Front. Chem. China 2011, 6(3): 213–220
DOI 10.1007/s11458-011-0253-6

RESEARCH ARTICLE

Facile synthesis of silica-polymer hybrids via simultaneous RAFT process and hydroxyl-alkoxysilane coupling reaction

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This study aimed at the synthesis of silica particles grafted with better-defined homopolymers and block copolymers by tandem approach. Z-functionalized *S*-benzyl *S*'-(3-trimethoxysilyl)propyltrithiocarbonate (BTPT) was used as a couplable RAFT agent to synthesize the target inorganic-organic hybrids. Simultaneous coupling reaction and RAFT process using silica particles and BTPT as raw materials efficiently afforded homopolymers grafted silica, and RAFT-synthesized macro chain transfer agents with *ω*-terminal trimethoxysilane moiety were utilized to mediate graft reaction to prepare silica particles grafted with di-, tri- and tetrablock copolymers comprised of polymer segments such as polystyrene, polyacrylamides and polyacrylates. When the grafted chains had molecular weights ranging between 3920 and 24800 g/mol, the molar grafting ratios, which were dependent on reaction conditions and types and compositions of grafted chains, were estimated to be in the range of 15.2–101 μmol/g, and grafted polymers usually had polydispersity indices lower than 1.3, revealing that the grafting process was almost controllable. To the best of our knowledge, this versatile tandem approach is one of the most facile techniques to prepare silica particles grafted with polymeric chains with controlled molecular weight, low polydispersity and precise composition due to its minimal reaction steps, mild conditions, straightforward synthesis and satisfactory controllability.

Received September 16, 2011; accepted September 21, 2011

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Keywords hybrid material, reversible addition fragmentation chain transfer (RAFT), coupling reaction, block copolymer, surface modification

1 Introduction

Synthesis and properties of inorganic-organic hybrid materials have attracted much attention due to their potential applications in many fields involving materials science and biotechnique [1–16]. Among them, silica particles are solid supports of choice to construct the target hybrids due to their excellent mechanical stability, low costs and variable particle sizes and specific surface area [1–4]. Development in controlled radical polymerization (CRP) techniques [17–24] enables the synthesis of silica particles grafted with complex macromolecular architectures such as block copolymers, comb-like copolymers and hyperbranched polymers. Among them, block copolymers grafted silica have been achieved via CRP approaches. However, examples of tri- and tetrablock copolymers grafted silica are scarce [25–27]. The introduction of multicomponent grafted chains into hybrid materials is of great importance since they may endow the materials with novel properties such as stimuli-responsive properties, microphase-separated structures and self-assembly behaviors different from their linear analogues. Thus, the development of synthetic methodology on facile synthesis of solid substrates grafted with well-defined multiblock copolymers is extremely urgent.

In general, both “grafting to” and “grafting from” approaches based on CRP techniques can be utilized for surface modification of solid substrates [28]. The former approach based on straightforward synthesis usually affords high grafting density. However, notable defects such as dead chains and low-component impurities on surface are always present due to unavoidable side reactions like chain termination and irreversible chain transfer, and thus the grafted copolymers are liable to lack precisely controlled chemical compositions. The latter approach using prefabricated polymers gives access to well-defined grafted chains on solid supports, but the grafting density is relatively low due to significant shielding effect. More recently, Z-supported RAFT graft reaction (a) [29–33] and its derivative methods such as coupling reaction (b) using Z-functionalized RAFT-synthesized polymers [25,26] and chain exchange reaction (c) using Z-supported chain transfer agent (CTA) and normal RAFT-synthesized polymers [27] have been developed to synthesize solid supports grafted with well-defined block copolymers up to tetrablock. Followed by a subsequent degrafting process, these methods can be generally used for the synthesis of highly pure block copolymers. Although approaches a, b and c possess many advantages and enable the synthesis of "living" polymeric chains grafted onto solid substrates in which the bonding position is of quantitative thiocarbonyl thio functionality, multistep syntheses are usually necessary, thus it is very urgent to develop a synthetic route with less reaction steps and similar controllability.

This study aimed at the synthesis of homopolymers and block copolymers grafted silica via tandem approach in which RAFT polymerization and hydroxyl-alkoxysilane coupling reaction were conducted simultaneously. Z-functionalized *S*-benzyl *S*'-(3-trimethoxysilyl)propyltrithiocarbonate (BTPT) and its derivative RAFT-synthesized polymers were used as couplable RAFT agents to synthesize the target inorganic-organic hybrids, and effects of reaction conditions on graft reaction were investigated. Since silica particles do not need further modification before graft reaction, and it only needs *n*-step reaction to obtain *n*-block copolymer grafted silica, this facile approach is very promising for surface modification. The success of this study paves way for chemical modification of hydroxyl-rich surface with polymeric segments with multicomposition and adjustable sequence.

