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Synthesis of Silica Particles Grafted with Well-Defined Living Polymeric Chains by Combination of RAFT Polymerization and Coupling Reaction

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ABSTRACT: A combinatorial approach based on reversible addition−fragmentation chain transfer (RAFT) polymerization and coupling reaction was used to prepare well-defined silica−polymer hybrids. Chain-end-functionalized homopolymers were synthesized by RAFT polymerization of vinyl monomers such as methyl acrylate, butyl acrylate, *N*,*N*-dimethylacrylamide, *N*-isopropylacrylamide, *N*-acrylomorpholine, methyl methacrylate, and styrene mediated by *S*-methoxycarbonylphenylmethyl *S*′-trimethoxysilylpropyltrithiocarbonate in toluene or dioxane at 60 °C, and di-, tri-, and tetrablock copolymers were further synthesized by successive chain extension polymerization. These polymers comprising a trimethoxysilane functionality in the chain end were then grafted to the surface of flash silica by coupling reaction between trimethoxysilane and hydroxyl groups. IR and thermogravimetric analyses results indicated the grafting ratios of polymeric chains on the surface of silica were relatively high. The grafted polymeric chains were cleaved from the surface of silica by aminolysis, and gel permeation chromatography results revealed all the grafted polymers possessed low polydispersity (typically less than 1.2) and molecular weight similar to that of the "as-prepared" polymers. Furthermore, the solid-supported polymeric chains were almost 100% living, evident from highly efficient chain extension polymerization to prepare well-defined block copolymers grafted onto silica particles.

Introduction

The surface modification of inorganic particles and synthetic resins with polymeric chains to form functional core−shell hybrid structures has attracted much attention due to their variable interfacial, mechanical, and thermal properties and potential applications in optics, electronics, engineering, and biosciences.[1−27] Among various solid supports, silica particles are supports of choice to prepare the target inorganic−organic hybrids due to their chemical resistance, mechanical stability, relatively low costs, variable particle sizes, and high specific surface area.[1−4] So far, silica particles coated with well-defined polymeric chains have been achieved by various polymerization techniques. Among them, controlled radical polymerization (CRP) approaches such as nitroxide-mediated polymerization (NMP),[28] atom transfer radical polymerization (ATRP),[29−31] and reversible addition−fragmentation chain transfer (RAFT) polymerization[32−38] have been widely applied to graft polymeric chains onto solid supports since they can afford well-defined polymers with controlled molecular weight, low polydispersity, and variable functionality.

Although CRP techniques enable the functionality in the chain end of polymers, it is still difficult to achieve 100% chain-end functionality after polymerization due to the presence of dead polymers resulting from side reactions such as termination and chain chansfer reactions (Scheme 1, in which the ellipse represents the chain-end functionality).[31] The dead polymeric chains are usually chemically and physically similar to living chains, and they are difficult to be removed, leading to the production of mixtures of pure living block copolymers and dead polymers such as homopolymers and/or block copolymers after chain extension polymerization.[39] As such mixtures may affect physicochemical properties such as thermal properties and self-assembly behaviors of the polymers obtained, it is necessary to develop techniques to prepare highly pure polymers. CRP approaches using reagents bearing one functionality as an initiator (NMP[28] and ATRP)[29,30] or the R group of a RAFT chain transfer agent (CTA)[26,27] provide living polymers with chain-end functionality at the α-chain end as the major products. However, the formation of dead polymers with one or two chain-end functionalities or without functionality is unavoidable due to the occurrence of termination and irreversible chain transfer reactions during polymerization. When the functionality such as a functional group[40] and peptide[41,42] is attached to the CTA as a Z group, however, all the resultant living chains obtained via the RAFT process bear a single functionality at their ω chain end, and the number of dead chains, which do not bear the ω functionality, can be kept very low under optimized reaction conditions. Therefore, this route gives an unprecedented control over the structure of homopolymers and multiblock copolymers and enables the synthesis of well-defined solid-supported living polymers. To date, two major routes have been developed to this end: (a) the Z-group approach in which the RAFT process is directly conducted on the surface of solid supports[10−17] and (b) the grafting to approach in which the Z-functionalized polymers are synthesized by RAFT process, followed by organic reactions such as coupling reaction and click chemistry to attach the polymeric chains to the support. The first approach has been widely investigated, while the second route has not been reported until now to the best of our knowledge.

In our previous studies, the Z-group approach in which the CTA is attached to the backbone via the stabilizing Z group was

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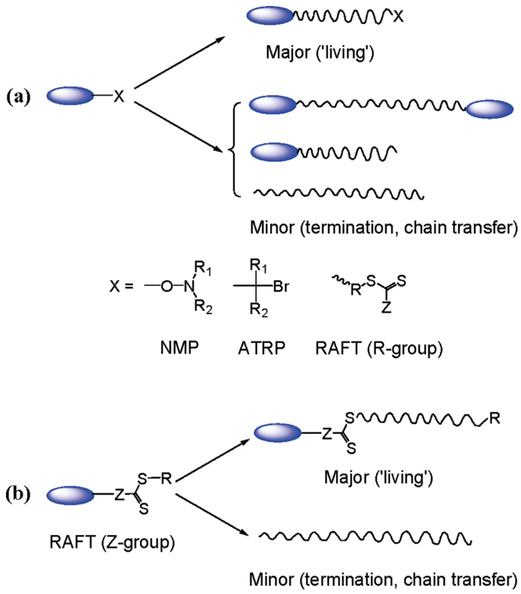
Scheme 1. Living and Dead Polymers Obtained by Controlled Radical Polymerization of Vinyl Monomers Using Various Initiators or Chain Transfer Agents with a Functional Group



developed to synthesize well-defined homopolymers and diblock copolymers grafted onto solid supports such as silica particles and synthetic resins.[10−14] The solid-supported CTAs were used to mediate Z-supported RAFT polymerization of various types of monomers in the presence of a free CTA, leading to the production of well-defined solid-supported polymers. Furthermore, the resultant macro-CTAs were utilized to mediate chain extension polymerization to prepare solid-supported diblock copolymers, demonstrating near perfect living polymers could be attached to the surface of solid supports by Z-supported RAFT polymerization.[13] However, the free and grafted diblock copolymers had quite different molecular weights due to shielding effect, and this phenomenon became increasingly noticeable with an increase in conversion. It is therefore of great challenge to obtain living multiblock copolymers by successive Z-supported RAFT polymerization. More recently, magnetite nanoparticles were successfully utilized by Saoud et al. to prepare ultrapure RAFT polymers such as polystyrene;[39] however, the isolated polymeric chains were relatively short (with molecular weight less than 5000 g/mol). It is still a challenge to prepare highly pure block copolymers with high molecular weight and without dead polymeric chains comprising homopolymers and block copolymers. An alternative approach by combination of RAFT polymerization and coupling reaction was developed to obtain well-defined living grafted polymers in this study. The silica-supported polymers were near 100% living, evident from highly efficient chain extension polymerization of methacrylate to prepare silica-supported block copolymers.

