

## Supporting Information

### The Influence of Spacers in Tetherable Initiators on Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP)

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#### Materials.

Methyl methacrylate (MMA, Aldrich, 99%) was passed through a column filled with basic alumina to remove the inhibitor. 10-phenylphenothiazine (PhPTZ) was synthesized according to previously reported procedures.<sup>1</sup> Silica nanoparticles (MIBK-ST) were kindly donated by Nissan Chemical. Dry THF was collected from a SciMatCo solvent purification system. *N,N*-Dimethylacetamide (DMA, Aldrich, 99%), methanol (EMD, 99.8%), tetrahydrofuran (THF, EMD, 99.5%), hexane (EMD, 98.5%), ethyl ether (Fisher, 99%), anisole (Aldrich, 99%), 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%), 10-undecen-1-ol (Aldrich, 98%), 2-bromoisobutyryl bromide (2BiB, Aldrich, 98%), triethylamine (TEA, Aldrich, 99.5%), platinum cyclovinyldimethylsiloxane complex (Gelest, 2% in cyclovinyldimethylsiloxane), tris(2-(dimethylamino)ethyl)amine (Me<sub>6</sub>TREN, Alfa, 99%), 4,4'-di-*n*-nonyl-2,2'-bipyridine (dNbpy, Alfa, 97%), copper(II) bromide (CuBr<sub>2</sub>, Aldrich, 99%), copper(II) chloride (Aldrich, 99%), copper(I) chloride (CuCl, Alfa, 99.999%) were used as received without further purification.

#### Characterization

The number-average MW ( $M_n$ ) and the 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  $10^5$ ,  $10^3$ ,  $10^2$  Å) in THF as an eluent at 35 °C and at a flow rate of 1 mL min<sup>-1</sup>. Linear PMMA standards were used for GPC calibration. <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy was performed on a Bruker Avance 300 MHz spectroscope with CDCl<sub>3</sub> as the solvent. The conversion was calculated by following the decrease of the monomer peak area relative to the peak areas of methoxy proton. 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 up at 20 °C/min to 120 °C; (2) hold at 120 °C for 20 min; (3) high-resolution ramp up at 20 °C/min to 800 °C; (4) hold at 800 °C for 10 min. The organic content of the samples were normalized to the weight loss between 120 °C and 800 °C. The graft densities were calculated using a previously reported equation.<sup>2</sup>

$$\sigma_{\text{TGA}} = \frac{(1 - f_{\text{SiO}_2}) N_A \rho_{\text{SiO}_2} d}{6 f_{\text{SiO}_2} M_n} \quad (\text{S1})$$

The value for  $f_{\text{SiO}_2}$ , in the equation, is the silica fraction measured by TGA after exclusion of any residual solvent;  $N_A$  is the Avogadro number;  $\rho_{\text{SiO}_2}$  is the density of silica NPs;  $d$  is the average diameter of silica NPs;  $M_n$  is the number average MW of polymer brushes. 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. The average interparticle distances were measured with the ImageJ software.

Elemental analysis was performed via Schoniger Combustion by Midwest Microlab, Inc (Indianapolis, USA).

### Synthesis of tetherable initiators

The tetherable initiators were synthesized using slight modification of procedures previously reported in the literature.<sup>2-3</sup> Allyl alcohol/5-hexen-1-ol/10-undecen-1-ol (2.8/4.9/8.1 mL, 40 mmol) and TEA (7.0 mL, 51 mmol) were dissolved in 50 mL dry THF. The solution was cooled to 0 °C in an ice bath. 2BiB (5.1 mL, 41 mmol) was added dropwise into the vigorously stirred solution. The reaction proceeded at room temperature overnight. The mixture was filtered and washed with THF. The solvents were removed from the filtrate under rotary evaporation. The concentrated crude product was purified via the silica column chromatography eluted with 20:1 hexane-ethyl acetate mixture.

Allyl/5-hexen-1-yl/10-undecen-1-yl 2-bromoisobutyrate was obtained as a transparent liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 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 (allyl 2-bromoisobutyrate); 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 (5-hexen-1-yl 2-bromoisobutyrate); 5.81 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.06-4.89 (m, 2H), 4.18 (t, *J* = 6.6 Hz, 2H), 2.11-2.00 (m, 2H), 1.96 (s, 6H), 1.72-1.22 (m, 14H) ppm (10-undecen-1-yl 2-bromoisobutyrate).

Allyl/5-hexen-1-yl/10-undecen-1-yl 2-bromoisobutyrate (6.5/7.8/10.0 g, 31 mmol) was dissolved in chlorodimethylsilane (8.5 mL, 78 mmol). The solution was purged with nitrogen then 2 wt % platinum cyclovinyldimethylsiloxane complex (0.10 mL, 10 μmol) was added. The reaction was stirred at room temperature overnight and the conversion was followed by <sup>1</sup>H NMR

until full conversion of the vinyl signals. The unreacted chlorodimethylsilane was removed via rotary evaporation.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 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 (C3 initiator); 4.19 (t,  $J = 6.6$  Hz, 2H), 1.95 (s, 6H), 1.83-1.22 (m, 8H), 0.93-0.75 (m, 2H), 0.42 (s, 6H) ppm (C6 initiator); 4.17 (t,  $J = 6.6$  Hz, 2H), 1.93 (s, 6H), 1.77-1.18 (m, 18H), 0.93-0.75 (m, 2H), 0.40 (s, 6H) ppm (C11 initiator).