2 Experimental

2.1 Materials

All solvents, monomers, and other chemicals were purchased from Alfa Aesar unless otherwise stated. Silica gel (Qingdao Haiyang Chemical Co., Ltd) had an average particle size of 10 µm, BET specific surface area of 297.1 m^2/g, and an average pore size of 11.5 nm. 3-(Mercaptopropyl)trimethoxysilane (95%) was purchased from Lancaster. *S*-benzyl *S*'-(3-trimethoxysilyl)propyltrithiocarbonate (BTPT) was synthesized according to our previous method [31]. Methyl acrylate (MA, 99%), *tert*-butyl acrylate (*t*BA, 98%), butyl acrylate (BA, 99%), *N*,*N*-dimethylacrylamide (DMA, 99%), and styrene (St, 99%) were passed through basic alumina column, dried over CaH_2 and distilled under reduced pressure. *N*-Isopropylacrylamide (NIPAM, 97%) was recrystallized twice from mixtures of hexane and toluene. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol. Toluene and dioxane were distilled over sodium and benzophenone before use. Other solvents that are of analytical grade were obtained from Sinopharm Chemical Reagent Co., Ltd. and used as received.

2.2 Synthesis of PMA grafted silica by one-pot method

0.29 g (0.80 mmol) of BTPT, 13.2 mg (0.080 mmol) of AIBN, 13.8 g (160 mmol) of MA and 38.0 mL of dry toluene under nitrogen were added into a 100 mL round flask. The mixtures were stirred for 30 min and equally subdivided into 8 portions. After adding 0.20 g of silica particles into each Shlenk tube, the reaction mixture was degassed with three freeze-evacuate-thaw cycles and polymerized in a sealed tube at 60°C. At timed intervals, the glass tube was removed from the oil bath and cooled to room temperature. The contents were diluted with dry THF and concentrated under reduced pressure until a constant weight, and then monomer conversion was determined by gravimetry. Free PMA produced in solution was isolated by filtration and precipitation into cold hexane; and PMA grafted silica was recovered by extraction with dichloromethane in a Soxhlet apparatus overnight.

Other homopolymers tethered silica was synthesized and purified according to similar procedures, and free polymers were recovered by concentration under reduced pressure (for PBA) or precipitation into cold methanol, hexane or diethyl ether (for other polymers).

2.3 Synthesis of macro chain transfer agents via RAFT process

St (41.7 g, 400 mmol), BTPT (0.725 g, 2.0 mmol), and AIBN (33.0 mg, 0.20 mmol) were added into 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 30 min. The tube was subsequently immersed into an oil bath preheated to 60°C. After 20 h, the polymerization was stopped by cooling the tube in ice water. Z-functionalized PSt (11.7 g, 26.3% of conversion) was obtained by concentration and precipitation into cold methanol twice. The molecular weight and polydispersity of PSt obtained by GPC were $M_n(\mathrm{GPC}) = 5390$, PDI = 1.19.

Other homopolymers, di-, and triblock copolymers were synthesized and purified according to similar procedures with use of BTPT and its derivative macro CTAs as mediators.

2.4 Synthesis of silica particles grafted with block copolymers by tandem approach

In a typical run, MA (1.72 g, 20 mmol), PSt (0.54 g, 0.10 mmol), AIBN (2.0 mg, 0.012 mmol) and silica particles (0.20 g) were added into a glass tube. The contents were stirred for 15 min and degassed with three freeze-evacuate-thaw cycles. After the contents had been polymerized in a sealed tube at 60°C for 20 h, the glass tube was immediately cooled to room temperature. The contents were diluted with dry THF and concentrated under reduced pressure until a constant weight, and monomer conversion (70.9%) was determined by gravimetry. Free PSt-*b*-PMA produced in solution was isolated by filtration and precipitation into cold hexane; and PSt-*b*-PMA grafted silica (about 0.26 g) was recovered by extraction with dichloromethane in a Soxhlet apparatus overnight.

