Supporting Information

Synthesis of silica-polymer hybrids by combination of RAFT polymerization and azide-alkyne cycloaddition 'click' reaction

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Synthesis of *S*-azidepropoxycarbonylethyl *S'*-methoxycarbonylphenylmethyltrithiocarbonate (AMP). To a 250-mL round flask was added 3.30 g (10.0 mmol) of MPPA, 1.05 g (10.4 mmol) of 3-azide-1-propanol, 0.15 g of (1.23 mmol) of 4-dimethylaminopyridine (DMAP) and 100 mL of freshly distilled dichloromethane under nitrogen, and then to the stirring reaction mixtures cooled with ice-water bath was added dropwise 2.26 g (99%, 10.8 mmol) of *N,N'*-dicyclohexylcarbodiimide (DCC) in 20 mL of dichloromethane in 1 h. After warming to room temperature, the solution was stirred overnight. The resultant precipitate was removed by filtration, and the crude products were subjected to flash chromatography using petroleum ether/ dichloromethane mixtures (2:1, v/v). The desired chain transfer agent AMP (4.05 g, 98.1% yield) was isolated as a yellow viscous oil. ^{1}H NMR ($CDCl_3$): δ 7.35 (m, 5H, PhH), 5.80 (s, 1H, CH), 4.19 (t, *J*6.0, 2H, CH_2O), 3.74 (s, 3H, CH_3), 3.60 (t, *J*6.8, 2H, CH_2S), 3.38 (t, *J*6.8, 2H, CH_2N_3), 2.76 (t, *J*6.8, 2H, CH_2CO), 1.90 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 221.2 (C=S), 171.1, 169.3 (C=O), 132.9, 129.1, 129.0, 128.7 (PhC), 61.9, 57.9, 53.2, 48.1, 32.9, 31.5, 28.0. FTIR (cm^{-1}): 3545, 3472, 3414, 3063, 3031, 2953, 2099 (C-N_3), 1732 (C=O), 1638, 1617, 1601, 1585, 1495, 1454, 1434, 1413, 1392, 1355, 1159, 1070, 1008, 924, 820, 697. Anal. calcd for $C_{16}H_{19}N_3O_4S_3$: C, 46.47%; H, 4.63%; N, 10.16%; S, 23.26%. Found: C, 46.65%; H, 4.61%; N, 10.09%; S, 23.14%. EI-TOF-MS: m/z = 413.0541; theoretical value: 413.0538.

Synthesis of Si-alkyne. The alkyne-functionalized silica was synthesized according to a method similar to the literature.[1] To a slurry of 20 g of activated flash silica in 150 mL of toluene was added 5.20 g (95%, 20 mmol) of 4-(chloromethyl)phenyltrimethoxysilane under nitrogen. The reaction mixtures were heated to 85 ^{o}C for 16 h. After cooling to room temperature, the benzylchloride-functionalized silica (Si-Cl) was filtered and thoroughly washed with toluene and diethyl ether. After drying under vacuum at 40 ^{o}C overnight, 20.5 g of Si-Cl was obtained. Elemental analysis: C, 4.251%, H, 0.472%, Cl, 1.60% (loading of 0.451 mmol/g). FT-IR: 1614, 1558, 1454, 1400, 1099, 946, 809, 733, 702, 470 cm^{-1}.

To a round flask was added 1.20 g (30 mmol) of NaOH, 8.44 g (151 mmol) of propynol and 100 mL of DMF. The mixtures were stirred at ambient temperature for 1 h, and 10 g (4.51 mmol) of Si-Cl was then added to the flask under nitrogen. The mixtures were reacted at 40 ^{o}C for 18 h and then cooled to room temperature. The alkyne-functionalized silica particles (Si-alkyne) were filtered, washed with THF, THF/water (1:1) mixture, distilled water, acetone, toluene and acetone, respectively. After drying under vacuum, 9.8 g of Si-alkyne was obtained. Elemental analysis: C, 5.810%, H, 0.622% (loading of 0.433 mmol/g, 96% substitution). FT-IR: 3325, 3250, 1641, 1547, 1480, 1099, 960, 807, 725, 676, 468 cm^{-1}.

Reference

1 Urbani, C. N.; Bell, C. A.; Lonsdale, D. E.; Whittaker, M. R.; Monteiro, M. J. *Macromolecules* **2007**, *40,* 7056–7059.

