Supporting Information

Enhancing Initiation Efficiency in Metal-free Surface-initiated Atom Transfer Radical Polymerization (SI-ATRP)

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EXPERIMENTAL PROCEDURES

Materials

Methyl methacrylate (MMA, Aldrich, 99%) was purified by passing through a basic alumina column before use. *N*,*N*-dimethylacetamide (DMA, Aldrich, 99%), methanol (EMD, 99.8%), tetrahydrofuran (THF, EMD, 99.5%), ethyl ether (Fisher, 99%), toluene (Aldrich, 99.8%), ethanol (EMD, 94.9-96.0%), 48 wt % aqueous hydrofluoric acid (HF, Aldrich, 99.99%), ammonium hydroxide (Fisher, 28.0-30.0%), allyl alcohol (Aldrich, 99%), 5-hexen-1-ol (Aldrich,

98%), triethylamine (TEA, Aldrich, 99.5%), 2-bromoisobutyryl bromide (2BiB, Aldrich, 98%) α-bromophenylacetic acid (Aldrich, 98%), *N*,*N*'-dicyclohexylcarbodiimide (DCC, Aldrich, 99%), 4-(*N*,*N*-dimethylamino)pyridine (DMAP, Aldrich, 99%), platinum(0)-1,3-divinyl-1,1,3,3-tetramethylsiloxane complex in xylene (Karstedt's catalyst, Aldrich, 2% Pt), chlorodimethylsilane (Aldrich, 98%), triethoxysilane (Aldrich, 95%), hexamethyldisilazane (HMDZ, Aldrich, 99%) were used as received unless otherwise stated. Methylene chloride (DCM, Fisher, 99.5%) was treated with calcium hydride and distilled to remove water. Dry THF was collected from a SciMatCo solvent purification system. 10-Phenylphenothiazine was synthesized according to a reported literature procedure.[1] Silica nanoparticles (SiO_2) 30 wt % dispersion in methyl isobutyl ketone (MIBK-ST) and isopropanol (IPA-ST-ZL), with effective radius 7.9 nm and 56.6 nm, respectively, measured by transmission electron microscope (TEM), were kindly donated by Nissan Chemical America Corp.

Characterization

Number-average molecular weight (M_n) and dispersity (M_w/M_n) were determined by size exclusion chromatography (SEC). Polymer-grafted nanoparticles were dispersed in THF and treated with HF before analysis in SEC. The SEC was conducted with a Waters 515 pump and Waters 410 differential refractometer using PSS columns (Styrogel 105, 103, 102 Å) in THF as an eluent at 35 °C and at a flow rate of 1 mL min^{-1}. Linear PMMA standards were used for calibration. ^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy was performed on a Bruker Advance 300 MHz spectroscope with $CDCl_3$ as solvent. Conversion was calculated by following the decrease of the monomer peak area relative to the peak areas of methoxy proton. Dynamic light scattering (DLS) measurements were performed on a Malvern Zetasizer Nano ZS at 25 °C

with THF as dispersant. Thermogravimetric analysis (TGA) was performed on a TA Instrument TGA 2950 and the data was processed with TA Universal Analysis software. The heating procedure involved four steps: (1) ramp at 20 °C/min to 120 °C; (2) isotherm at 120 °C for 20 min; (3) high-resolution ramp at 20 °C/min to 800 °C; (4) isotherm at 800 °C for 10 min. The organic contents of the samples were normalized to the weight loss between 120 °C and 800 °C.