Grafted PSt-*b*-PMA was obtained by aminolysis with use of 10-fold excess of *n*-hexylamine and 20-fold excess of methyl methanethiosulfonate in THF at ambient temperature [34]. The molecular weight and polydispersity of free and grafted PSt-*b*-PMA copolymers estimated by GPC analysis were $M_n(f) = 19600$, PDI(f) = 1.25; $M_n(g) = 14400$, PDI(g) = 1.20. The weight ($G_r = 33.2\%$) and molar ($G_p = 23.1$ μmol/g) grafting ratios were obtained by TGA using equations $G_r = W_{\text{Si-polymer},100}/W_{\text{Si-polymer},800} - W_{\text{SiO}_2,100}/W_{\text{SiO}_2,800}$ and $G_p = G_r/M_n(g)$, where $W_{\text{Si-polymer},T}$ and $W_{\text{SiO}_2,T}$ are the residual weight percent of silica-polymer hybrids and silica particles at temperature of T, and $M_n(g)$ is the molecular weight of grafted polymer.

2.5 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 Ultrastyragel columns with 10 μm 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, polystyrene samples were calibrated with PSt standard samples; other samples were calibrated using PMMA standard samples. ^{1}H NMR spectra (400 MHz) were recorded on a Varian spectrometer at 25°C using $CDCl_3$ as a solvent. Thermal gravimetric analysis (TGA) was carried out using a Perkin-Elmer Pyris 6 TGA instrument with a heating rate of 10°C/min under nitrogen. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer 2000 spectrometer using KBr disks.

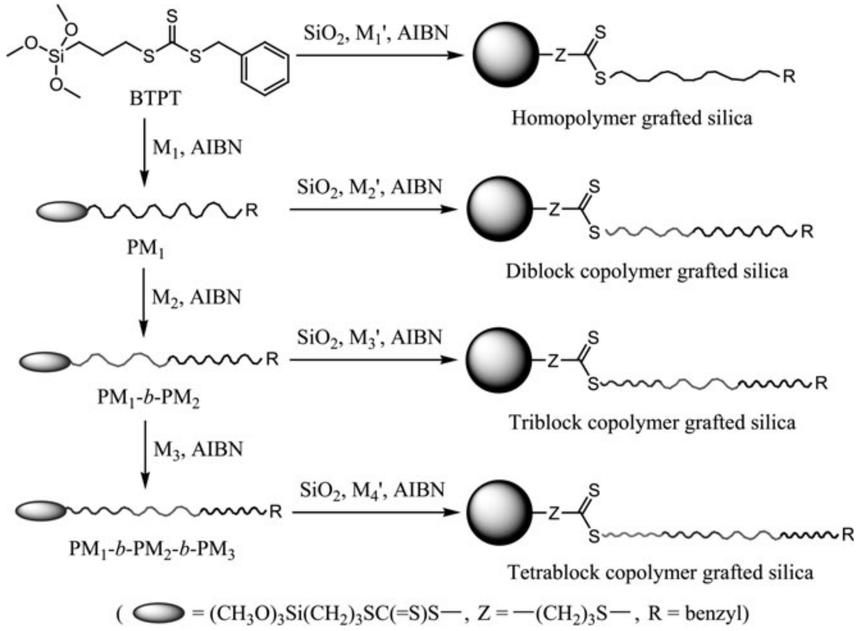
3 Results and discussion

In this study, Z-alkoxysilane-functionalized BTPT was used as an original couplable RAFT agent to prepare silica-polymer hybrids via one-pot method. RAFT polymerization of MA in the presence of silica particles was performed to investigate effects of reaction time and feed ratio on the graft reaction. On this basis, silica particles grafted with other homopolymers and block copolymers up to tetrablock were synthesized to confirm the versatility and generality of this tandem approach using Z-functionalized RAFT agents (Scheme 1).