Experimental Section

Materials. All solvents, monomers, and other chemicals were purchased from Aldrich unless otherwise stated. Silica gel (grade 710) with nominal particle size of 9.5−11 μm, BET specific surface area of 472.3 m^2/g, and average pore size of 6.89 nm was purchased from Aldrich. 3-(Mercaptopropyl)trimethoxysilane (95%) was purchased from Lancaster. *S*-Methoxycarbonylphenylmethyl *S*′-trimethoxysilylpropyltrithiocarbonate (MPTT) was synthesized and purified according to our previous method.[13] Methyl acrylate (MA, 99%), *N*,*N*-dimethylacrylamide (DMA, 99%), *N*-acrylomorpholine (NAM, 97%), methyl methacrylate (MMA, 99%), butyl acrylate (BA, 99%), *tert*-butyl acrylate (*t*BA, 98%), and styrene (St, 99%) were distilled over CaH_2 under reduced pressure before use. *N*-Isopropylacrylamide (NIPAM, 97%) was recrystallized twice from mixtures of hexane and toluene prior to use. Dioxane was distilled from CaH_2, and toluene was distilled from metallic sodium and benzophenone. 2,2′-Azobis(isobutyronitrile) (AIBN, 98%) was recrystallized twice from ethanol. Other chemicals were of analytical grade and used as received.

General Procedure for RAFT Homopolymerization. Polymerizations were conducted in dioxane or toluene using AIBN as the primary radical source and MPTT as the functional chain transfer agent. In a typical polymerization (run 5 of Table 1), DMA (1.983 g, 20.0 mmol), MPTT (0.105 g, 0.25 mmol), and AIBN (4.1 mg, 0.025 mmol) were added to a glass tube with a magnetic stirring bar, and dioxane was added until the total volume was 6.67 mL. The tube was sealed with a rubber septum, and the contents were degassed with nitrogen for 10 min. The tube was subsequently immersed into an oil bath preheated to 60 °C. After 21 h, the polymerization was quenched by placing the tube into an ice−water bath. The polymerization solution was drawn and dissolved into $CDCl_3$ to check ^1H NMR, and the monomer conversion was determined to be 99.6% by comparing the integrated areas of characteristic signals of monomer and polymer. After precipitating into a large amount of cold hexane, 2.05 g of PDMA was isolated, and its molecular weight and polydispersity were obtained by gel permeation chromatography (GPC): $M_n = 8460$, PDI = 1.08. Other polymers were synthesized according to a similar approach and obtained by precipitation into cold hexane, diethyl ether, or methanol.

General Procedure for Chain Extension Polymerization. Polymerizations were conducted in dioxane or toluene using trimethoxysilane-functionalized polymers as macro-chain-transfer agents. In a typical polymerization (run 1 of Table 2), PSt (M_n = 8060, PDI = 1.12, 2.42 g, 0.30 mmol), NAM (3.39 g, 24.0 mmol), and AIBN (4.9 mg, 0.030 mmol) were added to a glass tube with a magnetic stirring bar, and dioxane was added until the total volume was 15.0 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 19 h and then quenched by placing the tube into an ice−water bath. The diblock copolymer (3.91 g) was recovered by precipitating its solution into cold hexane, and the monomer conversion was determined to be 44.0% by gravimetry. The molecular weight and polydispersity of PSt-*b*-PNAM were determined by GPC: $M_n = 12\,800$, PDI = 1.15. Other block copolymers were synthesized and recovered according to a similar approach using various macro-CTAs.

Synthesis of Flash Silica Grafted with Homopolymers and Block Copolymers by Coupling Reaction. The coupling reaction between trimethoxysilane in the chain end of functionalized polymers and hydroxyl groups at the surface of silica gel was performed in dioxane or toluene at 80 °C. In a typical run (run 2 of Table 4), PSt (M_n = 8060, PDI = 1.12, 1.00 g), silica gel (0.20 g), and toluene (10.0 mL) were added to a round flask under nitrogen. The reaction was conducted with stirring at 80 °C for 20 h and then cooled to room temperature. The resultant silica−polystyrene hybrid (SiO_2-*g*-PSt) was filtered and washed thoroughly with toluene and THF. After drying at 60 °C under vacuum, 0.27 g of hybrid sample was obtained. The flash silica carrying surface-bound PSt was subjected to aminolysis and TGA measurement. GPC analysis: cleaved grafted PSt, $M_n(g)$ = 8240, PDI(g) = 1.10. The weight (G_r = 37.2%) and molar (G_p = 45.1 μmol/g) grafting ratio of polymeric chains on solid surface was determined by TGA using eqs 1 and 2,[12,13,43] 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, $W_{\text{Si-polymer},800}$ and $W_{\text{SiO}_2,800}$ are the residual weight percent of silica−polymer hybrid and flash silica

Table 1. Reversible Addition–Fragmentation Chain Transfer Polymerization of Various Monomers Mediated by *S*-Methoxycarbonylphenylmethyl *S'*-Trimethoxysilylpropyltrithiocarbonate (MPTT)[a]

run	M	solvent	$[M]_0/[MPTT]_0/[AIBN]_0$	C%[b]	M_n(th)[c]	M_n(GPC)[d]	PDI[d]	M_n(NMR)[e]	f[f]
1	MMA	toluene	100/1/0.1	86.8	9100	13200	1.58	15100	0.87
2	St	bulk	250/1/0.1	29.5	8120	8060	1.12	8200	0.98
3	NAM	dioxane	70/1/0.1	84.5	8780	7250	1.16	7480	0.97
4	NIPAM	dioxane	80/1/0.1	91.8	8750	8570	1.11	9120	0.94
5	DMA	dioxane	80/1/0.1	99.6	8340	8460	1.08	8580	0.99
6	MA	toluene	100/1/0.1	99.2	8980	11600	1.15	12000	0.97
7	BA	toluene	100/1/0.1	98.3	13000	13300	1.15	13600	0.98

[a] Reaction conditions: $[M]_0 = 3.0$ mol/L (for runs except run 2), at 60 °C for 21 h, in which MMA, St, NAM, NIPAM, DMA, MA, and BA stand for methyl methacrylate, styrene, *N*-acryloylmorpholine, *N*-isopropylacrylamide, *N,N*-dimethylacrylamide, methyl acrylate, and butyl acrylate, respectively. [b] Monomer conversion determined by ^{1}H NMR. [c] Theoretically calculated number-average molecular weight, $M_n(\text{th}) = M_{w,m} \times C\% \times [M]_0/[MPTT]_0 + M_{w,MPTT}$, where $M_{w,m}$ and $M_{w,MPTT}$ are the molecular weights of monomer and MPTT. [d] Molecular weight and polydispersity determined by gel permeation chromatography (GPC). [e] Apparent molecular weight determined by comparing the integral of the end-group resonance (ph*H* for PNAM and PMA, CH_2S for PMMA, and $(CH_3O)_3Si$ for other polymers) with that for the characteristic signal of polymeric chains in ^{1}H NMR spectra. [f] Apparent degree of functionality estimated by the equation $f = M_n(\text{GPC})/M_n(\text{NMR})$.

at 800 °C, and $M_{n,GPC}(g)$ is the apparent molecular weight of grafted polymer determined by GPC.

