

Supporting Information

Synthesis of well-defined polymers grafted onto fumed silica by chain exchange reaction and highly pure block copolymers thereby

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Experimental

Materials. Fumed silica with a nominal particle size of 7 nm and a specific surface area of 390 m²/g was purchased from Aldrich. 3-(Mercaptopropyl)trimethoxysilane (95%) was purchased from Lancaster. 1-Propanethiol (98%) was purchased from Alfa Aesar. (4-Cyanopentanoic acid)-4-dithiobenzoate (CPADB),¹ *S*-methoxycarbonylphenylmethyl *S'*-propyltrithiocarbonate (MPPT)² and *S*-benzyl *S'*-trimethoxysilylpropyltrithiocarbonate (BTPT)² were synthesized and purified according to literature methods. Fumed silica supported BTPT (Si-BTPT) with a CTA loading of 0.203 mmol/g was synthesized according to previous method.² Methyl acrylate (MA, 99%), *tert*-butyl acrylate (*t*BA, 98%), *N,N*-dimethylacrylamide (DMA, 99%), *N*-acrylomorpholine (NAM, 97%), methyl methacrylate (MMA, 99%), and styrene (St, 99%) were passed through a basic alumina column to remove the inhibitor before use. *N*-Isopropylacrylamide (NIPAM, 97%) was recrystallized twice from mixtures of hexane and toluene. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol. Other chemicals were of analytical grade and used as received.

General Procedure for RAFT Polymerization. Polymerizations were conducted in bulk, dioxane or toluene using AIBN as the primary radical source and MPPT or CPADB as the chain transfer agent (CTA). In a typical polymerization, St (18.7 g, 180 mmol), MPPT (0.301 g, 1.0 mmol), and AIBN (16.4 mg, 0.10 mmol) were added to a glass tube with a magnetic stirring bar. The tube was sealed with a rubber septum, and the contents cooled with ice-water bath were degassed with nitrogen for 20 min. The tube was subsequently immersed into an oil bath preheated to 60 °C. After 22 h, the polymerization was stopped by cooling the tube in ice water. PSt (7.56 g, 38.8% of conversion) was obtained by concentration and precipitation into cold methanol. The molecular weight and polydispersity of PSt obtained by GPC were $M_n = 7880$, PDI = 1.06. Other homopolymers were synthesized according to a similar approach, and obtained by precipitation into hexane, methanol or mixtures of deionized water and methanol (1:1, v/v, for *Pt*BA).

General Procedure for Chain Extension Polymerization. Polymerizations were conducted in dioxane or toluene using PSt or PMMA as a macro chain transfer agent. In a typical polymerization, PSt ($M_n = 7880$, PDI = 1.06, 1.58 g, 0.20 mmol), NAM (2.26 g, 16.0 mmol), and AIBN (3.3 mg, 0.020 mmol) were added to a glass tube with a magnetic stirring bar, and dioxane was added until the total volume was 10.0 mL. The tube was sealed with a rubber septum, and the contents were degassed with nitrogen for 15 min. The polymerization was performed at 60 °C for 20 h and then stopped by cooling the tube in ice water. The diblock copolymer (3.17 g) was recovered by precipitation into cold hexane, and the monomer conversion was determined to be 70.4% by gravimetry. The molecular weight and polydispersity of PSt-*b*-PNAM determined by GPC were $M_n = 14600$ and PDI = 1.11. Other di- and triblock copolymers were synthesized according to a similar approach using various macro CTAs as mediators, and isolated by precipitation into hexane or methanol.