3.1 Synthesis of PMA grafted silica by tandem approach

To investigate the controllability of simultaneous RAFT polymerization and coupling reaction, BTPT mediated RAFT polymerization in the presence of silica particles was performed. Graft polymerization of MA was taken as a typical example to investigate the effects of reaction time and feed ratio on tandem reaction. First, the graft reaction under fixed conditions ($[\text{MA}]_0:[\text{BTPT}]_0:[\text{AIBN}]_0 = 200:1:0.1$, $[\text{MA}]_0 = 3.0$ mol/L, $m_{\text{BTPT}}/W_{\text{SiO2}} = 0.50$ mmol/g) was conducted in toluene at 60°C for different time, and the reaction kinetics was investigated. Pseudo-first-order kinetics was observed when monomer conversion was less than 83.1%, and an induction period of about 0.6 h was noted in kinetic curves (Fig. 1). With increasing conversion, the molecular weights of free and grafted polymers were almost linearly increased, and the polydispersity indices (PDI) of free and grafted polymers were usually comparable and ranged between 1.16 and 1.25 (Fig. 2), revealing that the grafting process was of satisfactory controllability. When monomer conversion increased from 25.3% to 93.2%, the $M_n(g)$ values increased from 4050 to 11200 g/mol, and the $M_n(g)/M_n(f)$ values gradually decreased from 0.84 to 0.63. SiO_2-*g*-PMA obtained at 25.3% conversion had molar grafting ratio (G_p) of 53.3 μmol/g, but no significant change in G_p values was noted as monomer conversion got beyond 52.4% (Fig. 3). These results could be ascribed to different degrees of shielding effect and rates of addition-fragmentation chain transfer in solution and on surface. The graft reaction using Z-functionalized RAFT agent was similar to Z-supported RAFT graft polymerization [29–33], in which all the chain propagation and termination reactions happened in solution, chain transfer reactions existed in solution and on surface, and only efficient addition-fragmentation chain transfer on substrate surface could result in the target silica-polymer hybrids. At low conversion, the steric hindrance was not obvious owing to relatively short chains, and the rates of addition-fragmentation chain transfer in solution and on surface were similar. Therefore, $M_n(g)$ was close to $M_n(f)$. At high conversion, the chains were long enough to hinder polymeric radicals from approaching the surface in order to conduct further coupling reaction and addition-fragmentation chain transfer, thus $M_n(g)/M_n(f)$ tended to decrease gradually. Two major factors can affect the grafting density during the tandem reaction. One is the coupling reaction which is liable to enhance the grafting density as it can be theoretically performed from start to end if the surface hydroxyl is active enough. The other factor is the shielding effect which usually results in decreased grafting density especially at high conversion. Our results showed that the molar grafting ratios only fluctuated between 41.0 and 42.6 μmol/g as monomer conversion was beyond 52.4%, which indicated that both the roles roughly counteracted each other at high conversion.

Second, effects of feed ratios of monomer to CTA on graft reaction were investigated. The tandem reactions ($[\text{MA}]_0$:



Scheme 1 Synthesis of homopolymers and block copolymers grafted silica via tandem coupling reaction and RAFT polymerization mediated by Z-alkoxysilane-functionalized RAFT agent

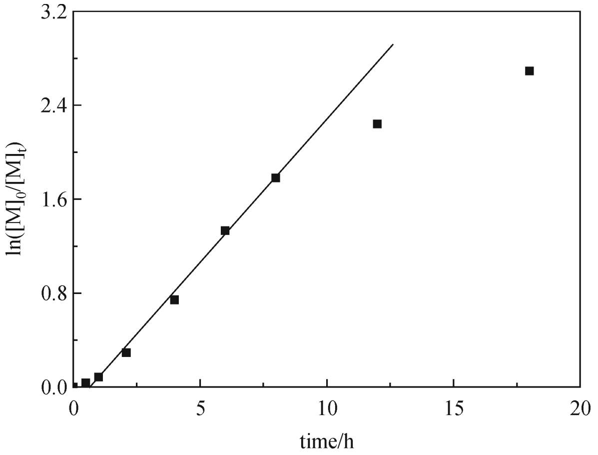


Figure 1 Pseudo-first-order kinetic curves for one-pot RAFT graft polymerization of MA mediated by BTPT. Reaction conditions: $[MA]_0$:$[BTPT]_0$:$[AIBN]_0$ = 200:1:0.1, $[MA]_0$ = 3.0 mol/L, m_{BTPT}/W_{SiO_2} = 0.50 mmol/g, in toluene at 60°C.

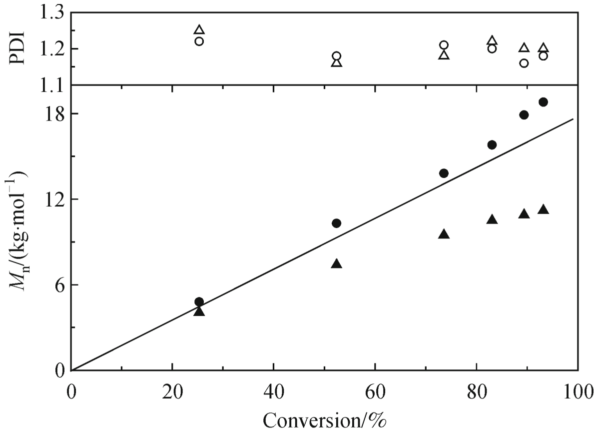


Figure 2 Dependence of M_n and PDI of free (circle) and grafted (triangle) PMAs on conversion. See Fig. 1 for polymerization conditions.