### Surface modification of silica nanoparticles

Silica nanoparticles were modified as described in our previous report.<sup>2</sup> The molar concentration of tetherable initiator was controlled to provide ca. 1.5 initiator molecules per  $\text{nm}^2$  of silica nanoparticles (assuming sphere with a diameter of 15.8 nm).<sup>4</sup>

### Surface-initiated Atom Transfer Radical Polymerization

**Normal ATRP:** Silica nanoparticles (0.20 g, 58  $\mu\text{mol}$ , assuming  $\sim 1$  accessible  $\text{Br}/\text{nm}^2$ ), MMA (3.1 mL, 29 mmol), 10.0 mg/mL  $\text{CuCl}_2$  in DMF (19  $\mu\text{L}$ , 1.4  $\mu\text{mol}$ ), dNbpy (24 mg, 58  $\mu\text{mol}$ ), and 3.1 mL anisole were mixed in a 10 mL Schlenk flask. The mixture was purged with nitrogen for 13 min then it was flash-frozen in liquid nitrogen.  $\text{CuCl}$  (2.7 mg, 27  $\mu\text{mol}$ ) was added to the frozen mixture which was purged with nitrogen for another 5 min. The reaction was allowed to thaw in warm water and heated in an oil bath at 60  $^\circ\text{C}$ . The progress of the reaction was followed by  $^1\text{H}$  NMR and SEC until the 25 mm $\times$ 12 mm oval rare earth extra power stir-bar stopped moving. The reaction was immediately diluted with 5 mL THF and sonicated for 30 min. The final product was recovered by precipitation in methanol.

**PhotoATRP:** Silica nanoparticles (0.20 g, 58  $\mu\text{mol}$ , assuming  $\sim 1$  accessible  $\text{Br}/\text{nm}^2$ ), MMA (3.1 mL, 29 mmol), 20.0 mg/mL  $\text{CuBr}_2$  in DMF (32  $\mu\text{L}$ , 2.9  $\mu\text{mol}$ ),  $\text{Me}_6\text{TREN}$  (4.6  $\mu\text{L}$ , 17  $\mu\text{mol}$ ), and 3.1 mL anisole were mixed in a 10 mL Schlenk flask. The mixture was purged with nitrogen for 13 min then irradiated with a 4.9  $\text{mW}/\text{cm}^2$  MelodySusie® DR-0901 UV lamp at 365

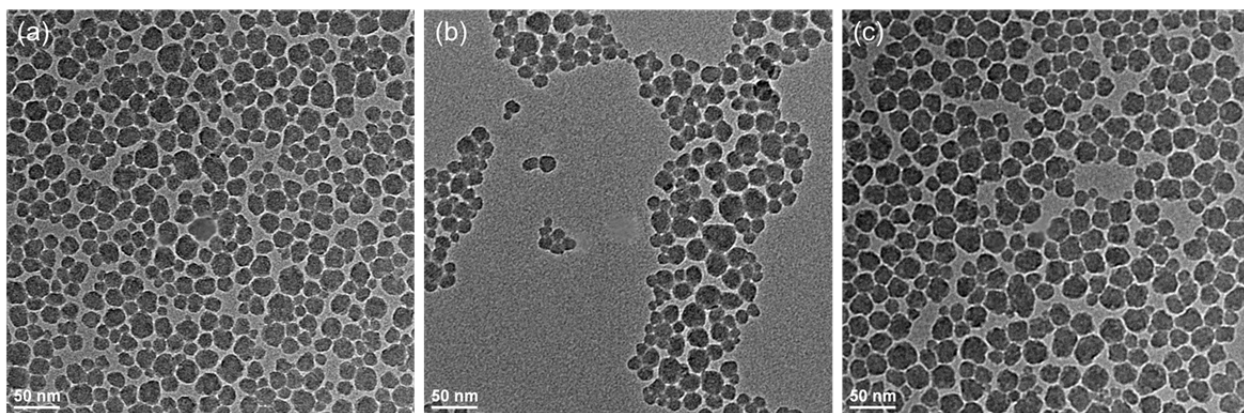
nm while stirred at room temperature. The progress of the reaction was followed by  $^1\text{H}$  NMR and SEC until the 25 mm×12 mm oval rare earth extra power stir-bar stopped moving. The reaction was immediately diluted with 5 mL THF and sonicated for 30 min. The final product was recovered by precipitation in methanol.