$$G_r = \frac{W_{\text{Si-polymer, 100}}}{W_{\text{Si-polymer, 800}}} - \frac{W_{\text{SiO}_2\text{, 100}}}{W_{\text{SiO}_2\text{, 800}}} \qquad (1)$$

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

Chain Extension Polymerization To Synthesize Block Copolymer–Silica Hybrids. In a typical experiment (run 1 of Table 5), SiO_2-*g*-PSt (macro-CTA, 0.200 g, 6.58 μmol), PSt ($M_n = 8060$, PDI = 1.12, 266 mg, 33.0 μmol), MA (0.850 g, 9.87 mmol), AIBN (50.2 mg of toluene solution with concentration of 12.9 mg/g, 3.95 μmol), and toluene (1.90 mL) were added to a Schlenk tube. The tube was degassed by three freeze–pump–thaw cycles and then put into an oil bath preset to 60 °C for 18 h. After polymerization, the samples were diluted with THF and precipitated into a large amount of hexane thrice. The monomer conversion was determined to be 40.2% by gravimetry. The mixture was diluted with 10 mL of THF, and the clear solution was decanted and precipitated into cold hexane to recover the free polymer. The residual mixture was dispersed and stirred in THF, filtered, and washed thoroughly with toluene and THF. After drying under vacuum, 0.233 g of isolated diblock copolymer–silica hybrid (SiO_2-*g*-PMA-*b*-PSt) was obtained. The weight grafting ratio of block copolymer chains were determined to be 56.2% by TGA. GPC analyses showed that the degrafted PSt-*b*-PMA diblock copolymer had molecular weight of 13 800 and polydispersity of 1.10, and free PSt-*b*-PMA produced in solution had molecular weight of 18 600 and polydispersity of 1.11. Other chain extension polymerizations were performed according to similar procedures in which diblock and triblock copolymers were used as free polymers.

General Procedure for Cleaving the Grafted Polymers. The grafted polymers were cleaved from the solid supports according to a similar method developed by Roth et al.[44] In a typical run, to a glass tube was added 100 mg of SiO_2-*g*-PMA sample, 4.0 mL of THF, and 20.0 μL (0.212 mmol) of methyl methanethiosulfonate. The solution was degassed with nitrogen for 5 min, and then 14.0 μL (0.106 mmol) of degassed *n*-hexylamine was injected into the mixture. After stirring at ambient temperature overnight, the solution was filtered off, and the recovered polymer was subjected to GPC analysis. Other grafted polymeric chains were cleaved according to a similar procedure.

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 100–10 000 for Styragel HT2, 500–30 000 for Styragel HT3, and 5000–600 000 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. ^{1}H NMR spectra (300 MHz) were recorded on a Varian spectrometer at 25 °C using $CDCl_3$ 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 800 °C at a rate of 10 °C/min under nitrogen.

Results and Discussion

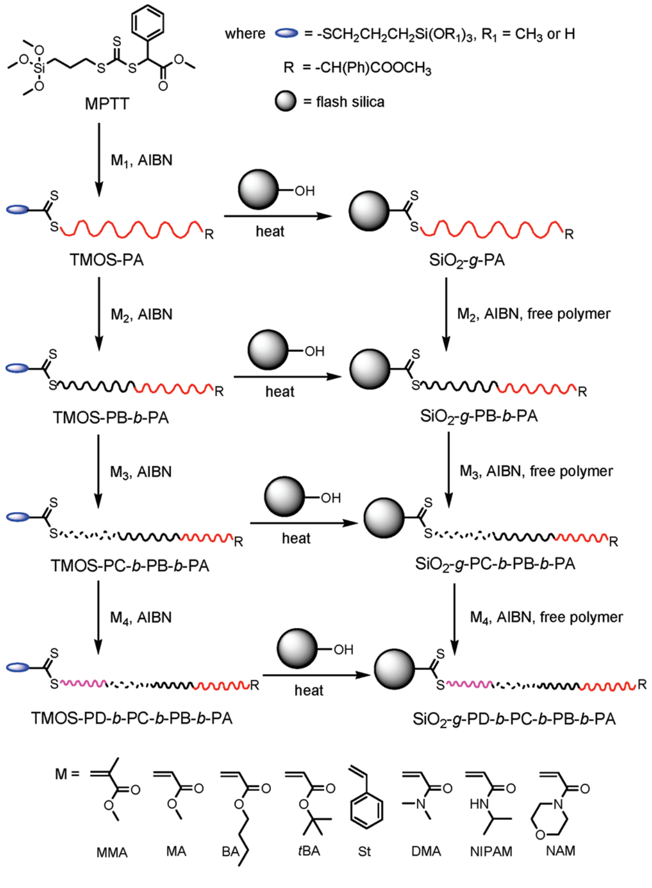
Synthesis of TMOS-Functionalized Polymers by RAFT Process. To prepare the Z-functionalized polymers, *S*-methoxycarbonylphenylmethyl *S'*-trimethoxysilylpropyltrithiocarbonate (MPTT)[13] with a functionality of trimethoxysilane (TMOS) was synthesized. MPTT was used to mediate RAFT polymerization of various types of monomers such as methyl methacrylate (MMA), styrene (St), *N*-acrylomorpholine (NAM), *N*-isopropylacrylamide (NIPAM), *N,N*-dimethylacrylamide (DMA), methyl acrylate (MA), and butyl acrylate (BA), and RAFT polymerization was conducted in bulk (for St), toluene (for MMA, MA, and BA), or dioxane (for NAM, NIPAM, and DMA) at 60 °C for 21 h. In Table 1, the monomer conversion (C%) was determined by ^{1}H NMR by comparing the integrated areas of characteristic signals of monomer and polymer using the following equations: $C_{MMA} = I_{3.59}/I_{3.5-3.8}$, $C_{MA} = 1 - I_{5.7-6.5}/I_{3.5-3.9}$, $C_{BA} = 1 - (2I_{5.7-6.5})/(3I_{3.8-4.3})$, $C_{St} = (2I_{1.0-2.2})/(3I_{5.1-5.9} + 2I_{1.0-2.2})$, $C_{NAM} = (3I_{2.0-2.9})/(3I_{2.0-2.9} + I_{5.4-6.9})$, $C_{DMA} = (I_{1.0-3.4} - 2I_{5.4-6.7})/(I_{1.0-3.4} + I_{5.4-6.7})$, and $C_{NIPAM} = 1 - I_{5.2-6.6}/(3I_{3.7-4.4})$, where I_{a-b} means the integrated areas from a to b ppm in ^{1}H NMR spectra of mixtures obtained by RAFT polymerization. The results in Table 1 showed that MPTT was a good RAFT agent for polymerization of acrylate and acrylamido monomers and styrene, for which the polymerization led to well-defined polymers with controlled molecular weight and low polydispersity (1.08 < PDI < 1.16). For polymerization of MMA, the molecular weight was higher than the theoretically calculated value (M_n(th)) based on conversion and feed ratio, and the polydispersity was 1.58, corresponding to a relatively poor controlled system. This result is similar to RAFT polymerization of MMA mediated by other trithiocarbonates with the methoxycarbonylphenylmethyl group as the R group,[40] which can be attributed to the fact that trithiocarbonates are not good chain transfer agents to mediate the RAFT polymerization of methacrylate-type monomers.