$[BTPT]_0$ = 50, 100, 300 or 400, $[BTPT]_0$:$[AIBN]_0$ = 10, $[MA]_0$ = 3.0 mol/L, m_{BTPT}/W_{SiO_2} = 0.50 mmol/g) were performed in toluene at 60°C for 18 h, and the results are listed in runs 1–5 of Table 1. As can be seen, typically, free polymers had molecular weights similar to the theoretical values, and both of them were higher than those of grafted polymers. As the feed ratio of monomer to CTA increased from 50 to 400, molecular weights of grafted PMA increased from 3920 to 17100 g/mol, while molar grafting ratio gradually decreased from 101 to 24.8 μmol/g. The shielding effect during grafting process became increasingly pronounced, evident from gradually broadened molecular weight distribution, lowered molar grafting ratios and decreased $M_n(g)/M_n(f)$ values with the increasing chain length of grafted polymers (Fig. 4). The polydispersity indices of grafted polymers varied between 1.17 and 1.32, suggesting that better-defined PMA grafted silica could be obtained even if the grafted polymers had molecular weight up to 17100 g/mol.

Last, the one-pot method was also used to prepare silica particles grafted with other homopolymers such as PSt, PDMA and PBA (runs 6–8 of Table 1). As expected, free polymers usually had molecular weight similar to the theoretical value, while grafted polymers were of shorter

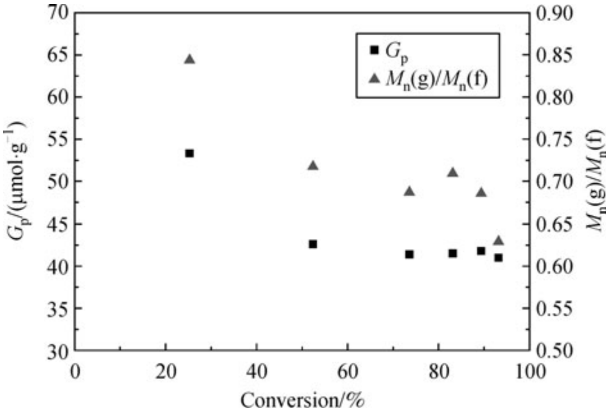


Figure 3 Effects of conversion on weight and molar grafting ratios of PMA grafted silica. See Fig. 1 for polymerization conditions.

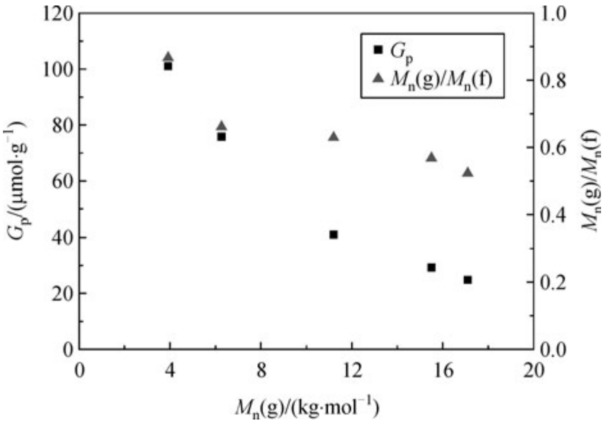


Figure 4 Dependence of molar grafting ratio and $M_n(g)/M_n(f)$ on molecular weight of grafted chains during tandem reaction to synthesize PMA grafted silica. See runs 1–5 of Table 1 for reaction conditions.

chain length due to obvious shielding effect and lowered rate of addition-fragmentation chain transfer on surface than that in solution. The grafted polymers had polydispersity indices in the range of 1.16–1.28, which were close to those of their corresponding free polymers. These results were in good agreement with “living”/controlled radical polymerization and confirmed the versatility and generality of the tandem approach for surface modification. Another finding is that the grafting density is significantly affected by the types of grafted chains. With a careful inspection of the results in Table 1, it was found that the molar grafting ratios decreased in the order PMA> PBA> PDMA> PSt as the molecular weights of grafted chains were comparable. For instance, when the tandem reaction using a feed ratio of 100 was utilized to synthesize the silica-polymer hybrids, the molar grafting ratio of PMA grafted silica (75.8 μmol/g) was much higher than that of PDMA grafted silica (52.2 μmol/g) although the $M_n(g)$ values were quite similar. This phenomenon could be attributed to different radical stability and steric hindrance during graft reaction and distinct chain flexibility and conformation originated from different chain rigidity. The radical stability would affect the rate of addition-fragmentation chain transfer on surface and in solution, and other factors also played a crucial role in affecting the probability and rate of polymeric radicals to approach the substrate surface in the performance of the graft process. As compared with previously developed Z-supported RAFT graft polymerization [29–33], the tandem approach has at least some advantages as follow. First, it uses the least reaction steps lacking any catalyst due to its straightforward synthesis. Second, other free CTA is unnecessary during polymerization since Z-alkoxysilane-functionalized RAFT agent acts as both free CTA and the coupling agent during the tandem process. Last, higher grafting density is expected to be achieved now that the unmodified substrate possesses larger specific surface area than CTA-tethered solid support, which endows the RAFT agent and chain radical with enhanced probability to approach the substrate surface in the performance of the graft reaction. The grafting density, as listed in Table 1, was estimated to be in the range of 0.05–0.20 chains/nm^2. This result was similar to or better than that obtained from Z-supported RAFT graft reaction [29–33] or the coupling reaction using Z-functionalized RAFT-synthesized polymers [25,26], supporting the above-mentioned viewpoints.