Synthesis of Silica-Polymers Hybrids by Chain Exchange Reaction. The chain exchange reaction using Si-BTPT, macro CTAs and AIBN as raw materials was performed in dioxane or toluene at desired temperatures. In a typical run, PSt ($M_n = 7880$, PDI = 1.06, 0.394 g, 0.050 mmol), Si-BTPT (0.247 g, 0.050 mmol), AIBN (8.2 mg, 0.050 mmol), and toluene (24.5 mL) were added to a round flask, and the mixtures were degassed with nitrogen for 15 min. The reaction was conducted with stirring at 60 °C for 24 h and then cooled down to room temperature. The PSt-grafted silica (SiO₂-*g*-PSt) was purified by five cycles of centrifugation, redispersion and stirring in toluene (3 × 20 mL) and THF (2 × 20 mL). After drying at 45 °C under vacuum, 0.287 g of SiO₂-*g*-PSt was obtained. The hybrid sample was then subjected to aminolysis and TGA measurement. GPC analysis: grafted PSt, $M_n(g) = 7960$, PDI(g) = 1.05. The weight ($G_r = 19.2\%$) and molar ($G_p = 24.1 \mu\text{mol/g}$) grafting ratios of polymeric chains on substrate surface were determined by TGA using equations 1 and 2,^{2,3} where G_r and G_p mean the weight and molar ratio of grafted polymer to solid support, $W_{\text{Si-polymer},100}$ and $W_{\text{SiO}_2,100}$ are the residual weight percent of silica-polymer hybrid and flash silica at 100 °C, $W_{\text{Si-polymer},600}$ and $W_{\text{SiO}_2,600}$ are the residual weight percent of silica-polymer hybrid and flash silica at 600 °C, and $M_{n,\text{GPC}(g)}$ is the apparent molecular weight of grafted polymer determined by GPC.

$$G_r = \frac{W_{\text{Si-polymer}, 100}}{W_{\text{Si-polymer}, 600}} - \frac{W_{\text{SiO}_2, 100}}{W_{\text{SiO}_2, 600}} \quad (1)$$

$$G_p = \frac{G_r}{M_{n,\text{GPC}(g)}} \quad (2)$$

General Procedure to Cleave Grafted Chains from the Substrate Surface Using Large Excess of Thermal Initiators. Polymer-grafted silica, macro CTAs, thermal initiators and solvent were combined to produce the desired hybrid product under heating. In a typical run, AIBN (394 mg, 2.4 mmol), LPO (47.8 mg, 0.12 mmol), SiO₂-*g*-PSt (0.15 g, comprising about 0.024 mmol of RAFT agent) were added to

a round flask, and toluene was added until the total volume was 12.0 mL. The mixtures were stirred for 5 min and then degassed with nitrogen for 20 min. The reaction was carried out with stirring at 80 °C for 6 h and immediately cooled down to room temperature. Silica-supported CTA (Si-CTA, 120 mg) was isolated by five cycles of centrifugation and redispersion THF (5×10 mL), and the recovered PSt was concentrated and precipitated into methanol. The hybrid sample was then subjected to aminolysis and TGA measurement. GPC analysis: grafted PSt, $M_n(g) = 7920$, $PDI(g) = 1.06$. The weight grafting ratio of recycled Si-CTA determined by TGA was 1.52%.

General Procedure to Cleave Grafted Chains from the Substrate Surface by Aminolysis. The grafted polymers were cleaved from the substrate surface according to a method similar to the literature.⁴ In a typical run, to a glass tube was added 90 mg of silica-polymer hybrid sample, 3.0 mL of THF, and 20.0 μ L (0.212 mmol) of methyl methanethiosulfonate. The solution was degassed with nitrogen for 5 min, and then 14.0 μ L (0.106 mmol) of degassed *n*-hexylamine was injected into the mixture. After stirring at room temperature overnight, the solution was subjected to centrifugation, and the recovered polymer was used for GPC analysis.

Characterization. The number-average molecular weight (M_n) and polydispersity (PDI) of polymer samples were measured on a Waters 150-C gel permeation chromatography equipped with three Ultrastyrigel columns with 10 μ m bead size at 35 °C. Their effective molecular weight ranges were 100-10000 for Styragel HT2, 500-30000 for Styragel HT3, and 5000-600000 for Styragel HT4. The pore sizes are 50, 100, and 1000 nm for Styragels HT2, HT3, and HT4, respectively. THF was used as an eluent at a flow rate of 1.0 mL/min, and polystyrene samples were calibrated with PS standard samples; other samples were calibrated using PMMA standard samples. ¹H NMR (400 MHz) and ¹³C (100 MHz) spectra were recorded on a Varian UNITY INOVA 400 spectrometer at 25 °C using CDCl₃ as a solvent. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer 2000 spectrometer using KBr disks. Thermogravimetric analyses (TGA) were carried out using a TA Instruments TGA 2050 thermogravimetric analyzer from room temperature to 600 °C at a rate of 10 °C/min under nitrogen. C, H, N and S were determined by combustion followed by chromatographic separation and thermal conductivity detection using a Carlo-Erba EA 1110CHNO-S Elemental Analyzer.

