

## Electronic Supplementary Information

### A novel strategy for enhancing propagation rate of polystyrene grown from silica nanoparticles or carbon nanotubes

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**General.** CuBr (Shanghai Chemical Reagent Co, 99%) was purified by stirring in glacial acetic acid, washing with ethanol, and then drying in a vacuum oven at 70°C overnight. Tetraethoxysilane (TEOS, 99%, Shanghai Chemical Reagent Co) was distilled under reduced pressure before use. Anisole was stirred with sodium at 80°C overnight, and then distilled under reduced pressure. 2-Bromobutyryl bromide (Aldrich, 98%), *N,N,N',N'N''*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 98%) and other reagents with analytical grade (Shanghai Chemical Reagent Co) were used as received. Glycidol 2-bromoisobutyrate was synthesized according to reference 1, <sup>1</sup>H NMR (500Hz, CDCl<sub>3</sub>, ppm) δ: 4.43-4.54, 4.02-4.11 (m, COOCH<sub>2</sub>, 2H), 3.19-3.29 (m, CH in epoxy ring, 1H), 2.81-2.89, 2.65-2.73 (m, CH<sub>2</sub> in epoxy ring, 2H), δ: 1.85-2.01(s, CH<sub>3</sub>, 6H).

**Instrumental Analysis.** The molecular weight,  $M_{n, GPC}$  and the molecular weight distribution ( $M_w/M_n$ ) were measured on a Waters 150C and Waters 1515 gel permeation chromatography (GPC) respectively. The former equipped with three ultrastyrigel columns ( $10^3$ ,  $10^4$ ,  $10^5$  Å), and the latter equipped with linear columns, monodisperse polystyrenes were used as calibration standard and THF was used as eluent at a flow rate of 1.0 mL/min for Waters 150C and 0.3 mL/min for Waters 1515.  $^1\text{H}$  NMR spectra were determined on a Bruker DMX-300 nuclear magnetic resonance instrument with  $\text{CDCl}_3$  as solvent and tetramethylsilane (TMS) as internal standard. FTIR spectra were recorded on a Bruker VECTOR-22 IR spectrometer. Thermal gravimetric analyses (TGA) were carried out on a PE TGA-7 instrument with a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere. Transmission electron microscopy (TEM) image was made on a Hitach-7650 microscopy operated at 100kv.

**Synthesis of ATRP initiator-anchored silica nanoparticles.** Into a 500 mL flask, ethanol (400 mL) and aqueous ammonia solution (22 mL, 28%) were added. After the mixture was stirred at  $40^\circ\text{C}$  for 2 h, TEOS (21 mL) was added rapidly. The reaction mixture was stirred at  $40^\circ\text{C}$  vigorously overnight. 3-Aminopropyltriethoxysilane (APTES, 2 mL) was added, the mixture was stirred slowly for 6 h, and then refluxed for 2 h. The nanoparticles (NPs) were isolated by centrifugation, and purified by re-dispersing in ethanol—separated by centrifugation for six cycles. The amino-functionalized silica NPs were finally re-dispersed in ethanol (100 mL) and glycidol 2-bromoisobutyrate (2 g) was added. After stirring at ambient temperature for 4 h, the suspension was heated at  $45^\circ\text{C}$  for 4 h. The NPs were purified and isolated

following similar procedures as those described for the synthesis of amino-functionalized silica NPs. The ATRP initiators anchored silica NPs (4.5 g) (designated as SiO<sub>2</sub>-Br) were obtained as white powder after drying in vacuum oven at 50 °C for 24 h. FT-IR (KBr, cm<sup>-1</sup>): 2950 (C-H), 1730 (C=O).

**SI-ATRP of St from silica nanoparticles.** Into a 5 mL glass tube, magnetic stir bar, SiO<sub>2</sub>-Br (0.1 g), CuBr (4.6 mg) and anisole (1.04 g) were added successively, and then the mixture was ultrasonicated for 30 s. The PMDETA (6.7 μl) and St/PS0.5 (or St/PS1.0 or St) (1.04 g) were added. After degassed by three freeze-evacuate-thaw cycles, the glass tube was sealed in vacuum. After the polymerization was carried out at 90 °C for a predetermined time, the polymerization mixture diluted with THF was poured into excess of methanol, the polymer coated silica was precipitated, collected by filtration and dried in vacuum at 60 °C until the weight was constant.

**Purification of PS-grafted silica.** The crude product (100 mg) was homogeneously dispersed in THF (10 mL). The suspension was centrifugated at 13,000 rpm for 30 min. The upper clean liquid was discarded, and the fresh THF (10 mL) was added into the residue. This procedure was repeated for three times until no polymer was in THF, the obtained PS-grafted silica was dried in vacuum at 60 °C and subjected to TGA determination.