Table 2. Synthesis of Block Copolymers by Chain Extension Polymerization Mediated by Various Macro-Chain-Transfer Agents (Macro-CTAs)[a]

run	macro-CTA	M	$[M]_0/[CTA]_0$	*t* (h)	C%[b]	M_n(th)[c]	M_n(GPC)[d]	PDI[d]	*f*[e]
1	PSt	NAM	80	19	44.0	13 000	12 800	1.15	0.97
2	PSt	DMA	100	19	47.8	12 800	12 500	1.19	0.96
3	PSt	NIPAM	100	19	49.3	13 600	12 800	1.20	0.94
4	PSt	MA	100	19	53.2	12 600	13 300	1.12	0.95
5	PSt-*b*-PNAM	NIPAM	120	21	43.4	18 700	18 500	1.18	0.94
6	PSt-*b*-PNAM	DMA	120	21	45.8	18 200	17 500	1.16	0.95
7	PSt-*b*-PNAM	*t*BA	100	21	44.3	18 500	18 100	1.13	0.97
8	PSt-*b*-PDMA	MA	200	21	47.6	20 700	19 400	1.16	0.93
9	PSt-*b*-PNIPAM	MA	200	21	50.2	21 400	21 600	1.25	0.92
10	PSt-*b*-PNAM-*b*-PNIPAM	MA	200	18	31.2	23 900	23 200	1.19	0.91
11	PSt-*b*-PNAM-*b*-PDMA	MA	200	18	38.8	24 200	25 100	1.18	0.93
12	PSt-*b*-PNAM-*b*-P*t*BA	MA	200	18	31.5	23 500	23 100	1.11	0.90

[a] Reaction conditions: $[\text{macro-CTA}]_0$:$[\text{AIBN}]_0$ = 10:1, $[\text{AIBN}]_0$ = 2.0 (runs 1−4), 1.0 (runs 5−9), and 0.80 mmol/L (runs 10−12), in dioxane at 60 °C. PSt was synthesized by run 2 in Table 1, and other macro-CTAs were synthesized by runs 1 (for PSt-*b*-PNAM), 2 (for PSt-*b*-PDMA), 3 (for PSt-*b*-PNIPAM), 5 (for PSt-*b*-PNAM-*b*-PNIPAM), 6 (for PSt-*b*-PNAM-*b*-PDMA), and 7 (for PSt-*b*-PNAM-*b*-P*t*BA) in Table 2. [b] Monomer conversion determined by gravimetry. [c] Theoretically calculated molecular weight, $M_n(\text{th}) = M_{w,m} \times C\% \times [M]_0/[\text{macro-CTA}]_0 + M_{w,\text{macro-CTA}}$, where $M_{w,m}$ and $M_{w,\text{macro-CTA}}$ are the molecular weights of monomer and macro-CTAs. [d] Molecular weight and polydispersity determined by GPC. [e] Apparent degree of functionality estimated by the equation $f = M_n(\text{GPC})/M_n(\text{NMR})$, where M_n(NMR) is the apparent molecular weight of block copolymers determined by comparing the integral of ArH resonance in PSt segment with that for the characteristic signal of other polymeric chains in ^{1}H NMR spectra.

Scheme 2. Synthesis of Flash Silica Grafted with Well-Defined "Living" Homopolymers and Block Copolymers by a Combinatorial Approach Based on Reversible Addition−Fragmentation Chain Transfer (RAFT) Process and Coupling Reaction or by Direct Chain Extension Polymerization Using Macro-Chain-Transfer Agents



The functionalized di-, tri-, and tetrablock copolymers were synthesized by successive chain extension polymerization based on the RAFT process (Scheme 2). First, the TMOS-functionalized PSt (M_n = 8060, PDI = 1.12) was used as a macro-CTA to mediate chain extension polymerization of monomers such as NAM, DMA, NIPAM, and MA, and diblock copolymers with a functionality of TMOS were obtained. When the polymerization was carried out in dioxane at 60 °C for 19 h, the results are listed in runs 1−4 of Table 2. The molecular weights of the resultant diblock copolymers determined by GPC were in good agreement with the theoretical values calculated from the conversion and macro-CTA concentration, and the polydispersity indices ranged between 1.12 and 1.20. Inspection of GPC traces reveals no significant shoulders and tailings, thus indicating the chain extension polymerization mediated by PSt had been efficiently performed. Chain extension polymerization of NIPAM, DMA, *t*BA, and MA mediated by various diblock copolymers comprising polystyrene segments was also conducted in dioxane at 60 °C for 21 h. Table 2 (runs 5−9) shows that the resultant triblock copolymers possessed molecular weights close to those expected, and the polydispersity was usually less than 1.25. Finally, three triblock copolymers, PSt-*b*-PNAM-*b*-PNIPAM, PSt-*b*-PNAM-*b*-PDMA, and PSt-*b*-PNAM-*b*-P*t*BA, were utilized as mediators for chain extension polymerization of MA, and the results are listed in runs 10−12 of Table 2. As expected, the molecular weights of tetrablock copolymers were similar to those calculated from the equation $M_n(\text{th}) = M_{w,m} \times C\% \times [M]_0/[\text{macro-CTA}]_0 + M_{w,\text{macro-CTA}}$ (where $M_{w,m}$ and $M_{w,\text{macro-CTA}}$ are the molecular weights of monomer and macro-CTA, respectively), and the polydispersity indices varied from 1.11 to 1.19. Although the polydispersity indices of tri- and tetrablock copolymers were low, significant shoulders and tailings could be noted from their GPC traces in some cases, corresponding to unavoidable side reactions during chain extension polymerization (see the Supporting Information and Figure 1). During RAFT polymerization, some side reactions such as chain termination (disproportionation and combination) and irreversible chain transfer reactions usually exist, leading to the formation of a variety of polymeric structures as side products. Usually a shoulder in GPC traces indicates the presence of combination reaction, while side products obtained by disproportionation reaction and irreversible chain transfer reactions are appearant as a tail in the GPC traces. All these side products cannot be used for chain extension polymerization of a second monomer due to lack of living chain ends.

During RAFT polymerization, some side reactions introduced undesirable chain ends, leading to decrease of the functionality of the chain ends of the polymer. The side products lack of TMOS functionality cannot further participate in the following coupling reaction, so it is necessary to determine the degree of functionality of the living chain ends. In ^{1}H NMR spectra of homopolymers and block copolymers,

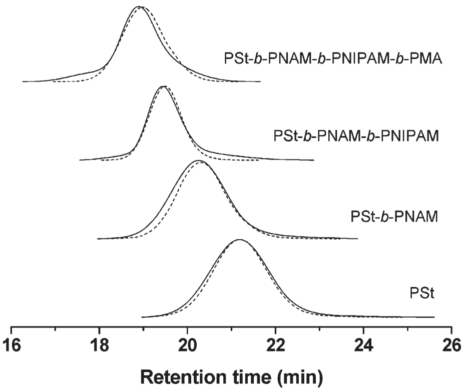


Figure 1. Gel permeation chromatography (GPC) traces of grafted PSt, PSt-*b*-PNAM, PSt-*b*-PNAM-*b*-PNIPAM, and PSt-*b*-PNAM-*b*-PNIPAM-*b*-PMA (dashed line) and their precursors (solid line), in which PSt, PNAM, PNIPAM, and PMA mean polystyrene, poly(*N*-acrylomorpholine), poly(*N*-isopropylacrylamide), and poly(methyl acrylate), respectively.