References

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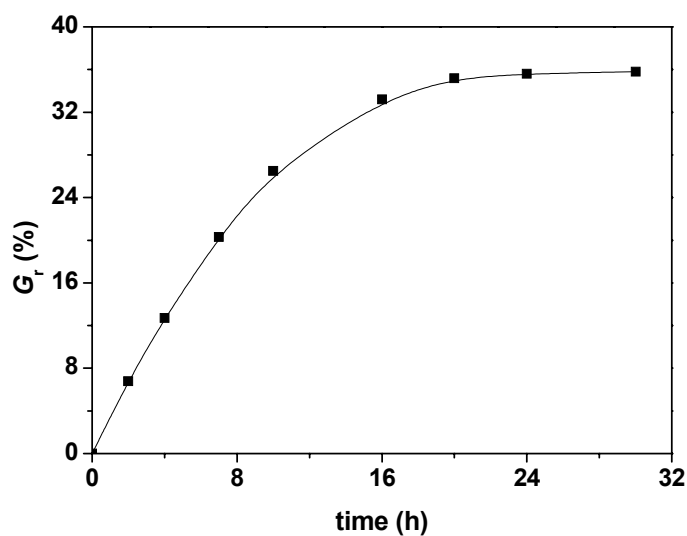


Figure 1S. Effects of reaction time on weight grafting ratio of PMA on the surface of fumed silica. Reaction conditions: $[PMA]_0:[Si-BTPT]_0:[AIBN]_0 = 1:1:1$, $[AIBN]_0 = 2.0$ mmol/L, in toluene at 60 °C, $M_n(PMA) = 20600$, PDI = 1.14, and the loading of Si-BTPT was 0.203 mmol CTA per g of fumed silica.

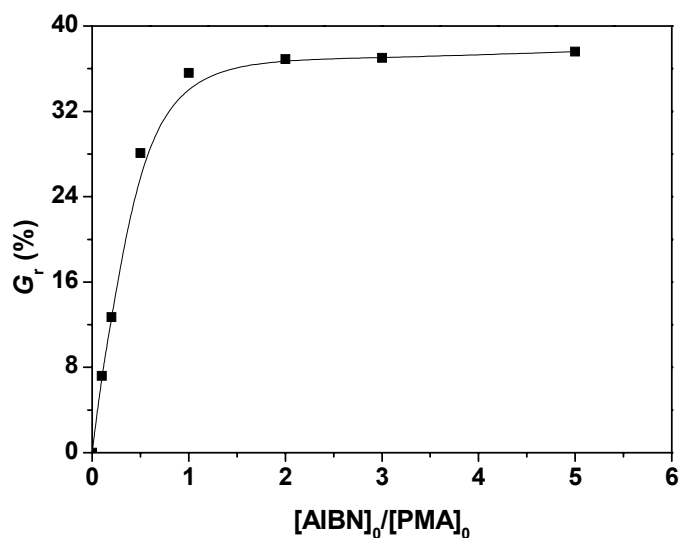


Figure 2S. Effects of $[AIBN]_0/[PMA]_0$ (x) on weight grafting ratio of PMA on the surface of fumed silica. Reaction conditions: $[PMA]_0:[FSi-BTPT]_0:[AIBN]_0 = 1:1:x$, $[PMA]_0 = 2.0$ mmol/L, in toluene at 60 °C for 24 h, $M_n(PMA) = 20600$, PDI = 1.14, and the loading of Si-BTPT was 0.203 mmol CTA per g of fumed silica.