**Metal-free ATRP:** Silica nanoparticles (0.20 g, 58  $\mu\text{mol}$ , assuming  $\sim 1$  accessible Br/nm<sup>2</sup>), MMA (3.1 mL, 29 mmol), PhPTZ (7.9 mg, 29  $\mu\text{mol}$ ), and 3.1 mL DMA were mixed in a 10 mL Schlenk flask. The mixture was purged with nitrogen for 13 min then irradiated with a 4.9 mW/cm<sup>2</sup> MelodySusie® UV lamp at 365 nm while stirred at room temperature. The reaction progress was followed by  $^1\text{H}$  NMR and SEC until the 25 mm×12 mm oval rare earth extra power stir-bar stopped moving. The reaction was immediately diluted with 5 mL THF and sonicated for 30 min. The final product was recovered by precipitation in methanol.

**Table S1.** Weight fractions ( $f_{\text{Br}}$ ), concentrations ( $c_{\text{Br}}$ ), and initiator densities ( $\sigma_i$ ) of Br, average interparticle distance ( $d_{\text{ip}}$ ), and relative scattering cross-sections of initiator-functionalized silica nanoparticles

Entry	Spacer	$f_{\text{Br}}$ (%) <sup>a</sup>	$c_{\text{Br}}$ (mmol/g)	$\sigma_i$ (nm <sup>-2</sup> )	$d_{\text{ip}}$ (nm) <sup>b</sup>	Relative scattering cross-section <sup>c</sup>
1	C3	3.44	0.431	1.50	21.10	1
2	C6	3.50	0.438	1.52	21.52	1.13
3	C11	3.31	0.415	1.44	22.51	1.47

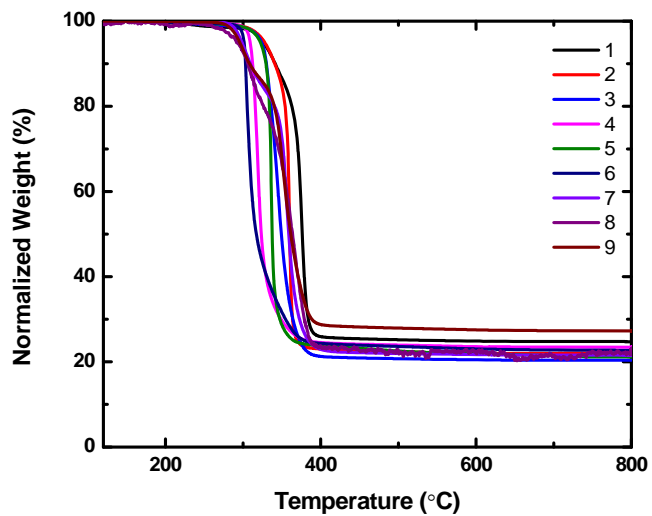
<sup>a</sup> Determined by elemental analysis. <sup>b</sup> Measured with ImageJ software from TEM images. <sup>c</sup> Calculated from  $d_{\text{ip}}$  based on the relation:  $I/I_0 \sim d^6$ , where  $I$  and  $I_0$  are the scattered and incident light intensities, and  $d$  is the average diameter of the nanoparticles.



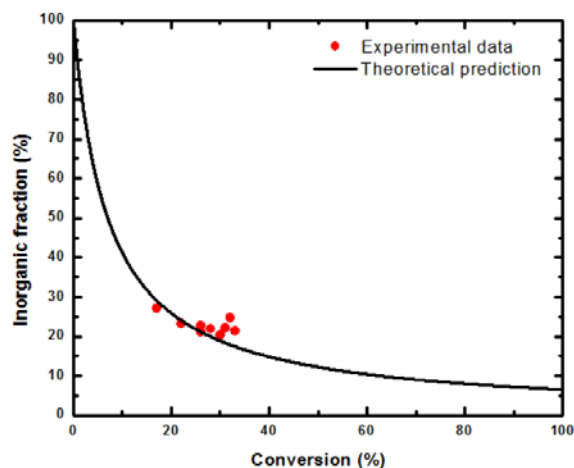
**Figure S1.** Characteristic TEM images of silica nanoparticles modified with C3 (a), C6 (b), and C11 (c) initiators.

**Table S2.** Inorganic contents ( $f_i$ ) of PMMA grafted silica nanoparticles

Entry	Spacer	Reaction method	Final Conversion	$f_i$
1	C3	Normal	32%	24.8%
2	C6	Normal	28%	22.0%
3	C11	Normal	30%	20.4%
4	C3	Photo	22%	23.4%
5	C6	Photo	26%	21.2%
6	C11	Photo	26%	22.8%
7	C3	Metal-free	33%	21.5%
8	C6	Metal-free	31%	22.2%
9	C11	Metal-free	17%	27.2%



**Figure S2.** TGA traces of PMMA grafted silica nanoparticles



**Figure S3.** Correlation between the inorganic fraction (measured by TGA) and the conversion (measured by NMR). The apparently too high conversion values could be due to monomer evaporation for slower polymerizations,

## References

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