Table S1. Synthesis of azide-functionalized polymers as listed in Table 1 by RAFT polymerization mediated by AMP and various macro chain transfer agents[a]

run	CTA	M	$[M]_0/[CTA]_0$	C%[b]	M_n(th)[c]	M_n(GPC)[d]	PDI[d]
1	AMP	MMA	100	60.2	6440	8700	1.43
2	AMP	St	200	26.3	5890	5830	1.10
3	AMP	NIPAM	100	78.6	9300	8760	1.12
4	PSt	NAM	100	45.6	12300	12200	1.10
5	PSt	NIPAM	80	44.4	9840	9360	1.15
6	PSt	SA	100	47.8	14700	13800	1.12
7	PSt	*t*BA	120	56.3	14500	14800	1.10
8	PSt-*b*-PNAM	NIPAM	100	41.2	16900	17400	1.17
9	PSt-*b*-PNAM	DMA	100	43.1	16500	16900	1.23
10	PSt-*b*-PSA	MA	100	46.2	17800	18300	1.11
11	PSt-*b*-PNAM-*b*-PNIPAM	*t*BA	200	32.4	25700	24800	1.20
12	PSt-*b*-PNAM-*b*-PDMA	*t*BA	200	34.7	25800	25500	1.22

[a] Reaction conditions: $[CTA]_0:[AIBN]_0 = 10:1$, $[M]_0 = 3.0$ mol/L (runs 1 to 3), $[AIBN]_0 = 2.0$ (runs 4 to 7), 1.0 (runs 8 to 10), and 0.80 (runs 11 and 12) mmol/L, in toluene (runs 1, 2 and 7) or dioxane (other runs) at 60 °C for 18 h. Macro CTAs were synthesized by runs 2 (PSt-N_3), 4 (PSt-*b*-PNAM-N_3), 6 (PSt-*b*-PSA-N_3), 8 (PSt-*b*-PNAM-*b*-PNIPAM-N_3) and 9 (PSt-*b*-PNAM-*b*-PDMA-N_3), respectively. [b] Monomer conversion determined by gravimetry. [c] Theoretically calculated molecular weight, $M_n(\text{th}) = M_{w,m} \times C\% \times [M]_0/[CTA]_0 + M_{w,CTA}$, where $M_{w,m}$ and $M_{w,CTA}$ were the molecular weights of monomer and CTA. [d] Molecular weight and polydispersity determined by GPC.

Table S2. Synthesis of azide-functionalized polymers as listed in Table 2 by RAFT polymerization mediated by AMP and various macro chain transfer agents[a]

run	CTA	M	$[M]_0/[CTA]_0$	t (h)	C%[b]	M_n(th)[c]	M_n(GPC)[d]	PDI[d]
1	AMP	St	200	16	23.5	5310	5360	1.08
2	PSt	SA	100	16	41.2	13000	12400	1.12
3	PSt	NAM	100	15	38.8	10800	10200	1.11
4	PSt-*b*-PNAM	NIPAM	100	21	49.5	15800	15600	1.13
5	PSt-*b*-PNAM	DMA	100	21	51.6	15300	14800	1.19

[a] Reaction conditions: $[CTA]_0:[AIBN]_0 = 10:1$, $[AIBN]_0 = 2.0$ (runs 1 to 3), and 1.0 (runs 4 and 5) mmol/L, in toluene (run 1) or dioxane (other runs) at 60 °C. Macro CTAs were synthesized by runs 1 ($PSt-N_3$) and 3 (PSt-*b*-$PNAM-N_3$). [b] Monomer conversion determined by gravimetry. [c] Theoretically calculated molecular weight, $M_n(th) = M_{w,m} \times C\% \times [M]_0/[CTA]_0 + M_{w,CTA}$, where $M_{w,m}$ and $M_{w,CTA}$ were the molecular weights of monomer and CTA. [d] Molecular weight and polydispersity determined by GPC.