The graft densities were calculated using the following equation:

$$\sigma_{\mathrm{TGA}} = \frac{(1 - f_{\mathrm{SiO_2}}) N_A \, \rho_{\mathrm{SiO_2}} d}{6 \, f_{\mathrm{SiO_2}} \, M_{\mathrm{n}}} \qquad \text{(S1)}$$

The value for $f_{\mathrm{SiO_2}}$, in the equation, is the silica fraction measured by TGA after exclusion of any residual solvent; N_{A} is the Avogadro number; $\rho_{\mathrm{SiO_2}}$ is the density of silica NPs; d is the average diameter of silica NPs; M_{n} is the number average MW of polymer brushes. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed on an Applied Biosystem Voyager DE-STR MALDI-TOF mass spectrometer with α-cyano-4-hydroxycinnamic acid (4HCCA) as matrix. Ultraviolent-visible-near infrared (UV-Vis-NIR) spectroscopy was performed on a Varian Cary 5000 spectrophotometer with DMA as reference. The scanning rate was 300 nm/min. Transmission electron microscopy (TEM) was performed using a JEOL EX2000 electron microscope operated at 200 kV. Images were taken by amplitude and phase contrast using a Gatan Orius SC600 high resolution camera. Elemental analysis was performed via Schoniger Combustion by Midwest Microlab, Inc (Indianapolis, USA).

Synthesis of tetherable initiators

BiB-based tetherable initiators were synthesized using modified procedures previously reported in the literature.[2]

3-(Chlorodimethylsilyl)propyl 2-bromoisobutyrate (BiBSiCl). 18.6 mL (273 mmol) of allyl alcohol and 38.1 mL (273 mmol) of TEA were dissolved in 100 mL of dry THF in a round bottom flask and cooled down to 0 ºC in an ice bath. 27.0 (218 mmol) mL of 2BiB was diluted with 50 mL of dry THF. The 2BiB solution was added dropwise to the reaction solution over 30 min while the reaction was stirred in the ice bath. The reaction mixture was then stirred at room temperature overnight. The resulting suspension was filtered and the residue washed with THF. The filtrate was diluted with 200 mL of ethyl ether and washed three times with deionized (DI) water, once with saturated $NaHCO_3$ solution and once with brine. The organic solution was dried over anhydrous Na_2SO_4. Upon removal of solvents *in vacuo*, allyl 2-bromoisobutyrate was obtained as a slightly yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.94 (ddt, J = 17.3, 10.5, 5.6 Hz, 1H), 5.39 (dq, J = 17.3, 1.5 Hz, 1H), 5.27 (dq, J = 10.5, 1.5 Hz, 1H), 4.67 (dt, J = 5.5, 1.4 Hz, 2H), 1.95 (s, 6H) ppm.

30.0 g (145 mmol) of allyl 2-bromoisobutyrate and 94.4 mL (869 mmol) of chlorodimethylsilane were mixed in a round bottom flask sealed with a rubber septum. The flask was placed in an ice bath and dry nitrogen was bubbled through the solution for 10 min. 1.2 mL of Karstedt's catalyst solution was added dropwise to the purged solution then the reaction solution was stirred for two days after returning to room temperature. Conversion was monitored by ^{1}H NMR. Unreacted silane was removed by rotary evaporation. The platinum catalyst was precipitated when the crude product was cooled down to -18 ºC, and was removed via filtration through a 450 nm PTFE syringe filter. The product was obtained as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.18 (t, J = 6.7 Hz, 2H), 1.94 (s, 6H), 1.86-1.78 (m, 2H), 0.93-0.83 (m, 2H), 0.44 (s, 6H) ppm.

6-(Triethoxysilyl)hexyl 2-bromoisobutyrate (BiBSiOEt). 4.9 mL (40 mmol) of 5-hexen-1-ol and 7.0 mL (50 mmol) of TEA were dissolved in 50 mL of dry THF in a round bottom flask then

cooled down to 0 ºC by immersion in an ice bath. 5.0 mL (40 mmol) of 2BiB was added dropwise to the solution over 30 min at 0 ºC. The reaction mixture was stirred at room temperature overnight. The resulting suspension was centrifuged and washed with ethyl ether. The resulting solution was washed once with 1M HCl, twice with saturate $NaHCO_3$ solution, and once with brine. The organic phase was dried over anhydrous Na_2SO_4. 5-hexen-1-yl 2-bromoisobutyrate was obtained upon removal of solvents *in vacuo* as a slightly yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.80 (ddt, J = 17.0, 10.3, 6.6 Hz, 1H), 5.07-4.93 (m, 2H), 4.14 (t, J = 3.4 Hz, 2H), 2.11-2.01 (m, 2H), 1.89 (s, 6H), 1.68-1.57 (m, 2H), 1.50-1.38 (m, 2H) ppm.