The above results proved that BTPT mediated RAFT graft polymerization in the presence of silica particles could afford surface-tethered polymeric chains with nearly controlled molecular weight, relatively low polydispersity and satisfactory grafting density.

3.2 Synthesis of block copolymers grafted silica via tandem approach

Although block copolymers up to tetrablock grafted silica has been achieved by us recently [25–27], synthesis of solid supports grafted with multiblock copolymer with high grafting density remains difficult. The approaches based on “grafting from” method can afford hybrid materials with high grafting density. However, the surface-bound block copolymers usually possess complex compositions. For example, in addition to the target block copolymers, undesired grafted chains such as homopolymers, low-component polymers and loop-like polymeric chains may be present due to the loss of reactive end functionality, low efficiency during chain extension polymerization, and unavoidable irreversible termination and chain transfer. In this study, the tandem

Table 1 Synthesis of homopolymers grafted silica by tandem approach using BTPT mediator[a]

Run	M	$[M]_0/[BTPT]_0$	C%[b]	M_n(th)[c]	M_n(g)[d]	PDI(g)[d]	M_n(f)[e]	PDI(f)[e]	G_r/%[f]	G_p /(μmol/g)[g]
1	MA	50	90.5	4260	3920	1.24	4520	1.22	39.6	101
2	MA	100	92.4	8320	6270	1.17	9480	1.15	47.5	75.8
3	MA	200	93.2	16400	11200	1.20	17800	1.18	45.9	41.0
4	MA	300	91.2	23900	15500	1.25	27300	1.27	45.2	29.2
5	MA	400	87.3	30400	17100	1.32	32700	1.25	42.4	24.8
6	St	150	30.8	5170	4320	1.28	6200	1.24	18.8	43.5
7	DMA	100	98.8	10200	6360	1.18	11300	1.14	33.2	52.2
8	BA	100	90.5	11900	6950	1.16	12800	1.15	39.7	57.1

a) Reaction conditions: $[BTPT]_0:[AIBN]_0 = 10$, $[M]_0 = 3.0$ mol/L, $m_{BTPT}/W_{SiO_2} = 0.50$ mmol/g, in dioxane (run 7) or toluene (other runs) at 60°C for 18 h; b) Monomer conversion determined by gravimetry; c) Theoretically calculated molecular weight; d) Molecular weight and polydispersity of grafted polymers obtained by aminolysis; e) Molecular weight and polydispersity of free polymers; f) Weight grafting ratio; g) Apparent molar grafting ratio

approach of the synthesis of block copolymer grafted silica was also investigated. To this end, Z-functionalized macro CTAs were synthesized by RAFT processes using BTPT as an original RAFT agent (Table 2). First, RAFT polymerization afforded PSt, PNIPAM and PDMA with predetermined molecular weight and polydispersity lower than 1.2. Second, diblock copolymers PSt-*b*-PNIPAM and PSt-*b*-PDMA were synthesized by chain extension polymerization mediated by PSt ($M_n = 5390$, PDI = 1.19). Last, triblock copolymers PSt-*b*-PNIPAM-*b*-P*t*BA and PSt-*b*-PDMA-*b*-P*t*BA with relatively low polydispersity were also obtained by successive chain extension reaction. Under rigorously unhydrous conditions, these alkoxysilane-functionalized polymers usually had desired molecular weights and polydispersity indices lower than 1.25, and the trimethoxysilane functionality estimated by ^{1}H NMR was usually higher than 0.8.