**Cleavage of the PS from silica.** Cleavage of the PS from the PS-grafted silica was carried out according to the procedure described in reference 2. In a polyethylene (PE) tube, the PS-grafted silica NPs (50 mg) were dissolved in 10 mL THF. Into the solution, aqueous HF (48 wt%, 0.5 mL) was added, and the reaction mixture was

stirred at room temperature for 6 h. The polymer was precipitated by adding the solution into 10-fold excess of methanol in a plastic beaker, the precipitate was collected by filtration. The PS obtained was dissolved in THF (10mL), aqueous NaOH (10 wt%, 0.5 mL) was added and the mixture was refluxed over 24 h. The polymer was precipitated by adding the solution into 10-fold excess of methanol, the precipitate was collected by filtration, and dried in a vacuum oven at 60 °C overnight. The recovered PS was then subjected to GPC analysis.

**Synthesis of ATRP initiator-anchored MWCNTs.** The ATRP initiator-anchored MWCNTs (MWCNT-Br) were prepared similar to the procedure described in reference 3.

**Homogeneous ATRP of St.** Into a 20 mL glass tube with a magnetic stir bar, 2-hydroxyethyl-2-bromoisobutyrate (52.2 mg, 2.5 mmol), CuBr (36 mg, 2.5 mmol), PMDETA (43.3 mg, 2.5mmol ), St (9.1 g, 0.0875 mol) or a solution of PS with  $M_n(\text{GPC}) = 200300$  and  $M_w/M_n = 2.23$  (45.5 mg) in freshly distilled St (9.1 g, St/PS0.5) and anisole (9.1 g) were added successively. After degassed by three freeze-evacuate-thaw cycles, the glass tube was sealed in vacuum. After the polymerization was carried out at 90 °C for 4 h, the polymerization mixture was diluted with THF and passed through a column of neutral alumina, concentrated on a rotary evaporator and poured into excess of methanol, the product was precipitated, collected by filtration and dried in vacuum at 60 °C until the weight was constant. The weights of PS were 3.43g (for St) and 3.46g (for PS/St0.5, the weights of added PS and SiO<sub>2</sub>-Br were already deducted) respectively.

**SI-ATRP of St from MWCNTs.** Into a 5 mL glass tube with a magnetic stir bar, MWCNT-Br (50 mg), CuBr (2.0 mg) and anisole (1.04 g) were added successively, and then the mixture was ultrasonicated for 5 min. The PMDETA (2.9  $\mu$ L) and St/PS05 (or St) (1.04 g) were added. After degassed by three freeze-evacuate-thaw cycles, the glass tube was sealed in vacuum. The polymerization was carried out at 90 °C for a predetermined time, and then the polymerization mixture diluted with THF was poured into excess of methanol, the polymer-grafted MWCNTs were precipitated and collected by filtration. The precipitates were dissolved in THF and vacuum-filtered using a 0.22  $\mu$ m poly(vinylidene fluoride) membrane for three times. After dried overnight under vacuum, the PS-grafted MWCNTs (MWCNT-g-PS) was obtained and subjected to TGA determination.

## References

1. S. M. Sirard, H. J. Castellanos, H. S. Hwang, K.-T. Lim, K. P. Johnston, *Ind. Eng. Chem. Res.* 2004, 43, 525
2. C.-H. Liu, C.-Y. Pan, *Polymer*, 2007, 48, 3679.
3. H. Kong, C. Gao, D. Yan, *J. Am. Chem. Soc.*, 2004, 126: 412



Table S1. Results and conditions of the surface-initiated ATRP from silica NPs<sup>a</sup>

Entry <sup>b</sup>	Time (min)	Conv (%) <sup>c</sup>	$M_n$ (GPC) <sup>d</sup> (g/mol)	$M_w/M_n$ <sup>d</sup>	Initiator efficiency (%) <sup>e</sup>
1	60	6.1	13300	1.12	17.1
2	120	11.0	25200	1.17	15.1
3	180	15.0	33300	1.20	15.4
4	240	18.7	42700	1.10	14.8
5	30	7.3	29200	1.02	8.9
6	60	18.0	51300	1.12	11.8
7	90	25.5	75100	1.19	11.4
8	120	35.3	96900	1.10	11.8