2.1 g (8.0 mmol) of 5-hexen-1-yl 2-bromoisobutyrate and 10 mL (53 mmol) of triethoxysilane were dissolved in 20 mL of toluene. Dry nitrogen was bubbled through the solution for 10 min after the flask was placed in an ice bath. 0.1 mL of Karstedt's catalyst solution was added to the reaction and the contents were allowed to return to room temperature and stirred for two days. Conversion was monitored by ^{1}H NMR. Toluene and unreacted silane were removed by rotary evaporation followed by distillation *in vacuo*. The platinum catalyst was precipitated as the crude product was cooled down to -18 ºC, and was removed via filtration through a 450 nm PTFE syringe filter. The product was obtained as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.11 (t, J = 6.5 Hz, 2H), 3.79 (q, J = 7.0 Hz, 6H), 1.87 (s, 6H), 1.72-1.53 (m, 4H), 1.38-1.28 (m, 4H), 1.17 (t, J = 7.0 Hz, 9H), 0.57 (t, J = 7.9 Hz, 2H) ppm.

6-(Chlorodimethylsilyl)hexyl 2-bromo-2-phenylacetate (BPASiCl). 6.8 mL (57 mmol) of 5-hexen-1-ol, 10 g (47 mmol) of α-bromophenylacetic acid, and 0.51 g (4.2 mmol) of DMAP were dissolved in 134 mL of dry DCM in a round bottom flask. 10.7 g (52 mmol) of DCC was dissolved in 40 mL of dry DCM. Both of the solutions were cooled down to 0 ºC in an ice bath. The DCC solution was then injected dropwise in the reaction flask over 30 min. The reaction was stirred at room temperature for 24 h followed by filtration and washing the solids with

DCM. The filtrate was concentrated with rotary evaporation to give the crude product. The crude product was purified via silica column chromatography eluted with 30:1 (v/v) hexane-ethyl acetate mixture. Upon removal of the solvent, 5-hexen-1-yl 2-bromo-2-phenylacetate was attained as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.64-7.51 (m, 2H), 7.44-7.31 (m, 3H), 5.78 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.37 (s, 1H), 5.08-4.91 (m, 2H), 4.21 (td, *J* = 6.6, 1.7 Hz, 2H), 2.07 (qt, *J* = 7.0, 1.4 Hz, 2H), 1.82 – 1.19 (m, 4H) ppm.

6.1 g (22 mmol) of 5-hexen-1-yl 2-bromo-2-phenylacetate and 4.8 mL (44 mmol) of chlorodimethylsilane were mixed and the solution was bubbled with dry nitrogen for 5 min while cooled in an ice bath. 0.2 mL of Karstedt's catalyst solution was added into the reaction solution and the flask allowed to warm up to room temperature then it was stirred for five days. Conversion was monitored by ^{1}H NMR. Toluene and unreacted silane were removed by rotary evaporation followed by distillation *in vacuo*. The platinum catalyst precipitated when the crude product was cooled down to -18 ºC, and was removed via filtration through a 450 nm PTFE syringe filter. The product was a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.63-7.49 (m, 2H), 7.41-7.31 (m, 3H), 5.35 (s, 1H), 4.17 (td, *J* = 6.6, 1.2 Hz, 2H), 1.73-1.57 (m, 2H), 1.48-1.23 (m, 6H), 0.83-0.70 (m, 2H), 0.40 (s, 6H) ppm.

The hydrosilylation between chlorodimethylsilane and allyl 2-bromo-2-phenylacetate had no conversion. Mass spectroscopy (MS) of the reaction solution was performed to understand the side reaction and facilitate our design of tetherable initiators. An M^+ signal with typical platinum isotope distribution and 100% abundance at m/z = 424 was observed.

