Supporting Information

One-Pot Synthesis of Robust Core/Shell Gold Nanoparticles

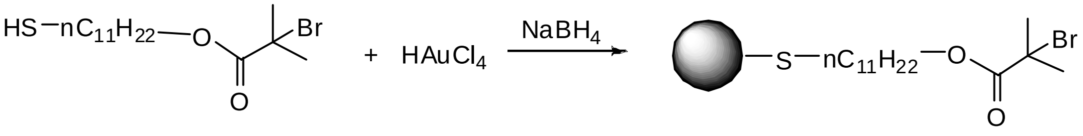
*Hongchen Dong, Manzhou Zhu, Jeong Ae Yoon, Haifeng Gao, Rongchao Jin, and Krzysztof Matyjaszewski**

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Experimental Section

Materials. The monomer, *n*-butyl acrylate (BA, Acros, 99%), and the crosslinker, ethylene glycol dimethacrylate (EGDMA, Aldrich, 98%), were purified twice by passing through a column filled with basic alumina to remove the inhibitor. The disulfide-based dimethacrylate, bis(2-methacryloyloxyethyl) disulfide (DSEDMA), was synthesized following a previously reported procedure.[1] Copper(I) bromide (Aldrich, 99%) was purified via several slurries in acetic acid, followed by filtration and washing with methanol and ethyl ether, and stored under nitrogen before use. All other reagents and solvents were purchased from Aldrich with the highest purity and used as received without further purification.

Synthesis of Initiator-Modified Gold Nanoparticles (Au-NPs). A thiol-capped polymerization initiator, 11-mercaptoundecyl 2-bromoisobutyrate ($Br(CH_3)_2COO(CH_2)_{11}SH$), **1**, was synthesized according to literatures.[2,3] Initiator-modified Au-NPs were directly prepared in the presence of compound **1** (Scheme S1). $HAuCl_4·3H_2O$ (79.3 mg, 0.201 mmol) and tetraoctylammonium bromide (TOAB, 228 mg, 0.417 mmol) were mixed with toluene (15 ml) in a 25 mL tri-neck round bottom flask. The solution was sonicated for 15 min to dissolve the $HAuCl_4 \cdot 3H_2O$. After the gold salt was completely dissolved, the solution was purged with dry N_2 for 30 min under constant magnetic stirring. Then, 205 mg of **1** (0.604 mmol, dissolved in 1 mL toluene) and 1 mL of aqueous solution of $NaBH_4$ (73 mg, 1.93 mmol, freshly made in ice-cold Nanopure water) were simultaneously added to the solution in a dropwise fashion within 15 min. The reaction was allowed to proceed for 3 h under nitrogen atmosphere before ethanol (60 mL) was added to the system to precipitate the Au-NPs. The turbid solution was allowed to stand on a bench overnight. The precipitate was collected and re-dispersed in toluene and precipitated again into ethanol. This precipitation and re-dispersion cycle was repeated twice before the pure Au- NPs (i.e. free of reaction byproducts) were obtained. The NPs were well dispersed in common organic solvents such as anisole, THF, and acetone without aggregation and the average diameter of the Au-NPs was about 5 nm.



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Scheme S1. Synthesis of Initiator-Modified Gold Nanoparticles (Au-NPs)

Synthesis of Initiator-Modified Silica NPs. The ATRP initiator-modified silica particles were used as a model system to explore the one-pot copolymerization reaction conditions for the Au-NP system. The procedures for the synthesis of 1-(chlorodimethylsilyl)propyl 2-bromoisobutyrate and the subsequent functionalization of the silica (30 % wt. silica in methyl isobutyl ketone, effective diameter D ~ 20 nm, MIBK-ST, Nissan) followed a previously described method.[4] Elemental analysis of the functionalized silica colloid confirmed the incorporation of bromine (2.84 wt%, 0.353 mmol of Br/g SiO_2).

