Reversible Addition−Fragmentation Chain Transfer Graft Polymerization Mediated by Fumed Silica Supported Chain Transfer Agents

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ABSTRACT: In this study, the Z supported reversible addition−fragmentation chain transfer (RAFT) graft polymerization to prepare silica-polymer hybrids was investigated. Two chain transfer agents (CTAs), *S*-benzyl *S′*-trimethoxysilylpropyltrithiocarbonate and *S*-methoxycarbonylphenylmethyl *S′*-trimethoxysilylpropyltrithiocarbonate, were synthesized and covalently attached to the surface of fumed silica. The resultant silica supported CTAs were used to mediate RAFT polymerization of vinyl monomers such as methyl acrylate, butyl acrylate, *N*,*N*-dimethylacrylamide, *N*-isopropylacrylamide, methyl methacrylate, and styrene in the presence of a free CTA to synthesize polymer grafted silica particles. Effects of CTA loadings on solid supports, types of free CTAs, and reaction media on graft polymerization were investigated in detail. Under optimal conditions such as using 2-(2-cyanopropyl)dithiobenzoate as a free CTA and controlling the polymerization at a low conversion (typically less than 40%), well-defined polymeric chains with polydispersity indices less than 1.2 and chain lengths similar to those of free polymers could be successfully grafted onto the surface of fumed silica, and relatively high grafting ratios could be achieved, as is evident from GPC, FT-IR, and TGA analyses. As compared with polymerization in toluene, RAFT graft polymerization of methyl acrylate in methanol could afford longer grafted chain lengths and significantly increased grafting efficiency at identical conditions, suggesting the potential effects of reaction media on graft polymerization.

Introduction

The surface functionalization of inorganic particles 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 a wide range of fields such as bioscience, engineering, and electronic and optical devices.[1−3] Among various solid supports, silica particles are supports of choice to prepare target inorganic-organic hybrids due to their chemical resistance, mechanical stability, relatively low costs, variable particle sizes (ranging from 1 nm to 100 μm), and high specific surface area (up to 1300 m^2/g).[3−5] Thus far, different types of silica particles such as porous flash silica,[6−12] mesoporous ordered silica particles,[4,13−15] nonporous silica nanoparticles,[16−23] and fumed silica[5,24] have been successfully grafted with well-defined polymeric chains, and the preparation of silica-polymer hybrids via surface initiated polymerization has been accomplished by ionic, ring-opening, conventional, and controlled radical polymerization techniques. Among them, reversible addition−fragmentation chain transfer (RAFT) polymerization has become one of the most promising controlled radical polymerization techniques to prepare polymer grafted solid supports due to its tolerance to a wide range of reaction conditions, its straightforward setup to result in block copolymers, and its versatility toward the range of monomers with variable functionalities.[25−31]

Thus far, five different approaches relative to the RAFT process have been developed to prepare silica-polymer hybrids. First, the initiating radicals are generated directly on the surface via surface-confined initiators,[13,32] or formed by reacting surface thiols with a radical initiator, and then followed by RAFT graft polymerization.[6] Second, the chain transfer agent (CTA) is attached to the backbone via the leaving and reinitiating R group (R-group approach).[20−22] Third, the CTA is attached to the backbone via the stabilizing Z group (Z-group approach).[5,8−11] Fourth, the functional polymer is first prepared by the RAFT process, followed by click chemistry[23] or reacting with a surface double bond in the presence of excess radical initiator[7] to obtain the functional hybrids. Last, functional block copolymers comprised of reactive trimethoxysilyl or triethoxysilyl groups were synthesized by RAFT polymerization and followed by self-assembly and a sol−gel process to form silica-polymer hybrid nanoobjects.[33,34] Among them, the first and second methods are similar to the "grafting from" technique in atom transfer radical polymerization (ATRP)[35,36] and nitroxide-mediated polymerization (NMP),[37] and the third and fourth methods are comparable to the "grafting to" approach. Various methods have their advantages and limitations. For instance, the R-group approach can afford a higher molecular weight of grafted polymers and grafting density, but the molecular weight distribution may be broadened by the possible chain coupling; the Z-group approach can yield better-defined grafted polymers with monomodal molecular weight distribution, although the grafting density is liable to decrease due to the shielding effect.[38−45] Until now, RAFT polymerization has been successfully utilized to graft various polymeric chains onto silica particles via the aforementioned methods, but reports on Z supported RAFT polymerization from silica particles are scarce.[5,8−11] Nguyen and Vana reported on Z supported RAFT polymerization of styrene and methyl methacrylate in bulk at 60 °C using nanometer-sized fumed silica immobilized cumyl dithiobenzoate (Si-CDB) as a mediating agent.[5] When the graft polymerization was performed without using free CTA in solution, Si-CDB with lower CDB loadings was beneficial to the polymerization to yield a grafted polymer with a higher molecular weight, and "living" polymeric