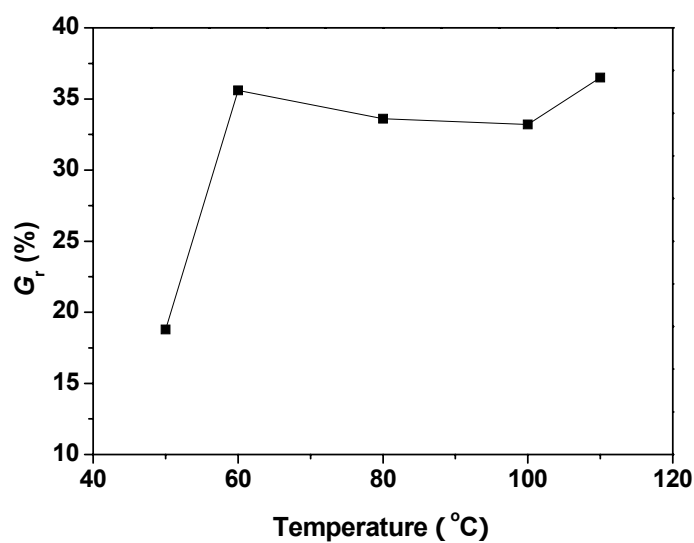


Figure 3S. Effects of reaction temperature on weight grafting ratio of PMA on the surface of fumed silica. Reaction conditions: $[PMA]_0:[Si-BTPT]_0:[AIBN]_0 = 1:1:1$, $[PMA]_0 = 2.0$ mmol/L, in toluene, $M_n(PMA) = 20600$, PDI = 1.14, and the loading of Si-BTPT was 0.203 mmol CTA per g of fumed silica.

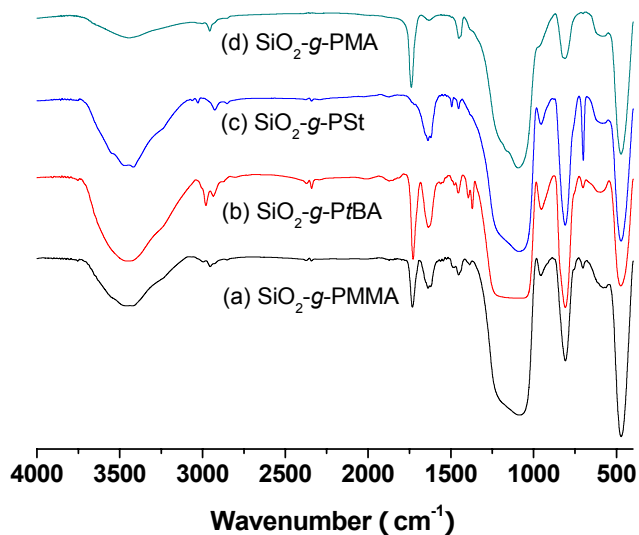


Figure 4S. FT-IR spectra of silica particles grafted with various homopolymers obtained via chain exchange reaction.

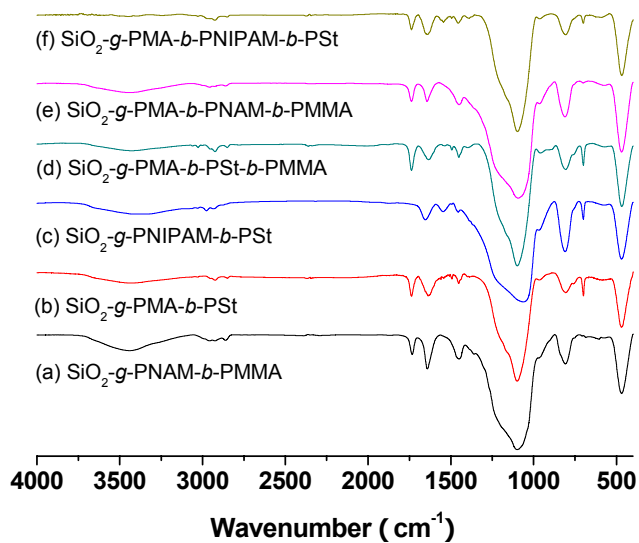


Figure 5S. FT-IR spectra of silica particles grafted with block copolymers obtained via chain exchange reaction.