Surface-Initiated ATRP from Silica NPs. In a typical ATRP of BA and EGDMA from the surface of silica NPs (Table 1, entry 1), the silica macroinitiator (SiO_2-Br, 50 mg, 0.0177 mmol), copper (II) bromide (0.79 mg, 3.54 μmol), ligand, *N,N,N',N",N"*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99 %) (16 μL, 0.0742 mmol), and 2.0 mL of anisole were added to a clean and dry Schlenk flask. After the solution became homogeneous, the monomer, BA (0.25 mL, 1.77 mmol), and the crosslinker, EGDMA (33 μL, 0.177 mmol), were added. The flask was sealed and deoxygenated by three freeze-pump-thaw cycles. During the final cycle the flask was filled with nitrogen and 10 mg (0.0706 mmol) of CuBr was added to the frozen mixture. The flask was sealed with a glass stopper then evacuated and back-filled with nitrogen four times before it was immersed in a thermostated oil bath at 65 ^{o}C. After 28 h, the conversion of EGDMA and BA reached 68% and 24%, respectively (Figure S1), when 2.3 mL of N_2-bubbled BA (15.9 mmol) was added to the reaction solution. At 73 h, 0.1 mL of tin(II) 2-ethylhexanoate ($Sn(EH)_2$, Aldrich, ~ 95%)/anisole solution (0.141 M) was added to the reaction. Samples were taken at timed intervals and analyzed by ^{1}H-NMR to determine the conversions of BA and EGDMA. The polymerization was stopped at 117 h by opening the flask and exposing the catalyst to air.

After polymerization, the polymer layer was cleaved from the particle surface by etching the silica NPs with an aqueous HF solution. The obtained grafted polymer layer was analyzed by THF GPC with linear polystyrene as standards.

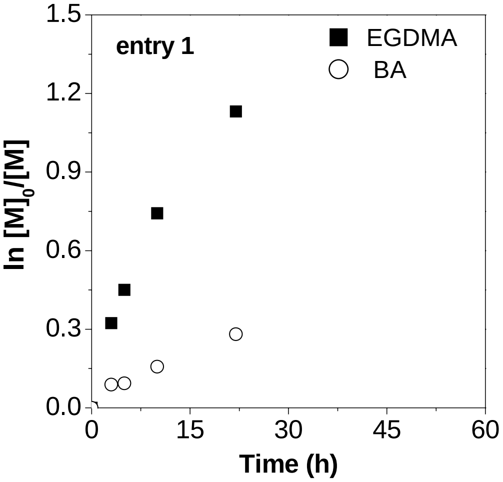

Figure S1. Semilogarithmic plot during the surface-initiated ATRP of BA and EGDMA from silica NPs before the addition of the second batch of BA monomer (Table 1, entry 1).

When a disulfide-based dimethacrylate crosslinker, DSEDMA, was used for copolymerization with BA under similar conditions, a hybrid silica NP with degradable polymer layer was obtained (Table 1, entry 2). Dynamic light scattering (DLS) measurements of the modified silica NPs in THF showed that the hydrodynamic diameter of the NPs before the second monomer addition was 67.9 ± 3.5 nm, and increased to 172.6 ± 5.9 nm before the polymerization was stopped (Figure S2). Since the diameter of silica NP was ca. 20 nm, the thickness of the crosslinked polymer shell was estimated to be 23.8 nm, and the linear polymer chain to be 52.4 nm. The cross-linked polymer shell could be degraded into linear polymers in the presence of tri-*n*-butylphosphine (*n*-Bu_3P, Aldrich, 97%) in tetrahydrofuran (THF) at room temperature for 10 h.