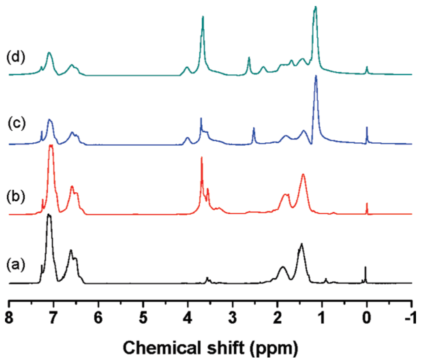


Figure 2. ^{1}H NMR spectra of PSt (a), PSt-*b*-PNAM (b), PSt-*b*-PNAM-*b*-PNIPAM (c), and PSt-*b*-PNAM-*b*-PNIPAM-*b*-PMA (d).

the signals corresponding to CH_3O of the TMOS functionality, CH_2S, and ph*H* resulting from the R group were observed at around 3.54, 3.37, and 7.33 ppm, respectively. The characteristic signals of various polymeric segments were noted at 3.59 (CH_3, PMMA), 6.2−7.2 (Ph*H*, PSt), 3.97 (C*H*, PNIPAM), 2.89 (CH_3, PDMA), 3.59 (CH_2, PNAM), 3.65 (CH_3, PMA), 4.03 (CH_2, PBA), and 1.43 ppm (CH_3, P*t*BA) (see the Supporting Information and Figure 2). On the basis of ^{1}H NMR spectra, apparent molecular weights of various polymers (M_n(NMR)) were determined by comparing the integral of the resonance of end group (ph*H* for PNAM and PMA, CH_2S for PMMA, and $(CH_3O)_3Si$ for other polymers) or side group (Ar*H* for PSt segment) with that for the characteristic signal of polymeric chains in ^{1}H NMR spectra, and the apparent degree of functionality (*f*) was then estimated by the equation $f = M_n(\text{GPC})/M_n(\text{NMR})$. From the results listed in Tables 1 and 2, it can be seen that the M_n(NMR) results are generally very close to the theoretical values, the *f* values of homopolymers were estimated to be 0.87−0.99, and the *f* values of block copolymers were around 0.90−0.97. These results further indicated that RAFT polymerization and successive chain extension reactions could be efficiently conducted to synthesize the target TMOS-functionalized polymers, and no significant decrease in degree of functionality of the living chain ends was noted during chain extension polymerization.

Table 3. Reversible Addition−Fragmentation Chain Transfer Polymerization Mediated by *S*-Methoxycarbonylphenylmethyl *S*′-Trimethoxysilylpropyltrithiocarbonate in Bulk (for St) or Toluene (for MA and MMA) at 60 °C[a]

run	M	$[M]_0/[CTA]_0$	*t* (h)	C%[b]	M_n (th)[c]	M_n (GPC)[d]	PDI[d]	C_{tr}[e]
1	MA	control	12	90.7		72 800	2.58	20.10 ± 0.21
2	MA	300	3	5.43	1820	1690	1.38	
3	MA	600	2.5	5.11	3060	2950	1.35	
4	MA	1500	1.5	5.42	7420	6920	1.35	
5	MA	3000	0.5	4.88	13000	12100	1.41	
6	St	control	12	22.5		184000	1.74	13.86 ± 0.18
7	St	300	3	8.93	3210	2640	1.21	
8	St	600	3	9.91	6610	4970	1.36	
9	St	1500	3	9.34	15000	11500	1.3	
10	St	3000	3	9.77	30900	19700	1.39	
11	MMA	control	12	52.9		166000	1.87	2.44 ± 0.06
12	MMA	300	0.3	2.78	1260	11800	1.71	
13	MMA	600	0.7	2.45	1890	23000	1.89	
14	MMA	1500	0.7	2.96	4870	43300	1.94	
15	MMA	3000	0.6	3.26	10200	72800	1.88	

[a] Reaction conditions: $[M]_0$ = 3.0 mol/L, $[AIBN]_0$ = 1.0 mmol/L (for polymerization of MA and MMA); $[St]_0$ = 8.7 mol/L, $[AIBN]_0$ = 2.9 mmol/L (for St polymerization). MMA, St, and MA are methyl methacrylate, styrene, and methyl acrylate, respectively. [b] Monomer conversion determined by ^{1}H NMR. [c] Theoretically calculated number-average molecular weight, $M_n(\text{th}) = M_{w,m} \times C\% \times [M]_0/[CTA]_0 + M_{w,CTA}$, where $M_{w,m}$ and $M_{w,CTA}$ are the molecular weights of monomer and RAFT agent. [d] Molecular weight and polydispersity determined by gel permeation chromatography. [e] Chain transfer constants determined by eq 3.

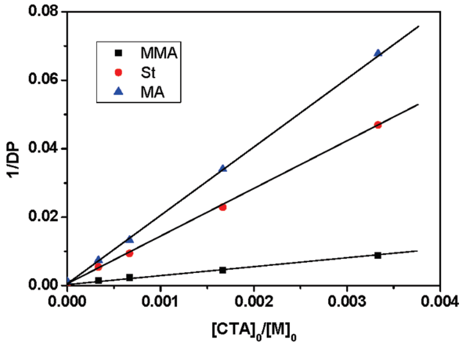


Figure 3. Plot of 1/DP vs $[CTA]_0/[M]_0$ for RAFT polymerization mediated by *S*-methoxycarbonylphenylmethyl *S*′-trimethoxysilylpropyltrithiocarbonate at 60 °C. Slopes from linear regression analysis provide the chain transfer constants as shown in Table 3.