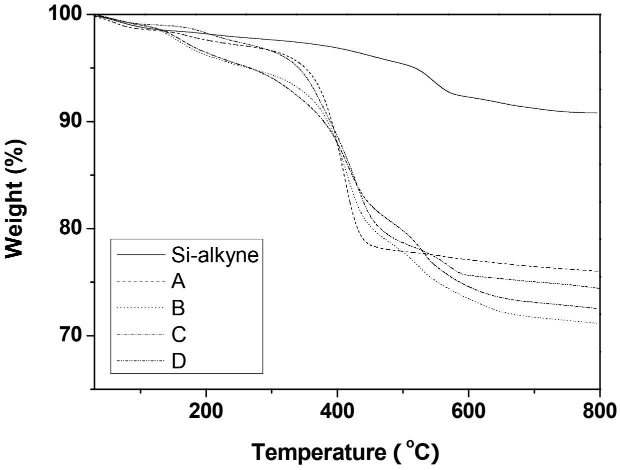

Fig. S1 TGA curves of Si-alkyne and typical silica-polymer hybrids obtained by simultaneous RAFT polymerization and click reaction: A, SiO_2-*g*-PSt; B, SiO_2-*g*-PNAM-*b*-PSt; C, SiO_2-*g*-PMA-*b*-PNAM-*b*-PSt; D, SiO_2-*g*-PMA-*b*-PNIPAM-*b*-PNAM-*b*-PSt.

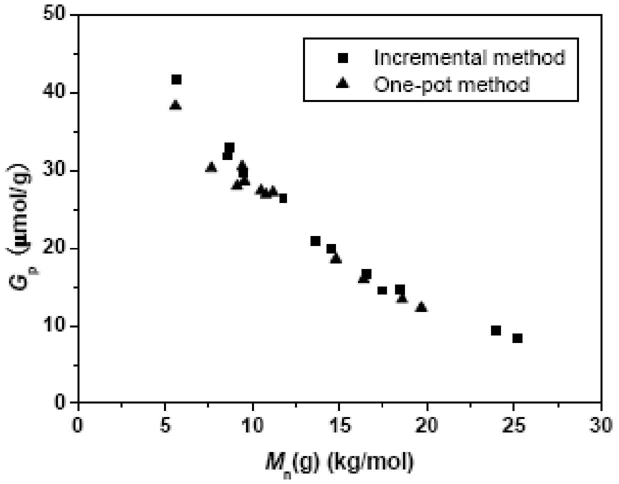

Fig. S2 Dependence of molar grafting ratio on molecular weight of various grafted polymers. See Tables 1 and 2 for detailed reaction conditions for both methods, and each symbol stands for a different grafted sample comprised of homopolymers, di-, tri- and tetrablock copolymers.

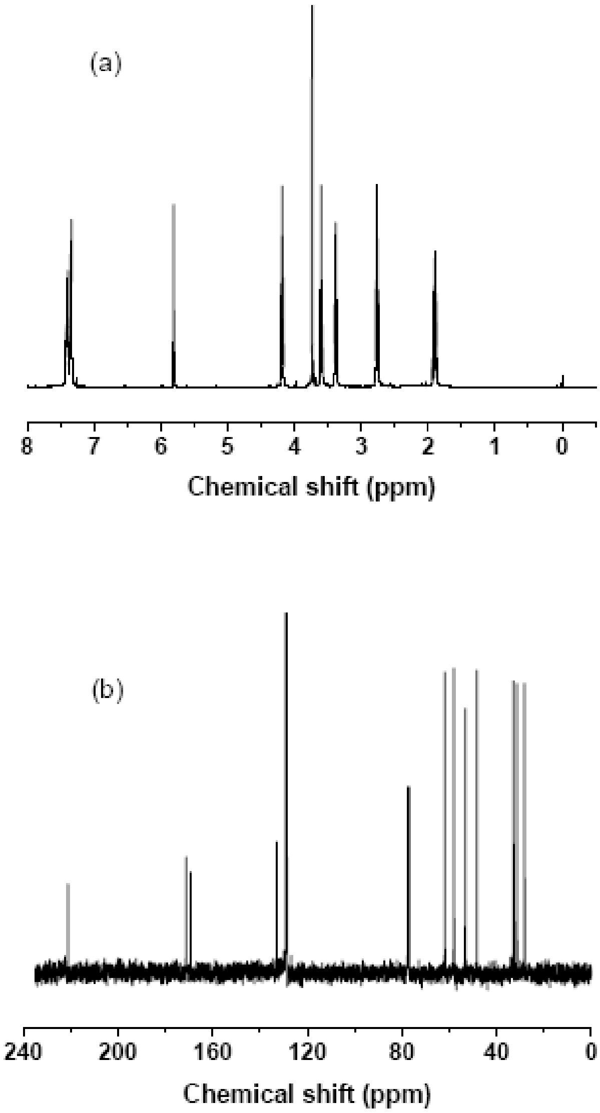

Fig. S3 ^{1}H (a) and ^{13}C (b) NMR spectra of *S*-azidepropoxycarbonylethyl *S'*-methoxycarbonyl phenylmethyl trithiocarbonate (AMP).