<sup>a</sup> [St]/[initiators]/[CuBr]/[PMDETA]=310:1:1:1; temperature: 90°C; solvent: anisole (1:1 to St, w/w). <sup>b</sup> Entry 1, 2, 3 and 4, St contained 0.5% PS; Entry 5, 6, 7 and 8, St contained 1.0% PS. <sup>c</sup> Calculated based on gravimetric method. <sup>d</sup>  $M_n$  and  $M_w/M_n$  of PS obtained from hydrolysis of PS-SiO<sub>2</sub>, entry 1, 2, 3 and 4, measured on Waters 150C equipped with three ultrastyrigel columns (10<sup>3</sup>, 10<sup>4</sup>, 10<sup>5</sup> Å) at 30 °C, THF was used as eluent at a flow rate of 1.0 mL/min; Entry 5, 6, 7 and 8, measured on Waters 1515 equipped with styragel linear columns at 30 °C, THF was used as eluent at a flow rate of 0.3 mL/min. <sup>e</sup> Calculated from the following equations: Initiator efficiency =  $M_n(\text{theory})/M_n(\text{GPC})$ ,  $M_n(\text{theory}) = [\text{St}]_0/[\text{initiator}]_0 \times M_{\text{St}} \times \text{conversion} + 167$ , where  $[\text{St}]_0$  and  $[\text{initiators}]_0$  are initial concentration of St and the amount of ATRP initiator-anchored on silica NPs, respectively;  $M_{\text{St}}$  and 167 are the molecular weights of St and the end group, respectively.

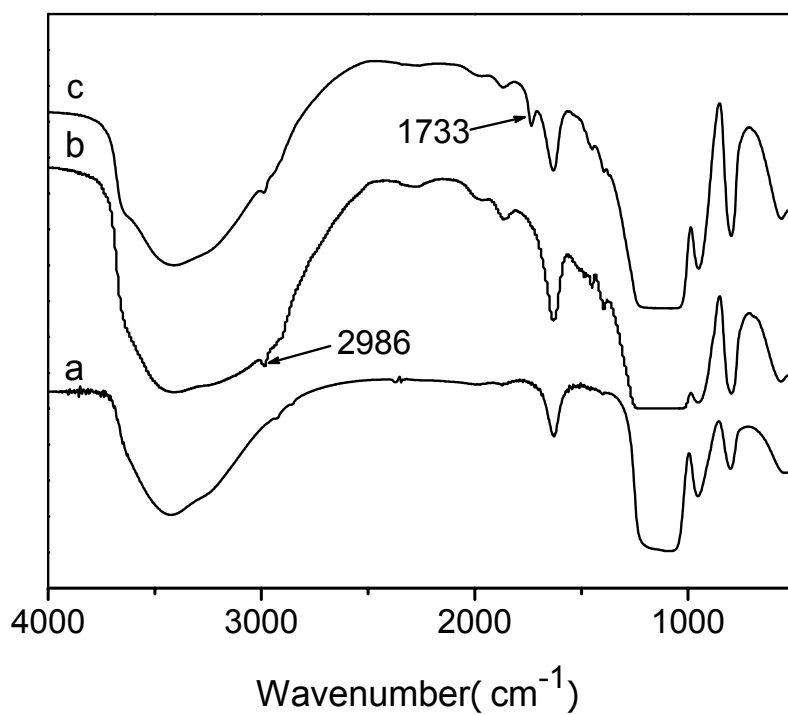


Fig. S1. FT-IR of spectra of bare SiO<sub>2</sub> (a), SiO<sub>2</sub>-NH<sub>2</sub> (b) and SiO<sub>2</sub>-Br (c)