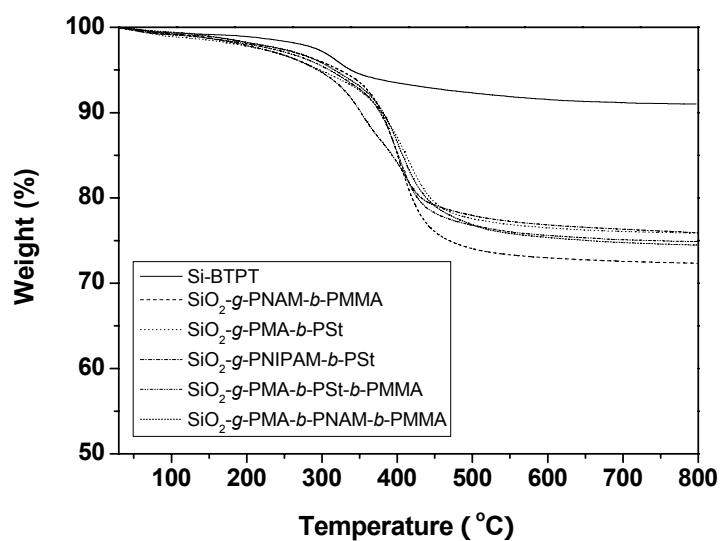


Figure 6S. TGA curves of Si-BTPT and fumed silica grafted with di- and triblock copolymers.

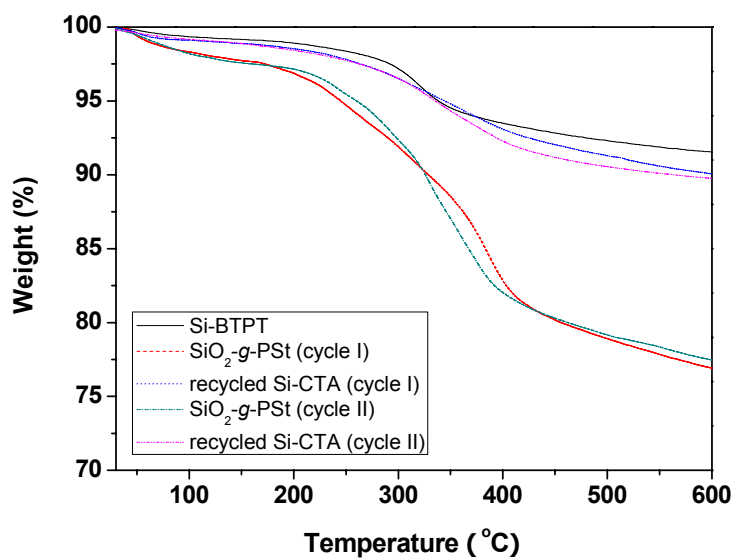


Figure 7S. TGA curves of Si-BTPT, SiO₂-g-PSt and recycled Si-CTA obtained by cycles I and II.