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chains grafted onto fumed silica could reach up to 70%; however, the polydispersities of grafted chains were usually higher than 1.5. More recently, we investigated Z supported RAFT polymerization mediated by flash silica supported 3-(methoxycarbonyl-phenyl-methylsulfanylthiocarbonylsulfanyl)-propionic acid (Si-MPPA) and 3-(benzylsulfanylthiocarbonylsulfanyl)propionic acid (Si-BSPA) in the presence of free CTA.[9−11] For RAFT polymerization of methyl acrylate mediated by Si-MPPA in the presence of MPPA, the polydispersity indices of free and grafted polymers were usually low (PDI < 1.2), while longer PMA chains could be grafted onto silica particles as Si-MPPA with a higher loading was used as the mediating agent. For RAFT polymerization mediated by Si-BSPA, however, the control over molecular weight and polydispersity was quite poor, and the polydispersity indices were usually very high (PDI > 1.4), even if free BSPA was introduced into the solution. Preliminary results revealed that RAFT graft polymerization was significantly affected by some factors such as the types and loading of silica supported CTAs and free CTA used in solution, and well-defined polymeric chains could be grafted onto the solid supports by the Z-group approach under optimized conditions.

During RAFT graft polymerization based on solid supported chain transfer agents, some other factors including particle sizes and specific surface area of solid supports and reaction media may also play an important role in polymerization; however, reports on the relative research are very scarce to date.[46] To further investigate the effects of these factors on polymerization, fumed silica with a nominal particle size of 7 nm and without surface pores was chosen as the solid support in this study, and the Z supported RAFT polymerization of vinyl monomers mediated by silica supported CTAs in the presence of various free CTAs in toluene and methanol was investigated.

Experimental Procedures

Materials. All solvents, monomers, and other chemicals were purchased from Aldrich unless otherwise stated. Fumed silica with a nominal particle size of 7 nm and a specific surface area of 390 m^2/g was purchased from Aldrich. 3-(Mercaptopropyl)trimethoxysilane (95%) was purchased from Lancaster. 1-Propanethiol (98%) was purchased from Alfa Aesar. 3-(Methoxycarbonyl-phenyl-methylsulfanylthiocarbonylsulfanyl)propionic acid (MPPA),[47] 3-(benzylsulfanylthiocarbonylsulfanyl)propionic acid (BSPA),[40] and 2-(2-cyanopropyl) dithiobenzoate (CPDB)[25] were synthesized and purified according to literature methods. Methyl acrylate (MA), *N*,*N*-dimethylacrylamide (DMA), methyl methacrylate (MMA), butyl acrylate (BA), and styrene (St) were passed through a basic alumina (Brockmann I) column to remove the inhibitor before use. *N*-Isopropylacrylamide (NIPAM) was recrystallized twice from mixtures of hexane and toluene prior to use. Tetrahydrofuran (THF) and toluene were dried over 4 Å molecular sieves. 2,2′-Azobisisobutyronitrile (AIBN, 99%, Fisher) was recrystallized twice from ethanol. Other chemicals were of analytical grade and used as received.

Characterization. The number-average molecular weight (M_n) and polydispersity index (PDI) of polymer samples were determined by GPC at ambient temperature using a system equipped with a Polymer Laboratories 5.0 μm bead-size guard column (50 mm × 7.5 mm) and two PLgel 5.0 μm MIXED-C columns with a differential refractive index detector (Shodex, RI-101). THF was used as an eluent at a flow rate of 1.0 mL/min, and toluene was used as a flow rate marker. Polystyrene samples were calibrated with PS standard samples with M_n values in the range of 7 500 000−7 500 580 g/mol, and other samples were calibrated using PMMA standard samples with M_n values in the range of 1 944 000-1 945 020 g/mol. The absolute molecular weight of PMA free polymers with a high molecular weight shoulder was determined by GPC-LS using a PL-GPC50 Plus Integrated GPC System with multidetectors and THF as an eluent. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker 400 UltraShield spectrometer at 25 °C using $CDCl_3$ as a solvent. C, H, and N were determined by combustion followed by chromatographic separation and thermal conductivity detection using a Carlo Erba 1108 Elemental Analyzer. Sulfur analyses were conducted using the Schoniger Oxygen Flask combustion method followed by the relevant titration. Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer using a single reflection horizontal ATR accessory. Electrospray ionization mass spectrometry (ESI-MS) was performed on a Bruker Daltonics micrOTOF mass spectrometer. Thermogravimetric analyses (TGA) were carried out using a TA Instrument TGA 2050 thermogravimetric analyzer from room temperature to 500 °C at a rate of 10 °C/min under nitrogen.