To investigate the ability to synthesize silica particles grafted with block copolymers via tandem process, simultaneous RAFT polymerization of MA and coupling reaction mediated by various macro CTAs were conducted in toluene or dioxane at 60°C for 20 h (Table 3). A series of di-, tri- and tetrablock copolymers comprising some polymer segments such as PSt, PNIPAM, PDMA, P*t*BA and PMA were covalently grafted onto the surface of silica particles, evident from IR and TGA. In IR spectra, a strong and broad absorption corresponding to the stretching vibration of Si-O bond of the solid supports was noted at about 1080 cm^{-1}, and characteristic absorptions of polymers grafted silica appeared at around 1600 (C = C stretching, PSt), 699 (C-H out of plane bending, PSt), 1654 (C = O stretching, PNIPAM), 1634 (C = O stretching, PDMA), 1740 (C = O stretching, PMA), 1736 (C = O stretching, PBA) and 1729 cm^{-1} (C = O stretching, P*t*BA). By comparing TGA curves of silica particles and silica-polymer hybrids (Fig. 5), the weight grafting ratios were estimated to be in the range of 31.4%–37.8%. On this basis, the apparent molar grafting ratios were obtained to be 15.2–25.4 μmol/g as the grafted copolymers had molecular weights ranging between 13600 and 24800 g/mol. The G_p values were similar to those obtained by Z-supported RAFT graft reaction or the coupling reaction.

The grafted chains were cleaved from silica surface by aminolysis [34], and highly pure block copolymers without or with very limited impurities were obtained. TGA results indicated that all the grafted chains could be quantitatively removed from the substrate surface by aminolysis in 3–5 h, and terminal functionalities such as hydroxyl, carboxyl and amine could be introduced into their chain end if radical-induced addition-fragmentation processes were used [27,29,35]. GPC traces of typical samples are listed in Fig. 6. As compared with macro CTAs, the GPC traces of grafted copolymers lacking notable shoulder and tailing shifted wholly to the higher molecular side, which was in

Table 2 RAFT polymerization of various monomers mediated by BTPT and macro CTAs

Run	CTA	M	$[M]_0/[CTA]_0$	*T* /h	C/%	M_n(th)	M_n(GPC)	PDI
1	BTPT	St	200	20	26.3	5840	5390	1.19
2	BTPT	NIPAM	60	15	88.2	6340	6300	1.16
3	BTPT	DMA	60	15	88.9	5640	5730	1.18
4	PSt	NIPAM	80	18	70.9	11800	11500	1.15
5	PSt	DMA	80	18	73.4	11200	11300	1.14
6	PSt-*b*-PNIPAM	*t*BA	100	20	48.4	17700	17800	1.20
7	PSt-*b*-PDMA	*t*BA	100	20	47.6	17400	18000	1.25

Reaction conditions: $[M]_0 = 3.0$ (runs 2 and 3), 1.5 (runs 4 and 5) or 1.2 (runs 6 and 7) mol/L, $[CTA]_0:[AIBN]_0 = 10$, in bulk (run 1) or dioxane (other runs) at 60°C

Table 3 Synthesis of silica particles grafted with block copolymers by RAFT polymerization of MA mediated by various macro CTAs via one-pot method[a)]

Run	Macro CTA	C/%[b)]	M_n(th)[c)]	M_n(g)[d)]	PDI(g)[d)]	M_n(f)[e)]	PDI(f)[f)]	G_r /%[g)]	G_p /(μmol·g^{-1})
1	PSt	70.9	17600	14400	1.20	19600	1.25	33.2	23.1
2	PNIPAM	61.0	16800	13800	1.22	18300	1.26	32.5	23.6
3	PDMA	67.2	17300	13600	1.25	18600	1.28	34.6	25.4
4	PSt-*b*-PNIPAM	48.2	19800	18200	1.21	22300	1.29	31.4	17.3
5	PSt-*b*-PDMA	53.4	20500	17600	1.18	21200	1.20	35.6	20.2
6	PSt-*b*-PNIPAM-*b*-P*t*BA	38.3	27700	24800	1.22	30200	1.24	37.7	15.2
7	PSt-*b*-PDMA-*b*-P*t*BA	37.5	27700	24200	1.24	29300	1.27	37.8	15.6

a) Reaction conditions: $[M]_0:[CTA]_0 = 200$ (runs 1–5) or 300 (runs 6 and 7), $[M]_0 = 2.0$ mol/L, $[AIBN]_0 = 1.2$ (runs 1–5) or 1.0 (runs 6 and 7) mmol/L, m_{CTA}/W_{SiO_2} = 0.50 mmol/g, in toluene (run 1) or dioxane (other runs) at 60°C for 20 h; b) Monomer conversion determined by gravimetry; c) Theoretically calculated molecular weight; d) Molecular weight and polydispersity of grafted polymers obtained by aminolysis; e) Molecular weight and polydispersity of free polymers; f) Weight grafting ratio; g) Apparent molar grafting ratio