6-(Triethoxysilyl)hexyl 2-bromo-2-phenylacetate (BPASiOEt). 5.0 g (17 mmol) of 5-hexen-1-yl 2-bromo-2-phenylacetate and 9.3 mL (50 mmol) of triethoxysilane were dissolved in 10 mL of dry toluene then the solution was bubbled with dry nitrogen for 5 min while cooled in an ice bath. 0.2 mL of Karstedt's catalyst solution was added into the reaction and after returning to

room temperature, the solution was stirred for five days. Conversion was monitored by ^{1}H NMR. Toluene and unreacted silane were removed under rotary evaporation followed by distillation *in vacuo*. The platinum catalyst precipitated as the crude product was cooled down to -18 ºC, and was removed via filtration through a 450 nm PTFE syringe filter. The product was obtained as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.60-7.48 (m, 2H), 7.41-7.30 (m, 3H), 5.34 (s, 1H), 4.17 (td, J = 6.7, 1.9 Hz, 2H), 3.81 (q, J = 7.0 Hz, 6H), 1.73-1.30 (m, 8H), 1.22 (t, J = 6.8 Hz, 9H), 0.67-0.52 (m, 2H) ppm.

Surface modification

16 nm silica nanoparticles. Dry nitrogen was bubbled through 10 mL of a dispersion of the silica particles (sample MIBK-ST) for 5 min then 1.5 mL of chlorodimethylsilane (**BiBSiCl** or **BPASiCl**) was slowly injected into the dispersion. The reaction was stirred at 60 ºC for 24 h then the flask was cooled down to room temperature and 1.1 mL (5.4 mmol) of HMDZ was slowly injected to the reaction. The pale brown dispersion was stirred at 35 ºC for another 12 h. The modified nanoparticles were dialyzed against methanol three times and acetone twice.

120 nm silica nanoparticles. 2.5 mL of silica particle dispersion (IPA-ST-ZL) was solvent-exchanged into 10 mL of ethanol via three centrifuge-dispersion cycles. A solution of 4.0 mL of ammonium hydroxide dissolved in 37 mL of ethanol was added dropwise to the dispersion. The reaction was stirred at 40 ºC for 2 h then 1.0 g of triethoxysilane (**BiBSiOEt** or **BPASiOEt**) dissolved in 3 mL of ethanol was added dropwise to the reaction. The reaction was stirred at 40 ºC for another 12 h. The dispersion was centrifuged at RCF = 4000 G to remove the solvents and base then the solids were dispersed again into ethanol. The particle dispersion was dialyzed against ethanol three times.

Total initiator densities were measured with elemental analysis after surface modification. The results are shown in Table S1. Apparently larger density for 120 nm particles / BiBSiOEt could be due to a multilayer formation but the error in Br elemental analysis is 0.3%.

Table S1. Elemental analysis and total initiator densities of surface-modified silica nanoparticles

Entry	Initiator	Particle size (nm)	Detected Br (wt %)	Br content (mmol/g)	Br density (nm^{-2})
1	**BiBSiOEt**	120	1.01	0.126	2.9
2	**BPASiOEt**	120	0.32	0.040	0.92
3	**BiBSiCl**	16	2.14	0.268	0.93
4	**BPASiCl**	16	1.97	0.247	0.86

Metal-free SI-ATRP

16 nm silica nanoparticles. 0.20 g of initiator-modified silica particles (containing 58 μmol of accessible initiation sites, assuming 0.5 accessible initiation sites per nm^2 of surface) and 1.6 mg (5.8 μmol) or 8.0 mg (20 μmol) of PhPTZ were dispersed in a mixture of 3.1 mL (29 mmol) of MMA and 3.1 mL of DMA. The reaction mixture was degassed by nitrogen purging for 15 min then the reaction mixture was irradiated with a 4.9 mW/cm^2 MelodySusie® UV lamp at 365 nm. Samples were taken from the reaction at desired time intervals. Reactions were terminated by exposure to air in the dark and addition of 5 mL of THF when the 10 mm×5 mm oval rare earth extra power stir bar (Sigma-Aldrich) powered with an IKA RET Basic stirring plate stopped moving. The final product was collected by precipitation in methanol.