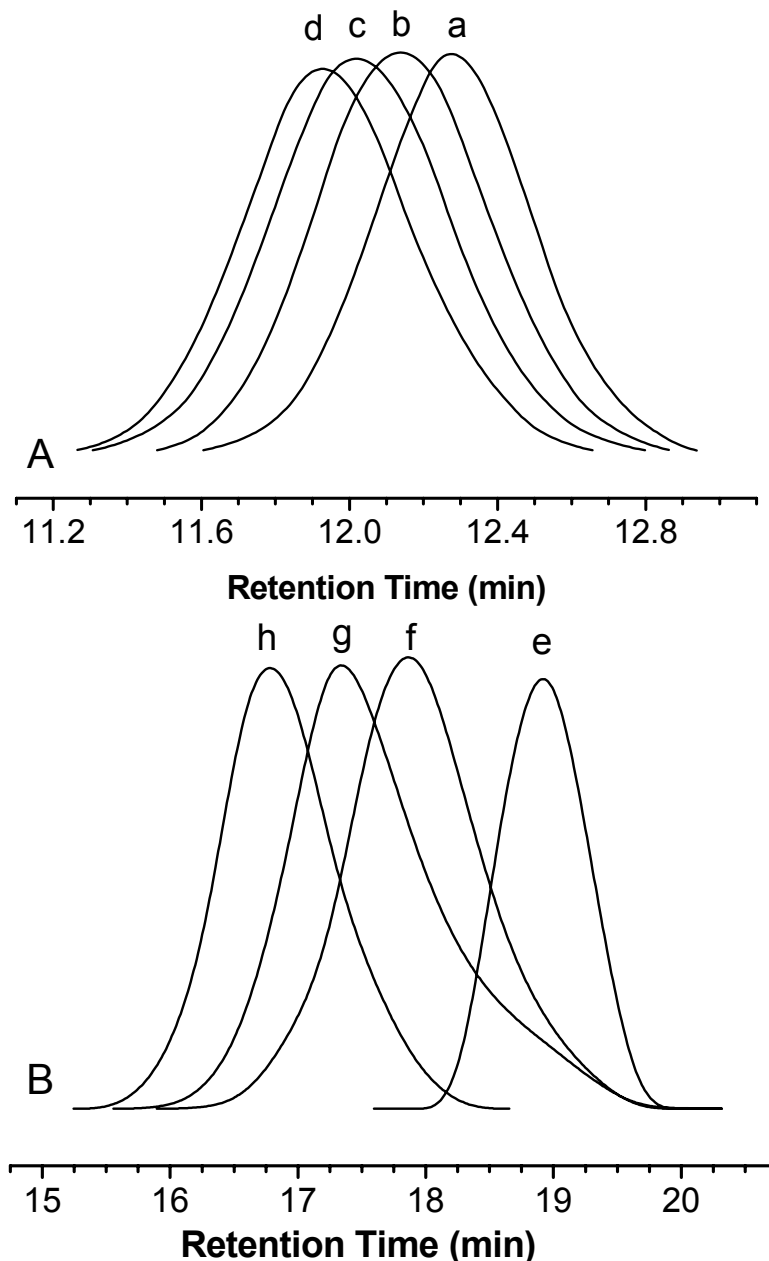


Fig. S2. GPC curves of PS cleaved from PS-SiO<sub>2</sub>, followed by hydrolyzation under alkali conditions. A) PS-SiO<sub>2</sub>s were prepared from SI-ATRP of St/PS0.5 at 1 h (a); 2 h (b); 3 h (c) and 4 h (d), measured on Waters 150C, (a)  $M_n=13300$  g/mol,  $M_w/M_n=1.12$ , (b)  $M_n=25200$ ,  $M_w/M_n=1.17$ ; (c)  $M_n=33300$ ,  $M_w/M_n=1.20$ , (d)  $M_n=42700$  g/mol,  $M_w/M_n=1.15$ . B) PS-SiO<sub>2</sub>s were prepared from SI-ATRP of St/PS1.0 at 0.5 h (e); 1 h (f); 1.5 h (g) and 2 h (h), measured on Waters 1515, (e)  $M_n=29200$ ,  $M_w/M_n=1.02$ , (f)  $M_n=51300$ ,  $M_w/M_n=1.12$ ; (g)  $M_n=75100$ ,  $M_w/M_n=1.10$ , (h)  $M_n=96900$  g/mol,  $M_w/M_n=1.10$ .

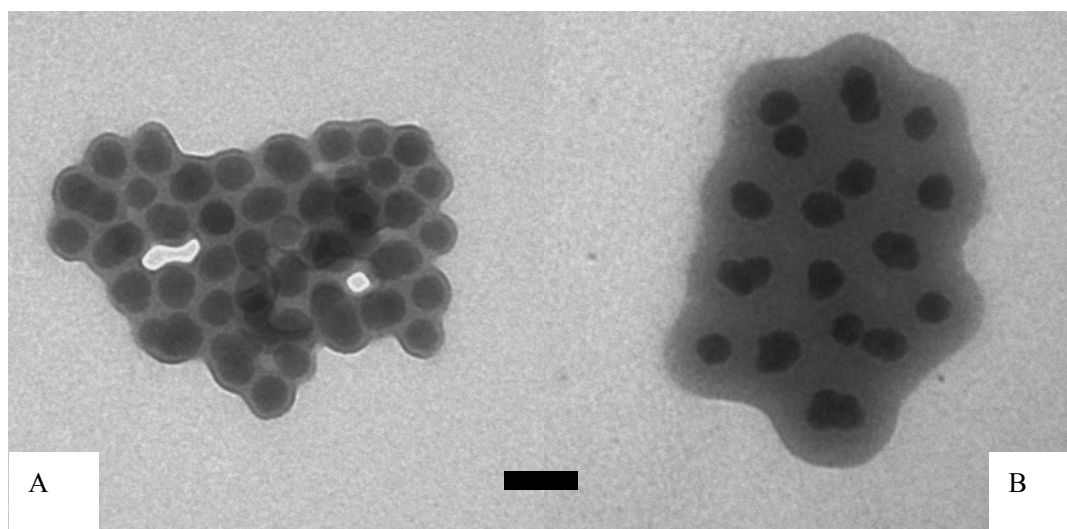


Fig. S3. TEM images of PS-grafted-silica NPs. A)  $M_n=29200$ , B)  $M_n=96900$ . Scale bar: 100nm.