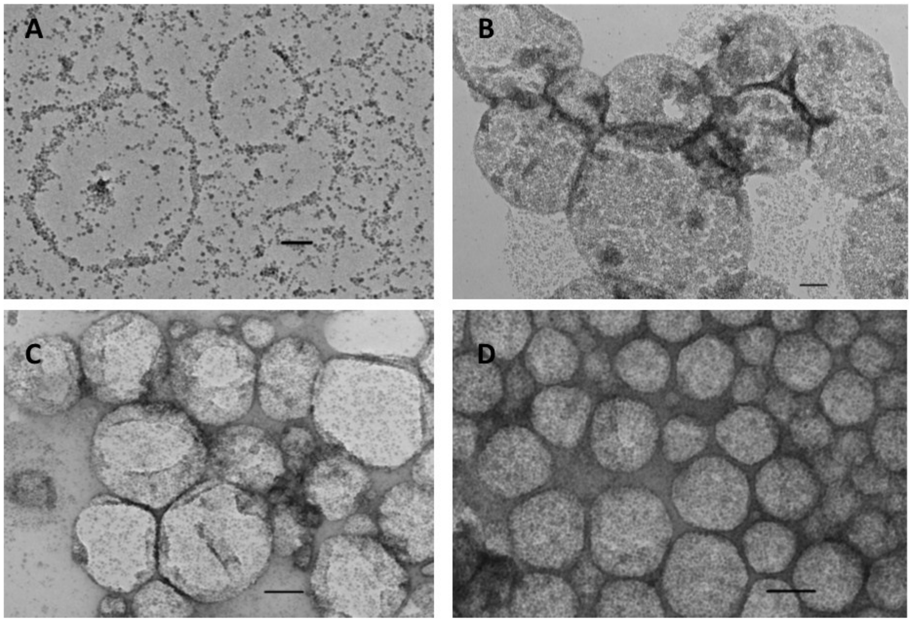


Figure S5. Representative TEM images of assembled structures from $SiO_2$-g-(PMAA, PBzMA) NPs with 23 kDa PMAA. All scale bars: 200nm.

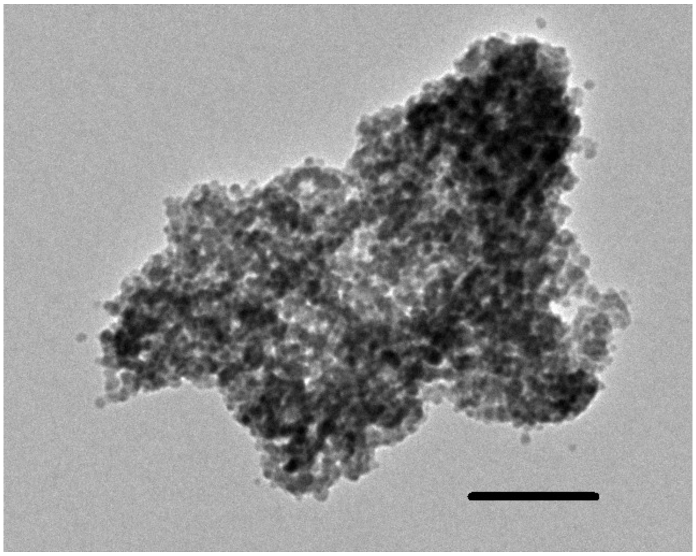


Figure S6. Representative TEM image of assembled structure from $SiO_2$-g-(PMAA, PBzMA) NPs with 5.8kDa PMAA. Scale bar: 200nm.