120 nm silica nanoparticles. 0.75 g initiator-modified silica particles (containing 44 μmol of accessible initiation sites when assuming ~1 accessible initiation sites per nm^2 of surface) and 1.2 mg (4.5 μmol) of PhPTZ were dispersed in a mixture of 2.4 mL (22 mmol) of MMA and 2.4 mL of DMA. The reaction was degassed by nitrogen purging for 10 min then the reaction

mixture was irradiated with the same 4.9 mW/cm^2 MelodySusie® UV lamp. Samples were taken from the reaction at desired time intervals. Reactions were terminated by exposure to air in the dark and addition of 5 mL of THF when the 10 mm×5 mm oval rare earth extra power stir bar stopped moving. The final product was collected by precipitation in methanol.

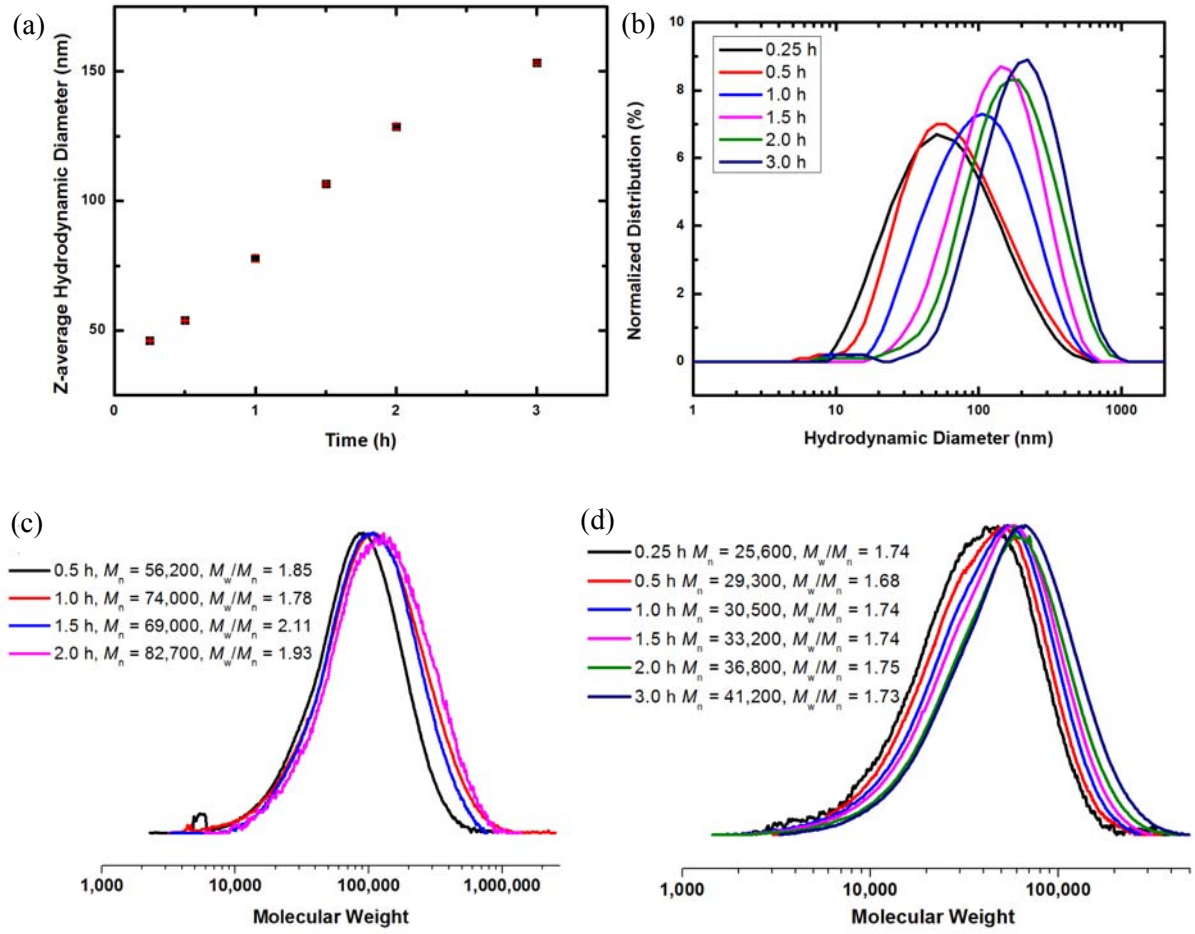

Figure S1. Evolution of z-average hydrodynamic diameters (a) and size distributions by intensity (b) of 16 nm silica nanoparticles modified with **BPASiCl** grafted with PMMA (**Error! Reference source not found.