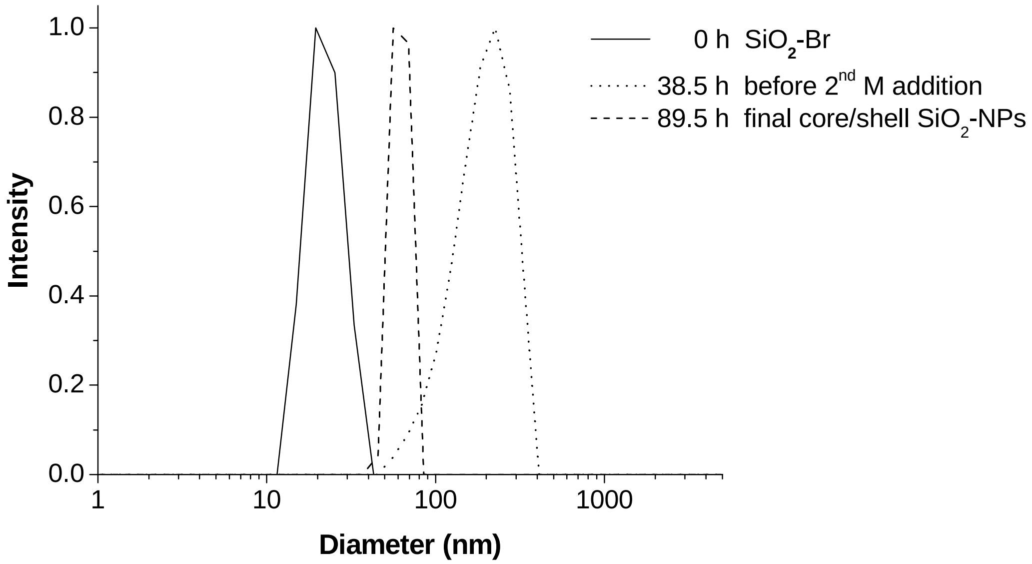

Figure S2. Hydrodynamic diameter distribution of the polymer/silica nanocomposites at varied reaction time, determined by DLS using CONTIN function (Table 1, entry 2).

Surface-Initiated ATRP from Au-NPs. The optimized experimental conditions from the one-pot synthesis of silica-polymer hybrid NPs were extended to the synthesis of Au-NPs with a crosslinked polymer shell and well-defined tethered polymer brushes. In a typical reaction (Table 1, entry 3), the initiator-modified Au-NPs (5.0 mg, 0.0053 mmol), $CuBr_2$ (0.23 mg, 1.05 μmol), and CuBr (3.0 mg, 0.0213 mmol) were added to a 10 mL Schlenk flask. The flask was thoroughly purged by vacuum and flushed with nitrogen before N_2-purged anisole (0.6 mL), PMDETA (4.6 μL, 0.0222 mmol), BA (76 μL, 0.530 mmol) and EGDMA (10.0 μL, 0.053 mmol) were sequentially added to the flask via syringe. The reaction mixture was homogenized by agitation on a vortex mixer for 5 min and the sealed flask was placed in a thermostated oil bath at 65 ^{o}C. Within 1 h, a color change from brown to purplish red was observed. This could be attributed to the dissociation of some initiator molecules from the Au NP surface, resulting in the coalescence and/or outright crystal growth of some NPs. At 24 h, 2.27 mL N_2-bubbled BA (15.9 mmol) was added to the reaction solution. Samples were taken at timed intervals and analyzed by ^{1}H-NMR to measure the conversions of BA and EGDMA. The polymerization was stopped at 43.5 h by opening the flask and exposing the catalyst to air. The polymer-modified Au-NPs were purified by precipitation into cold methanol several times, yielding sticky dark purple solid.

TEM image (Figure S3) of the core/shell Au NPs shows some clusters (< 30 %) with diameter about 15-25 nm. The polymerization was performed at 65 ^{o}C to achieve an appropriate polymerization rate. At this temperature, the initiator layer on Au NP was not stable and some coalescence occurred concurrently with the shell crosslinking reaction at the beginning of the polymerization, resulting in the initial color change of the reaction mixture. The coalescence was prevented after the formation of crosslinked polymer shell. The stabilized Au NPs with initiating sites on the surface further served as macroinitiators for polymerization of the remaining BA monomer and formed the brush with dangling PBA chains. AFM image in Figure S4 shows the thickness of the polymer layer (including the crosslinked shell and linear polymer brushes) on Au NPs about 35 nm. TGA analysis of the core/shell Au NPs indicates the weight fraction of polymers in the hybrid Au nanocomposites around 79 wt%, which could include some free polymer chains grown from the initially detached initiators (Figure S5).