The chain transfer constant of MPTT also permits to determine the chain-end functionality. To evaluate the activity of MPTT, the RAFT polymerization of typical vinyl monomers such as MA, St, and MMA was conducted at 60 °C, and monomer conversions were controlled to be less than 10%. As a comparison, free radical polymerization without MPTT was also conducted, and the results are listed in Table 3. The chain transfer constant (C_{tr}) was determined using variations of the Mayo equation (eq 3),[45,46] in which DP_n is the number-average degree of polymerization of the polymer, DP_{n0} is the number-average degree of polymerization for polymer produced under the same conditions in the absence of RAFT agent, and [CTA] and [M] are the concentrations of added chain transfer agent and monomer, respectively. Plots of 1/DP vs $[CTA]_0/[M]_0$ for RAFT polymerization mediated by MPTT at 60 °C are shown in Figure 3. The chain transfer constants for RAFT polymerization of MA, St, and MMA were determined to be 20.10 ± 0.21, 13.86 ± 0.18, and 2.44 ± 0.06, respectively. The chain transfer constants increase in the series where R is poly(methyl methacrylyl) < poly(styryl) < poly(methyl acrylyl), which is in good agreement with results reported by Moad et al.[32,47,48] The above results suggest the strong dependence of chain transfer constants on the radical leaving group

Table 4. Synthesis of Flash Silica Grafted with Homopolymers and Block Copolymers by Coupling Reaction[a]

run	graft polymer	M_n(a)[b]	PDI(a)[b]	M_n(g)[c]	PDI(g)[c]	G_r (%)[d]	G_p (μmol/g)[e]
1	PMMA	13 200	1.58	12 500	1.45	39.8	31.8
2	PSt	8 060	1.12	8 240	1.10	37.2	45.1
3	PNAM	7 250	1.16	7 560	1.11	45.1	59.7
4	PNIPAM	8 570	1.11	8 700	1.12	48.6	55.9
5	PDMA	8 460	1.08	8 550	1.06	51.0	59.6
6	PMA	11 600	1.14	11 500	1.12	63.5	53.8
7	PBA	13 300	1.15	13 200	1.12	49.8	37.7
8	PSt-*b*-PNAM	12 800	1.15	12 200	1.13	50.6	41.5
9	PSt-*b*-PDMA	12 500	1.19	12 600	1.15	50.2	39.8
10	PSt-*b*-PNIPAM	12 800	1.20	12 700	1.19	48.8	38.4
11	PSt-*b*-PMA	13 300	1.12	13 500	1.10	52.6	39.0
12	PSt-*b*-PNAM-*b*-PNIPAM	18 500	1.18	18 000	1.12	45.5	25.3
13	PSt-*b*-PNAM-*b*-PDMA	17 500	1.16	17 200	1.15	43.5	25.3
14	PSt-*b*-PNAM-*b*-P*t*BA	18 100	1.13	17 500	1.11	41.4	23.7
15	PSt-*b*-PDMA-*b*-PMA	19 400	1.16	18 800	1.15	48.3	25.7
16	PSt-*b*-PNIPAM-*b*-PMA	21 600	1.25	20 700	1.20	45.4	21.9
17	PSt-*b*-PNAM-*b*-PNIPAM-*b*-PMA	23 200	1.19	21 800	1.15	37.1	17.0
18	PSt-*b*-PNAM-*b*-PDMA-*b*-PMA	25 100	1.18	24 000	1.16	33.8	14.1
19	PSt-*b*-PNAM-*b*-P*t*BA-*b*-PMA	23 100	1.11	22 500	1.10	38.7	17.2

[a] Reaction conditions: $W_{\mathrm{polymer}}/W_{\mathrm{SiO_2}} = 5{:}1$, $W_{\mathrm{polymer}}/V_{\mathrm{solvent}} = 0.10$ g/mL, in dioxane (run 3) or toluene (other runs) at 80 °C for 20 h; see Tables 1 and 2 for precursors of graft polymers. [b] Molecular weight and polydispersity of "as-prepared" polymers. [c] Molecular weight and polydispersity of grafted polymers obtained by aminolysis. [d] Weight grafting ratio of grafted polymeric segments on the surface of flash silica obtained by thermogravimetric analyses. [e] Apparent molar grafting ratio calculated by the equation $G_p = G_r/M_n(\mathrm{g})$.

ability of the R group and can be ascribed to different radical stability and steric factors during polymerization.[32,47,48] The transfer constant of MPTT in MMA polymerization was significantly lower than that in polymerization of MA and St, which may account for poor control over molecular weight and polydispersity and relatively low degree of TMOS functionality ($f = 0.87$) of PMMA produced by RAFT polymerization of MMA mediated by MPTT.

$$\frac{1}{\mathrm{DP_n}} = \frac{1}{\mathrm{DP_{n0}}} + C_{\mathrm{tr}}\frac{[\mathrm{CTA}]}{[\mathrm{M}]} \qquad (3)$$

Synthesis of Flash Silica Grafted with Homopolymers and Block Copolymers by Coupling Reaction. In Z-supported RAFT graft polymerization, the chain length of grafted polymers was usually shorter than that of free polymers produced in solution, especially for polymerization conducted to high conversion. This effect is attributed to the significantly increased steric hindrance and slower rate of addition−fragmentation chain transfer reactions on surface when compared to that in solution.[10−14] However, this disadvantage is expected to be effectively overcome by using the grafting to approach. In this study, silica−polymer hybrids were prepared by coupling reaction between hydroxyl groups at the surface of silica gel and trimethoxylsilane in the chain end of various "as-prepared" Z-functionalized polymers prepared as aforementioned. The silica−polymer hybrids were isolated from ungrafted living polymers and dead polymers by filtration and thorough wash with toluene and THF. To do GPC analyses, the grafted polymeric chains were cleaved from the surface of flash silica by aminolysis using excess *n*-hexylamine and methyl methanethiosulfonate in THF at room temperature overnight.[44]

The coupling reaction ($W_{\mathrm{polymer}}/W_{\mathrm{SiO_2}} = 5{:}1$, $W_{\mathrm{polymer}}/V_{\mathrm{solvent}} = 0.10$ g/mL) was conducted in dioxane (run 3) or toluene (other runs) at 80 °C for 20 h. As expected, the grafted polymers and their precursors with TMOS functionality ("as-prepared" polymers) had similar molecular weights, while the polydispersity indices of grafted polymeric chains were usually slightly lower than those of their precursors (Table 4). These results indicated that the "grafting to" approach could significantly address the disadvantage of distinctly different chain lengths between grafted and free polymers in Z-supported RAFT graft polymerization.

Theoretically, all the dead polymeric chains without TMOS functionality cannot be grafted to the surface of solid supports, and only living polymeric chains comprising the TMOS functionality and the reactive thiocarbonyl−thio moiety can be covalently attached to the surface of flash silica during coupling reaction. As a comparison, the GPC traces of typical grafted samples up to tetrablock copolymer such as PSt, PSt-*b*-PNAM, PSt-*b*-PNAM-*b*-PNIPAM, and PSt-*b*-PNAM-*b*-PNIPAM-*b*-PMA (dashed line) and their precursors ("as-prepared" polymers, solid line) are listed in Figure 1. In some cases, the tailing and/or shoulder were observed in the GPC traces of functional precursors, indicating the existence of some side reactions in solution. However, the GPC traces of grafted polymers lack shoulder and significant tailing (see the Supporting Information for other grafted samples), which is in good agreement with the theoretical expectation. As a result, the polydispersity of grafted polymers was usually slightly lower than that of TMOS-functionalized polymers due to lack of dead polymeric chains.

The resultant silica−polymer hybrids were characterized by IR and TGA (see the Supporting Information). In IR spectra, a strong and broad absorption corresponding to the stretching vibration of Si−O bond of the solid supports was noted at around 1080 cm^{-1}, and typical absorptions corresponding to characteristic groups such as C═C (PSt) and C═O (other polymers) bonds in various polymeric segments were also observed (Figures 4 and 5).