** entry 4) in THF measured with DLS. The integrated size distributions were normalized to 100%. (c, d) SEC traces of metal free SI-ATRP from 16 nm silica nanoparticle modified with **BPASiCl** (c) and **BiBSiCl** (d). Molecular weight calibration with linear PMMA standards, toluene as internal standard. Reaction conditions: [SiO_2-Br, ~1 Br/nm^2]$_0$:[MMA]$_0$:[PhPTZ]$_0$ = 1:500:0.1; DMA = 50 vol%; UV irradiation at 365 nm, room temperature.

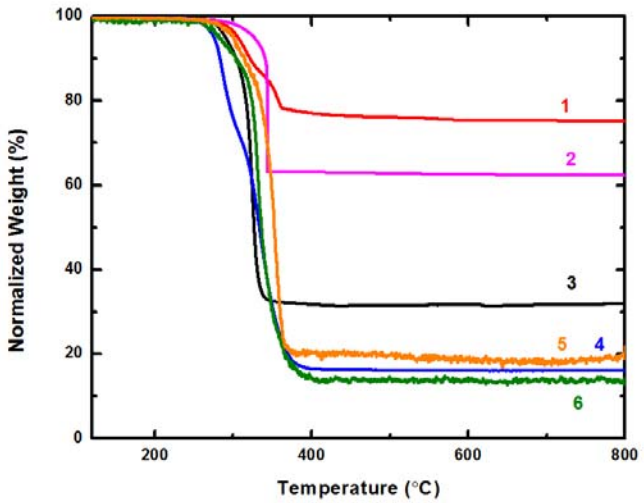

Figure S2. TGA plots of 5 final samples from **Table 1** and **Table S1**. All weights normalized to 100% after isotherm at 120 ºC.

Table S2. Inorganic fraction in final samples and corresponding graft densities.

Entry	Initiator	Particle size (nm)	$[PhPTZ]_0/[MMA]_0$ (ppm)	Final conversion	M_n	Inorganic fraction	σ (nm^{-2})
1	**BiBSiOEt**	120	200	6.4%	1.12×10^5	75.2%	0.03
2	**BPASiOEt**	120	200	18%	9.20×10^4	62.3%	0.15
3	**BiBSiCl**	16	200	16%	8.27×10^4	32.1%	0.09
4	**BPASiCl**	16	200	36%	4.70×10^4	16.0%	0.39
5	**BiBSiCl**	16	1000	31%	3.60×10^4	20.3%	0.38
6	**BPASiCl**	16	1000	57%	3.65×10^4	13.3%	0.60