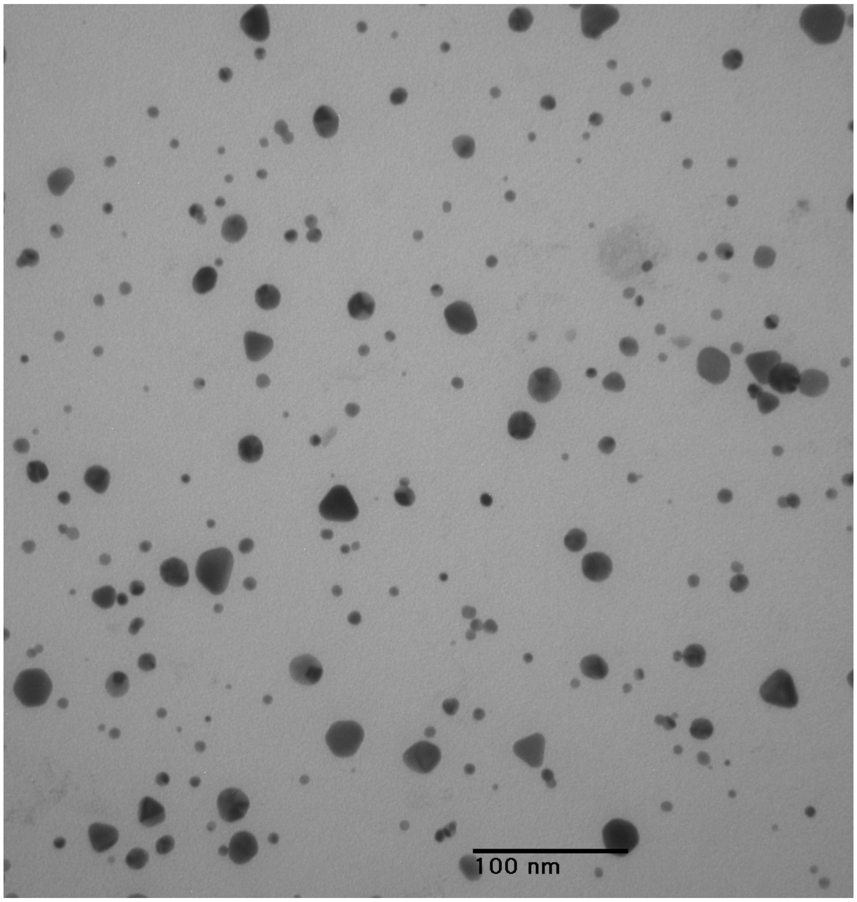

Figure S3. TEM image of robust gold NPs with cross-linked shell and dangling polymer hairs (Table 1, entry 3).

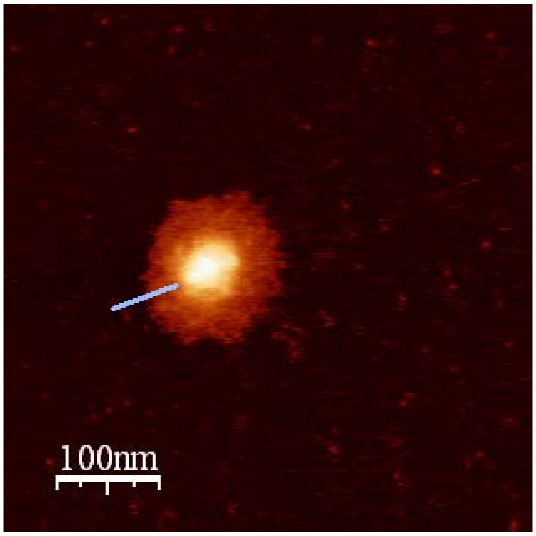

Figure S4. AFM images of robust gold NPs with cross-linked shell and dangling polymer hairs (Table 1, entry 3).