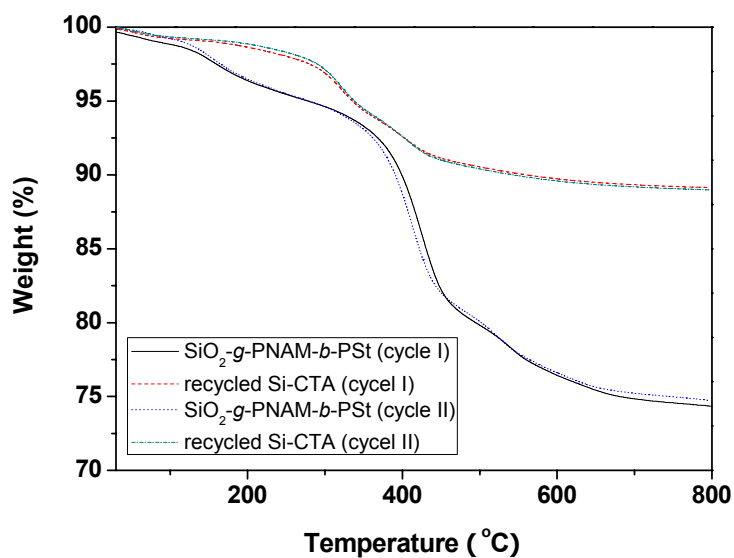


Figure 8S. TGA curves of Si-BTPT, SiO₂-g-PNAM-*b*-PSt and recycled Si-CTA obtained by cycles I and II.

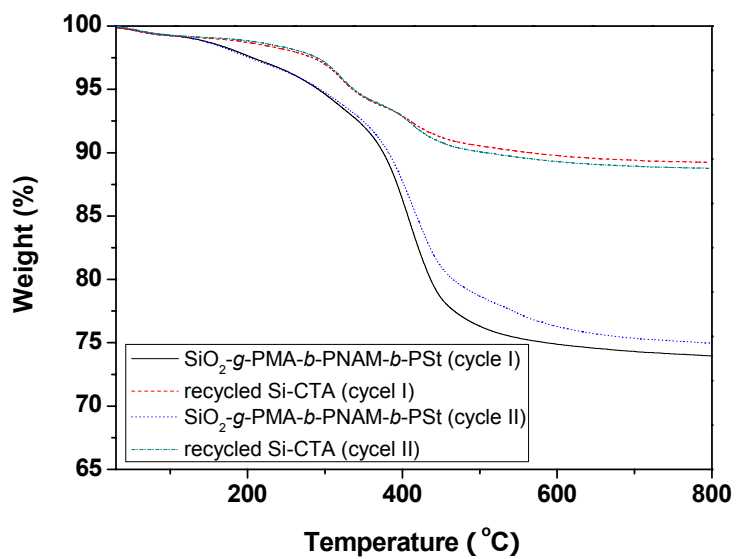


Figure 9S. TGA curves of Si-BTPT, SiO₂-g-PMA-*b*-PNAM-*b*-PSt and recycled Si-CTA obtained by cycles I and II.

Table S1. Synthesis of various polymers by RAFT polymerization using CPADB as an original CTA^a

run	CTA	M	solvent	[M] ₀ /[CTA] ₀	t (h)	C%	M _n (th)	M _n (GPC)	PDI
1	CPADB	MMA	toluene	160	21	62.3	10200	10100	1.15
2	PMMA	St	toluene	300	22	19.6	16200	16900	1.20
3	PMMA	MA	toluene	120	20	53.6	15700	16400	1.18
4	PMMA	NIPAM	dioxane	100	20	58.8	17700	17800	1.17
5	PMMA	NAM	dioxane	110	20	54.9	18800	17800	1.24
6	PMMA- <i>b</i> -PSt	MA	dioxane	160	21	28.7	20900	21500	1.25
7	PMMA- <i>b</i> -PNIPAM	MA	dioxane	150	21	32.3	22000	22500	1.21
8	PMMA- <i>b</i> -PNAM	MA	dioxane	200	21	32.8	23400	24200	1.22

^a Reaction conditions: [CTA]₀: [AIBN]₀ = 10:1, [AIBN]₀ = 2.0 (runs 1 to 5) or 1.0 mmol/L (runs 6 to 8), T = 60 °C. The macro CTAs PMMA (runs 2 to 5), PMMA-*b*-PSt (run 6), PMMA-*b*-PNIPAM (run 7) and PMMA-*b*-PNAM (run 8) were synthesized by runs 1, 2, 4 and 5, respectively.