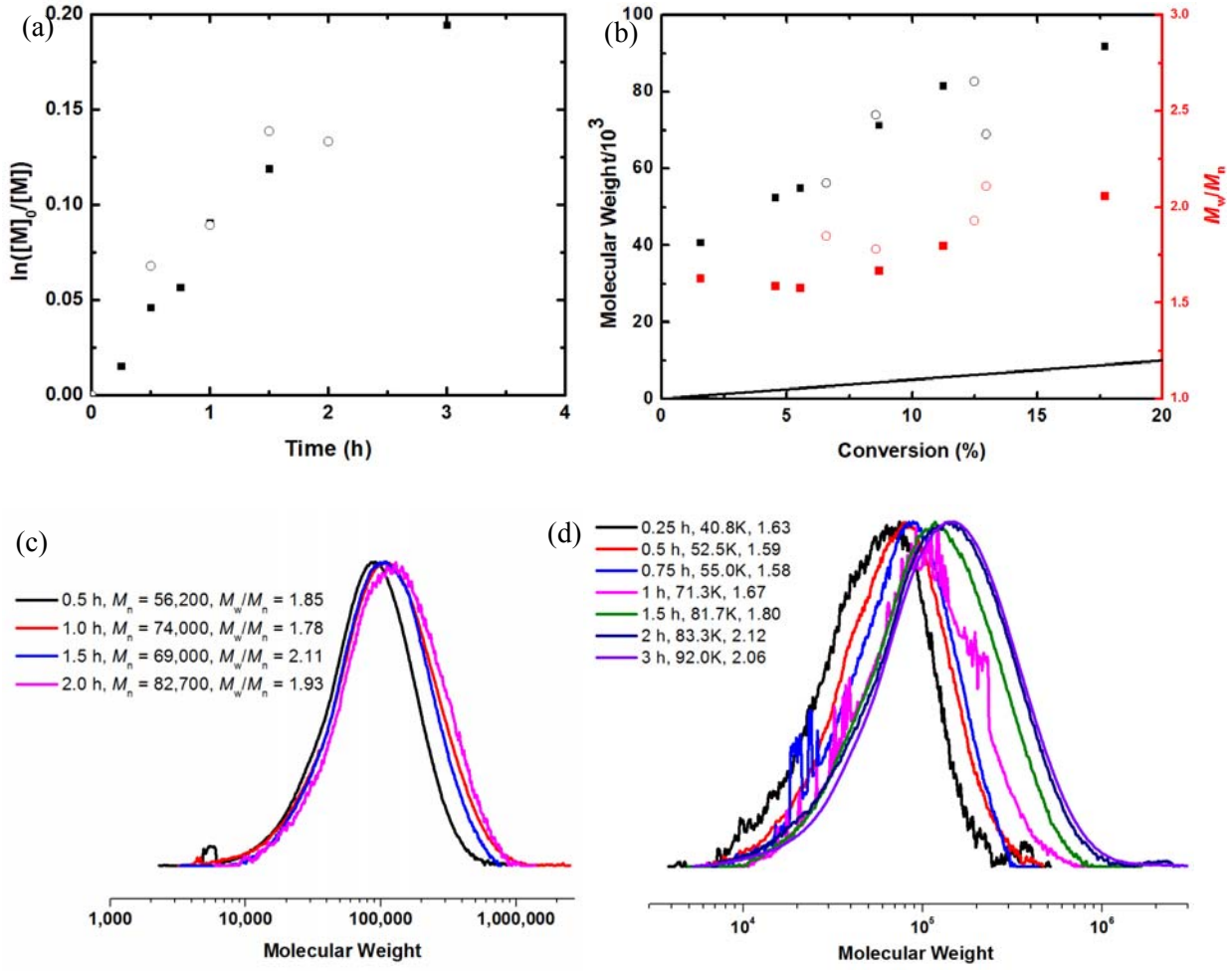

Figure S3. (a) Kinetic plot of metal free SI-ATRP from 120 nm silica nanoparticle modified with **BPASiOEt** (solid square) and **BiBSiOEt** (open circle). (b) Molecular weight (black) and dispersity (red) evolution of metal free SI-ATRP from 120 nm silica nanoparticle modified with **BPASiOEt** (solid square) and **BiBSiOEt** (open circle). (c, d) SEC traces of metal free SI-ATRP from 120 nm silica nanoparticle modified with **BPASiOEt** (c) and **BiBSiOEt** (d). Molecular weight calibration with linear PMMA standards, toluene as internal standard. Reaction conditions: $[SiO_2\text{-Br}, \sim 1\ Br/nm^2]_0$:$[MMA]_0$:$[PhPTZ]_0$ = 1:500:0.1; DMA = 50 vol%; UV irradiation at 365 nm, room temperature.