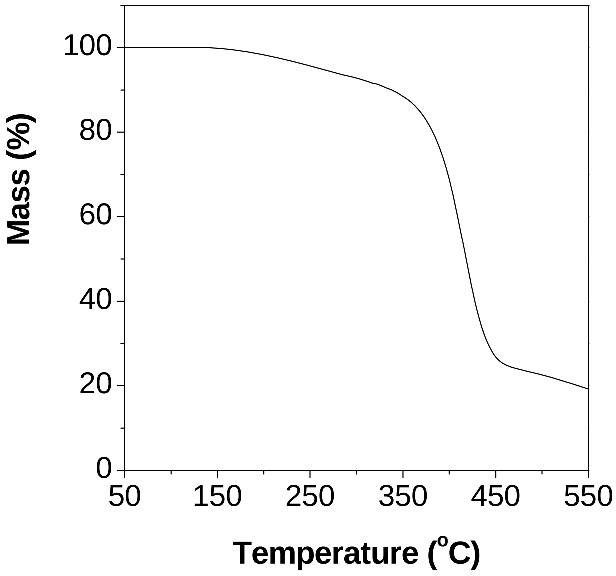

Figure S5. TGA curve of the robust gold NPs with and dangling polymer brush (Table 1, entry 3).

The Au-NPs modified with linear PBA brushes without cross-linked shell was synthesized via surface-initiated ATRP of BA with gold macroinitiator (Table 1, entry 4). The initiator-modified Au-NPs (5.0 mg, 0.0053 mmol), $CuBr_2$ (0.23 mg, 1.05 μmol), and CuBr (3.0 mg, 0.0213 mmol) were added to a 10 mL Schlenk flask. The flask was thoroughly purged by vacuum and flushed with nitrogen before nitrogen-purged anisole (0.6 mL), PMDETA (4.6 μL, 0.0222 mmol) and BA (2.27 mL, 15.9 mmol) were added to the flask via syringe. The reaction mixture was homogenized by agitation on a vortex mixer for 5 min and the sealed flask was placed in a thermostated oil bath at 65 ^{o}C. A color change from brown to purplish red was observed within the first hour. Samples were taken at timed intervals and analyzed by ^{1}H-NMR to measure the conversion of BA. At 27 h, the polymerization was stopped with 6.9% BA conversion by opening the flask and exposing the catalyst to air. The polymer-modified Au-NPs were purified by precipitation into cold methanol several times, yielding dark purple oil.

Analyses. Conversion of monomer and crosslinker were determined by ^{1}H NMR in $CDCl_3$ on a Bruker AM 300 MHz spectrometer at 27 ^oC. The cleaved polymers were separated by gel permeation chromatography (GPC) equipped with an autosampler (Waters, 717 plus), HPLC pump with THF as eluent at 1 mL/min (Waters, 515) and four columns (guard, 10^5 Å, 10^3 Å, 100 Å; Polymer Standards Services) in series. Toluene was used as internal standard. The apparent molecular weights and polydispersities (M_w/M_n) were determined with a calibration based on linear polystyrene standards using WinGPC 6.0 software from PSS. Bromine content in the initiator-modified NPs was determined using elemental analysis by Midwest Microlab, LLC. Thermogravimetric analysis (TGA) experiments were performed with samples placed in aluminum pans, using Polymer Laboratories TG1000 instrument operating in the 20-580 °C temperature range, under nitrogen, at a heating rate of 20 °C/min. Transmission electron microscopy (TEM) images were measured using a JEOL 200EX instrument operated at 200 kV. For TEM imaging, samples were dispersed in THF and deposited on carbon-coated copper grids. The particle size and size distribution were measured by dynamic light scattering (DLS) on a model HP5001 high-performance particle sizer from Malvern Instruments, Ltd. The sizes are expressed as $D_{av} \pm S$ (average diameter ± standard deviation). UV-vis spectra were recorded on a Varian Cary 5000 UV-vis-NIR spectrophotometer using a 1 cm-wide glass cuvette. Tapping mode atomic force microscopy (AFM) experiments were carried out using a Multimode Nanoscope III system (Digital Instruments, Santa Barbara, CA). The polymer-modified Au-NPs were suspended in chloroform (5 μg/mL). One drop of the suspension was deposited onto freshly cleaved mica surface, and the samples were dried under ambient condition overnight. The measurements were performed in air using commercial Si cantilevers with a nominal spring constant and resonance frequency respectively equal to 5 N/m and 130 kHz. The height and phase images were acquired simultaneously at set-point ratio A/A_o=0.7~0.9, where A and A_o refer to the "tapping" and "free" cantilever amplitude, respectively.

References

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