In Table 4, the weight (G_r) and molar (G_p) grafting ratio of polymeric chains on solid surface was determined by TGA. Theoretically, the grafting ratios may be affected by factors such as chain length and rigidity of polymeric chains, types of solvents, temperature, reaction time, and feed ratios of polymers to solid supports. In this study, the coupling reaction was only conducted under a certain condition ($W_{\mathrm{polymer}}/W_{\mathrm{SiO_2}} = 5{:}1$, $W_{\mathrm{polymer}}/V_{\mathrm{solvent}} = 0.10$ g/mL, at 80 °C for 20 h). The TGA curves of flash silica and flash silica grafted with various homopolymers are listed in Figure 6. When TGA was conducted from room temperature to 800 °C at a rate of 10 °C/min under nitrogen, the residual weight percent of flash silica at 800 °C was 94.6%, while the residual weight percents

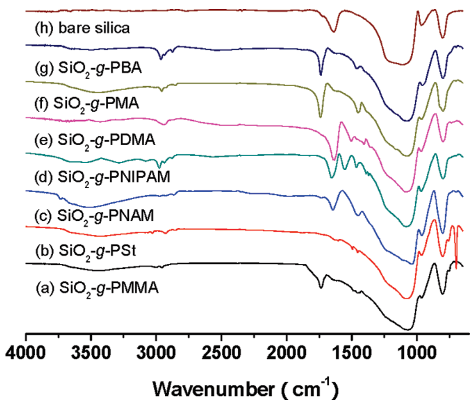


Figure 4. FT-IR spectra of flash silica grafted with homopolymers (a−g) and bare silica particles (h): SiO_2, 1638 (δ_{O-H}), 1109 (ν_{Si-O}); PMMA, 1736 ($\nu_{C=O}$); PSt, 1600 ($\nu_{C=C}$), 699 (δ_{C-H}); PNAM, 1645 ($\nu_{C=O}$); PNIPAM, 1654 ($\nu_{C=O}$); PDMA, 1634 ($\nu_{C=O}$); PMA, 1740 ($\nu_{C=O}$); and PBA, 1736 cm^{-1} ($\nu_{C=O}$).

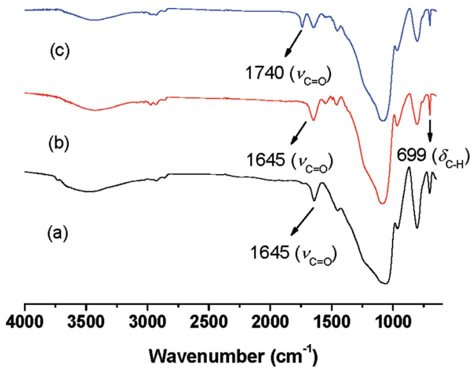


Figure 5. Typical FT-IR spectra of flash silica grafted with block copolymers: SiO_2-*g*-PNAM-*b*-PSt (a), SiO_2-*g*-PNIPAM-*b*-PNAM-*b*-PSt (b), and SiO_2-*g*-PMA-*b*- PNIPAM-*b*-PNAM-*b*-PSt (c).

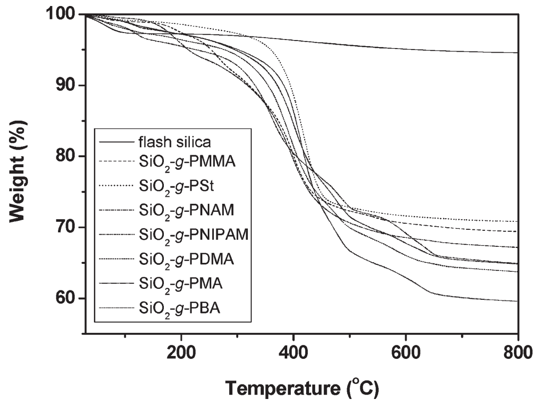


Figure 6. Thermogravimetric analyses (TGA) curves of flash silica and flash silica grafted with homopolymers.

of silica−polymer hybrids at 800 °C ranged between 59.6% and 70.8%. For silica grafted with homopolymers (SiO_2-*g*-PA) using weight feed ratio of $W_{polymer}/W_{SiO_2} = 5{:}1$, the weight grafting ratio was varied in a wide range from 37.2% to 63.5%, and the apparent molar grafting ratio was varied from 31.8 to 59.7 μmol/g. The grafting ratios of polymeric chains with similar chain length were quite different in some cases. For example, SiO_2-*g*-PMA had highest weight grafting ratio of 63.5% although the grafted polymeric chains were relatively long (M_n(g) = 11 500, PDI = 1.12), while SiO_2-*g*-PSt had lowest weight grafting ratio of 37.2% even if the grafted polymeric chains were relatively short (M_n(g) = 8240, PDI = 1.10). This phenomenon may be ascribed to dissimilar reactivity of TMOS functionality in the chain end originated from different molecular rigidity and modality of polymeric chains in solution. The molecular rigidity and modality of the polymeric chains tend to affect their diffusion and the positioning of the end groups during the coupling reaction, which can only occur if the reactive TMOS functionality reaches the surface of the silica particles. With prolonged reaction time, the diffusion of long polymeric chains to the available reactive sites can be sheltered by the existing grafted chains, and this effect becomes more pronounced with an increase in molecular rigidity, leading to significantly decreased grafting density of PSt chains on the surface of silica particles as compared to the other cases. In addition to chemical compositions, the grafting ratios are also dependent on molecular weights of functional precursors, evident from gradually decreased weight and molar grafting ratios with an increase in molecular weight as shown in Table 4. For instance, when a TMOS-functionalized tetrablock copolymer of PSt-*b*-PNAM-*b*-PDMA-*b*-PMA with molecular weight of 25 100 g/mol was used for the graft reaction, the weight grafting ratio was significantly decreased to be 33.8%, and the molar grafting ratio of polymeric chains on the surface of silica was estimated to be 14.1 μmol/g. Another example is the synthesis of silica−PMA hybrids by coupling reaction in toluene following the reaction conditions listed in Table 4. When the molecular weight of the grafted PMA chains increased from 5110 to 35 500 g/mol, the molar grafting ratio was significantly decreased from 104 to 8.62 μmol/g, while a maximum weight grafting ratio of 63.5% was observed when a PMA of M_n(GPC) = 11 500 g/mol was used for the graft reaction (see the Supporting Information).