Table S2. Synthesis of various polymers by RAFT polymerization using MPPT as an original CTA^a

No	CTA	M	solvent	[M] ₀ /[CTA] ₀	t (h)	C%	M _n (th)	M _n (GPC)	PDI
1	MPPT	St	bulk	180	22	38.8	7490	7880	1.06
2	MPPT	<i>t</i> BA	toluene	100	20	95.5	12500	11800	1.12
3	PSt	MA	toluene	110	20	82.5	15700	16600	1.10
4	PSt	NIPAM	dioxane	80	20	73.2	14500	13500	1.24
5	PSt	DMA	dioxane	80	20	72.8	13700	13800	1.22
6	PSt	NAM	dioxane	80	20	70.1	15800	14600	1.11
7	PSt- <i>b</i> -PNIPAM	MA	dioxane	120	21	50.8	18700	19500	1.24
8	PSt- <i>b</i> -PDMA	MA	dioxane	100	21	47.9	17900	18000	1.18
9	PSt- <i>b</i> -PNAM	MA	dioxane	160	21	54.8	22100	22600	1.19

^a Reaction conditions: [CTA]₀: [AIBN]₀ = 10:1, [AIBN]₀ = 3.0 (run 2), 2.0 (runs 3 to 6) or 1.0 mmol/L (runs 7 to 9), in bulk (run 1) or solution (other runs) at 60 °C. The macro CTAs PSt (runs 3 to 6), PSt-*b*-PNIPAM (run 7), PSt-*b*-PDMA (run 8) and PSt-*b*-PNAM (run 9) were synthesized by runs 1, 4, 5 and 6, respectively.

Table 3S. Synthesis of silica-polymer hybrids by chain exchange reaction^a

run	Macro CTA	$M_n(a)^b$	PDI(a) ^b	$M_n(g)^c$	PDI(g) ^c	$G_r(\%)^d$	$G_p(\mu\text{mol/g})^e$
1	PMMA	10100	1.15	9970	1.12	18.3	18.4
2	PSt	7880	1.06	7960	1.05	19.2	24.1
3	PMMA- <i>b</i> -PSt	16900	1.20	16600	1.13	22.8	13.7
4	PMMA- <i>b</i> -PMA	16400	1.18	16500	1.12	30.9	18.7
5	PMMA- <i>b</i> -PNIPAM	17800	1.17	18000	1.12	25.5	14.2
6	PMMA- <i>b</i> -PNAM	17800	1.24	18100	1.16	28.7	15.9
7	PSt- <i>b</i> -PMA	16600	1.10	16800	1.05	22.8	13.6
8	PSt- <i>b</i> -PNIPAM	13500	1.24	13600	1.17	22.5	16.5
9	PSt- <i>b</i> -PDMA	13800	1.22	13500	1.16	20.4	15.1
10	PSt- <i>b</i> -PNAM	14600	1.11	14800	1.06	23.6	15.9
11	PMMA- <i>b</i> -PSt- <i>b</i> -PMA	21500	1.25	21100	1.12	24.2	11.5
12	PMMA- <i>b</i> -PNIPAM- <i>b</i> -PMA	22500	1.21	22400	1.12	25.9	11.6
13	PMMA- <i>b</i> -PNAM- <i>b</i> -PMA	24200	1.22	23600	1.14	25.4	10.8
14	PSt- <i>b</i> -PNIPAM- <i>b</i> -PMA	19500	1.24	19300	1.15	24.6	12.7
15	PSt- <i>b</i> -PDMA- <i>b</i> -PMA	18000	1.18	18100	1.12	25.7	14.2
16	PSt- <i>b</i> -PNAM- <i>b</i> -PMA	22600	1.19	22200	1.08	24.1	10.9

^a Reaction conditions: [Macro CTA]₀: [Si-BTPT]₀: [AIBN]₀ = 1:1:1, [AIBN]₀ = 2.0 mmol/L, in toluene at 60 °C for 24 h, and the loading of Si-BTPT was 0.203 mmol CTA per g of fumed silica. ^b Molecular weight and polydispersity of as-prepared PMAs (macro CTAs) determined by GPC, and various macro CTAs were synthesized by RAFT process using MPPT as an original mediator. ^c Molecular weight and polydispersity of de-grafted PMAs obtained by aminolysis. ^d Weight grafting ratio determined by TGA. ^e Apparent molar grafting ratio calculated by $G_p = G_r/M_n(g)$.