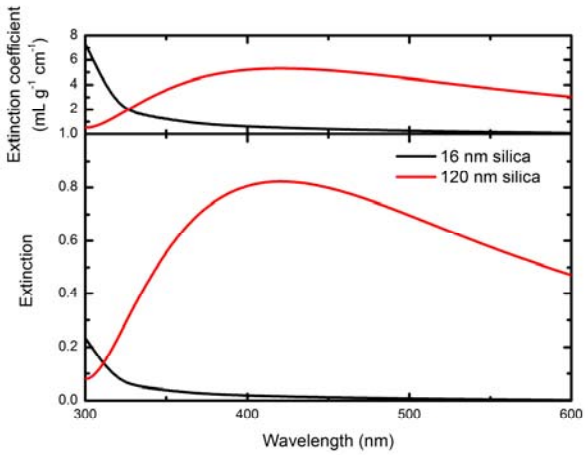

Figure S4. UV-Vis spectra of 16 nm silica nanoparticles (0.032 g/mL) and 120 nm silica nanoparticles (0.16 g/mL) in DMA and their respective extinction coefficient.

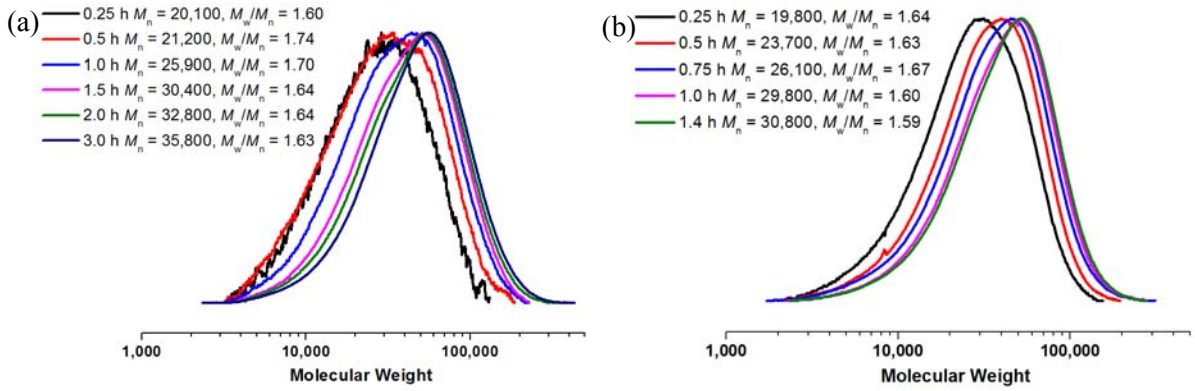

Figure S5. SEC traces of metal-free SI-ATRP of MMA from 16 nm silica nanoparticles modified with **BiBSiCl** (a, **Table 1** entry 5) or **BPASiCl** (b, **Table 1** entry 6). Molecular weight calibrated to standard PMMA, toluene as internal standard. Reaction conditions: [SiO_2-Br, ~1 Br/nm^2]$_0$:[MMA]$_0$:[PhPTZ]$_0$ = 1:500:0.5; DMA = 50 vol%; UV irradiation at 365 nm, room temperature.

References

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2. a) Ohno, K.; Morinaga, T.; Koh, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2005**, *38*, 2137-2142; b) Emmerling, S. G. J.; Langer, L. B. N.; Pihan, S. A.; Lellig, P.; Gutmann, J. S. *Macromolecules* **2010**, *43*, 5033-5042.