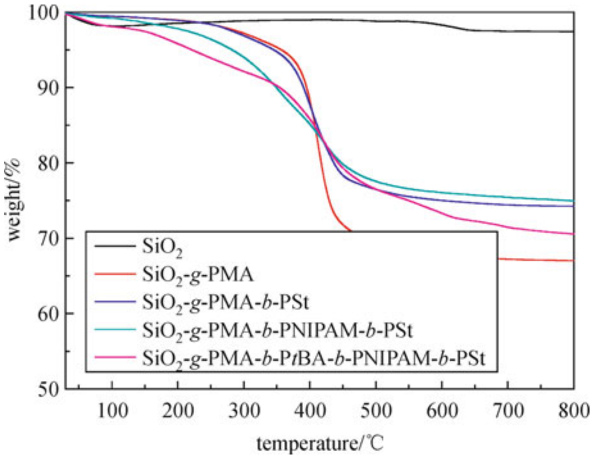


Figure 5 TGA curves of silica particles and typical silica-polymer hybrids. The hybrid samples were synthesized by run 2 of Table 1 and runs 1, 4 and 6 of Table 3.

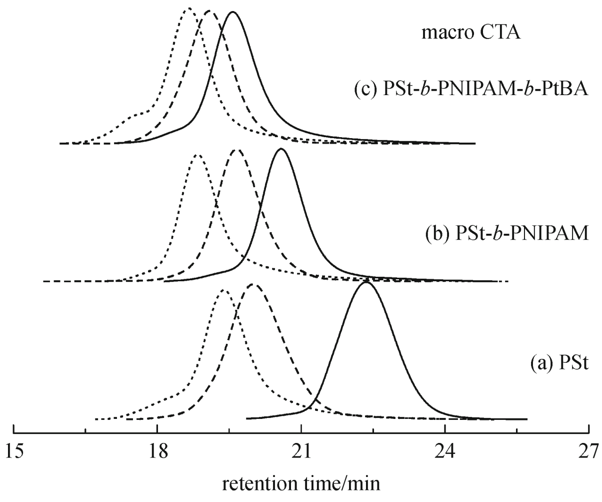


Figure 6 GPC traces of macro CTAs (solid line), free (dotted line) and grafted (dashed line) block copolymers obtained by tandem reaction. Free and grafted copolymers were PSt-*b*-PMA (a), PSt-*b*-PNIPAM-*b*-PMA (b) and PSt-*b*-PNIPAM-*b*-P*t*BA-*b*-PMA (c), respectively. See runs 1, 4 and 6 in Table 3 for detailed reaction conditions.

good agreement with controlled grafting process. On the contrary, significant shoulder and tailing were usually noted in GPC traces of free copolymers produced in solution, which were corresponding to dead chains and polymers resulting from condensation of terminal alkoxysilane. Since dead chains could not be grafted onto the substrate surface during the tandem reaction, the polydispersity indices of grafted copolymers (PDI = 1.18–1.25) were usually slightly lower than those of free polymers formed in solution. All the covalently bonded positions to link grafted chains and substrate surface quantitatively possessed reactive thiocarbonyl thio moieties. Accordingly, the resultant copolymers grafted silica was of 100% livingness in theory and could be utilized for highly efficient chain extension polymerization in the production of silica particles grafted with block copolymers with one more segment as the shielding effect was not significant [25,26,30].

In addition to their potential applications in hybrid materials [1–4] and synthesis of highly pure block copolymers [25–27], these silica-polymer hybrids can also be used as model samples in the investigation of the effects of grafting density and types, compositions and sequences of grafted chains on glass transition temperature of surface-tethered polymers as their relaxation behaviors on restricted surface are quite different from those in bulk and solution. These properties are under study in our laboratory and will be reported later.

4 Conclusions

An original strategy to synthesize silica-polymer hybrids via tandem approach was presented. Z-alkoxysilane-functionalized BTPT was used as an original couplable RAFT agent to prepare the target homopolymers block copolymers grafted silica. IR, TGA and GPC results indicated that the tandem RAFT process and coupling reaction could efficiently afford silica-polymer hybrids with nearly controlled molecular weight, relatively low polydispersity and grafting density similar to or better than that obtained by Z-supported RAFT graft polymerization or coupling reaction using as-prepared RAFT-synthesized polymers. A series of homopolymers, di-, tri- and tetrablock copolymers were successfully grafted onto silica surface, revealing the versatility and generality of the tandem approach. This approach is promising for surface modification of hydroxyl-rich substrate due to its many advantages such as less reaction steps, mild conditions, and satisfactory controllability.

Acknowledgements The financial support from the National Natural Science Foundation of China (Grant Nos. 20844001, 20874067 and 21074081) and the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions is gratefully acknowledged.

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