In Table 4, the weight grafting ratio of various grafted polymeric chains varied in the range 33.8−63.5%, suggesting about 6.7−12.7% of polymeric chains on average could be grafted to the surface of silica particles in this study. Flash silica has a BET surface area of 472.3 m^2/g, and the molar grafting ratios was varied between 14.1 and 59.7 μmol/g in various runs; thus, the grafting density of polymeric chains on the surface of silica particles was estimated to be 0.018−0.076 chains/nm^2, which is a little better than our previous study in which a grafting density of 0.016−0.049 chains/nm^2 were obtained by the Z-supported RAFT graft polymerization for grafted chains of molecular weight varying from 4450 to 17 500 g/mol.[12] It should be mentioned that the grafting density obtained by coupling reaction is relatively low as compared to that obtained by the "grafting from" approach due to a more pronounced shielding effect. For instance, it was found that the grafting density could reach up to 0.68 chains/nm^2 when the "grafting from" approach was used to modify silica nanoparticles via ATRP and RAFT polymerization.[6,22]

Chain Extension Polymerization of MA To Synthesize Block Copolymer Grafted onto Silica Particles. The solid-supported polymeric chains obtained by coupling reaction between Z-functionalized polymers and silica gel are expected to be 100% living since each polymeric chain attached to the surface of solid supports comprising one reactive thiocarbonyl−thio moiety. In our previous study, flash silica grafted with well-defined homopolymers was synthesized by Z-supported RAFT graft polymerization, and better-defined diblock copolymer grafted silica particles were achieved by the straightforward chain extension polymerization of a second monomer in the presence of 4-fold excess of free polymers, demonstrating near-perfect living polymers could be

Table 5. Chain Extension Polymerization of MA To Synthesize Block Copolymer−Silica Hybrids Using Various Macro-CTAs[a]

run	macro-CTA	C%	M_n(th)[b]	M_n(f)[c]	PDI(f)[c]	M_n(g)[d]	PDI(g)[d]	G_r (%)	G_p (μmol/g)
1	SiO_2-*g*-PSt	40.2	16 900	18 600	1.11	12 800	1.10	56.2	40.7
2	SiO_2-*g*-PNAM-*b*-PSt	39.5	20 700	22 600	1.14	15 600	1.12	61.3	39.3
3	SiO_2-*g*-PNIPAM-*b*-PNAM-*b*-PSt	33.8	25 300	28 100	1.24	22 100	1.16	51.1	23.4

[a] Polymerization conditions: $[M]_0$:[macro-CTA]$_0$:[free polymer]$_0$ = 1500:1:5, $[M]_0$ = 3.0 mol/L, $[AIBN]_0$ = 1.2 mmol/L, in toluene at 60 °C for 18 h. The macro-CTAs were synthesized by runs 2, 8, and 12 in Table 3, and the corresponding free polymers used in runs 1−3 were synthesized by run 2 in Table 1 (for PSt), run 1 (for PSt-*b*-PNAM), and run 5 (for PSt-*b*-PNAM-*b*-PNIPAM) in Table 2, respectively. [b] $M_n(\mathrm{th}) = 86.09 \times \mathrm{C\%} \times [M]_0/([\text{macro-CTA}]_0 + [\text{free polymer}]_0) + M_{w,\text{macro-CTA}}$, where $M_{w,\text{macro-CTA}}$ is the molecular weight of polymeric chains grafted onto silica particles. [c] Molecular weight and polydispersity of grafted block copolymers determined by GPC using PMMA standards. [d] Molecular weight and polydispersity of free block copolymers produced in solution.

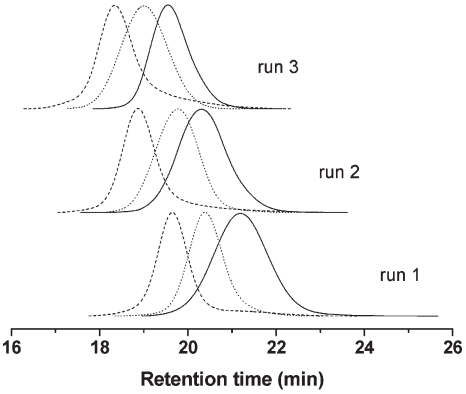


Figure 7. Gel permeation chromatography (GPC) traces of macro-chain-transfer agents (solid line) and free (dashed line) and grafted (dotted line) block copolymers. See Table 5 for polymerization conditions in various runs.

covalently attached to the surface of solid supports via Z-supported RAFT polymerization.[13] In this study, similar chain lengths could be achieved by the coupling reaction using TMOS-functionalized polymer precursors, while the molecular weights of grafted polymeric chains varied from 7560 to 24 000 g/mol. To understand the effects of chain length on the livingness of the solid-supported polymers, typical silica−polymer hybrids such as SiO_2-*g*-PSt, SiO_2-*g*-PNAM-*b*-PSt, and SiO_2-*g*-PNIPAM-*b*-PNAM-*b*-PSt were used as macro-CTAs to mediate chain extension polymerization of MA, and the corresponding "as-prepared" polymers with similar molecular weights were used as free polymers to reduce side reactions.

When the polymerization ($[M]_0$:[macro-CTA]$_0$:[free polymer]$_0$ = 1500:1:5, $[M]_0$ = 3.0 mol/L, $[AIBN]_0$ = 1.2 mmol/L) was conducted in toluene at 60 °C for 18 h, the results are listed in Table 5. As expected, the molecular weights of free polymers produced in solution were significantly higher than those of the grafted polymers due to the increased shielding effect and slower rate of addition−fragmentation chain transfer in solution than that at the surface of solid supports.[10−17] In GPC traces (Figure 7), free block copolymers usually exhibited tailings corresponding to the side products of irreversible termination and chain transfer during polymerization. As compared with the GPC traces of grafted polymers attached to macro-CTAs, the GPC traces of grafted block copolymers were completely shifted to higher molecular weights. Furthermore, no obvious tailing and shoulder were noted, with polydispersity indices below 1.16, suggesting well-defined block copolymer grafted silica particles could be obtained by chain extension polymerization in the presence of free polymer. Comparing the results listed in Tables 4 and 5 demonstrates that the apparent molar grafting ratios before and after chain extension polymerization are comparable, within experimental errors, thus suggesting almost no grafted polymeric chains were lost during polymerization. The highly efficient chain extension polymerization demonstrated the livingness and quantitative reinitiation efficiency of the macro-CTAs even if the solid-supported polymers had high molecular weight up to 18 000 g/mol.

Conclusion

A combinatorial approach based on RAFT polymerization and coupling reaction was developed to synthesize well-defined polymeric chains grafted onto silica particles. The TMOS-functionalized homopolymers were first synthesized by RAFT polymerization mediated by MPTT, and a series of functional di-, tri-, and tetrablock copolymers were obtained by successive chain extension polymerization. Then the "as-prepared" polymers with a TMOS functionality in the chain end were attached to the surface of silica particles by coupling reaction in toluene or dioxane at 80 °C. The silica−polymer hybrids were characterized by infrared spectra and TGA, and the grafting density of various polymeric chains at the surface of silica particles was determined to be 0.018−0.076 chains/nm^2. The degrafted polymers had molecular weights similar to their "as-prepared" polymer precursors, while their polydispersity indices were usually slightly lower than the latter, suggesting highly pure block copolymers could be achieved by the combinatorial approach. The flash silica grafted with polymeric chains are living and of almost quantitative reinitiation efficiency, evident from highly efficient chain extension polymerization to prepare well-defined block copolymers grafted onto silica particles.

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Supporting Information Available: GPC traces of grafted polymers and their precursors, IR spectra and TGA curves of flash silica grafted with di-, tri-, and tetrablock copolymers, and ^{1}H NMR spectra of TMOS-functionalized homopolymers and block copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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