Synthesis of Chain Transfer Agents. In a typical run, to a stirred solution of 3-(mercaptopropyl)trimethoxysilane (95%, 6.20 g, 30 mmol) in 50 mL of anhydrous methanol was added dropwise a solution of sodium methoxide in methanol (25 wt %, 6.48 g, 30 mmol) under nitrogen. After stirring for 30 min, CS_2 (3.05 g, 40 mmol) was added dropwise to the solution, and the mixture was then stirred at ambient temperature for 5 h. To the yellow solution was added benzyl bromide (98%, 5.24 g, 30 mmol), and the mixture was stirred overnight under nitrogen. The mixture was concentrated, diluted with dichloromethane, filtered off, and concentrated under reduced pressure until constant weight. *S*-Benzyl *S*′-trimethoxysilylpropyltrithiocarbonate (BTPT, 10.8 g, 30 mmol) was obtained as an orange oil and used without further purification. Other CTAs such as *S*-methoxycarbonylphenylmethyl *S*′-trimethoxysilylpropyltrithiocarbonate (MPTT), *S*-benzyl *S*′-propyltrithiocarbonate (BPTT), and *S*-methoxycarbonylphenylmethyl *S*′-propyltrithiocarbonate (MPPT) were synthesized according to a similar procedure using 3-(mercaptopropyl)trimethoxysilane and 1-propanethiol as raw materials and obtained in almost quantitative yield.

BTPT: ^1H NMR ($CDCl_3$): δ 7.30 (m, 5H, PhH), 4.60 (s, 2H, CH_2), 3.56 (s, 9H, CH_3O), 3.39 (t, *J*7, 2H, CH_2S), 1.84 (m, 2H, CH_2), 0.77 (t, *J*8, 2H, CH_2Si). ^{13}C NMR ($CDCl_3$): δ 223.2 (C=S), 135.0, 129.2, 128.6, 127.7 (PhC), 50.5, 41.3, 39.5, 21.8, 8.8.

MPTT: ^1H NMR ($CDCl_3$): δ 7.34 (m, 5H, PhH), 5.81 (s, 1H, CH), 3.74 (s, 3H, CH_3), 3.56 (s, 9H, CH_3O), 3.37 (t, *J*7, 2H, CH_2S), 1.81 (m, 2H, CH_2), 0.75 (t, *J*8, 2H, CH_2Si). ^{13}C NMR ($CDCl_3$): δ 221.8 (C=S), 169.5 (C=O), 133.2, 129.1, 128.9, 128.8 (PhC), 57.9, 53.3, 50.4, 39.8, 21.8, 8.9.

BPTT was purified by silica flash column chloromatography using 10:1 hexane/dichloromethane (v/v) as an eluent and obtained as a yellow liquid product in 98.5% isolated yield. ^1H NMR ($CDCl_3$): δ 7.33 (m, 5H, PhH), 4.61 (s, 2H, CH_2), 3.35 (t, *J*7, 2H, CH_2S), 1.75 (m, 2H, CH_2), 1.02 (t, *J*7, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 223.6 (C=S), 135.0, 129.2, 128.6, 127.7 (PhC), 41.3, 38.8, 21.5, 13.5. IR (cm^{-1}): 3062, 3030, 2962, 2928, 2871, 1602, 1585, 1494, 1453, 1421, 1397, 1378, 1337, 1288, 1236, 1194, 1082, 1060, 1044, 1030, 878, 800, 770, 695. Anal. calcd for $C_{11}H_{14}S_3$: C, 54.50%; H, 5.82%; S, 39.68%. Found: C, 54.55%; H, 5.84%; S, 39.62%. ESI-MS: $m/z = 243.0327$ $[M + H]^+$, theoretical value $= 243.0330$ (calcd for $C_{11}H_{15}S_3$).

MPPT was purified by silica flash column chloromatography using a gradient eluent of 4:1 hexane/dichloromethane (v/v) to pure dichloromethane and obtained as a yellow solid product in 98.7% isolated yield. mp 35−36 °C. ^1H NMR ($CDCl_3$): δ 7.34 (m, 5H, PhH), 5.82 (s, 1H, CH), 3.75 (s, 3H, CH_3O), 3.33 (t, *J*7, 2H, CH_2S), 1.74 (m, 2H, CH_2), 1.01 (t, *J*7, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 221.8 (C=S), 169.3 (C=O), 133.0, 128.9, 128.8, 128.6 (PhC), 57.7, 53.0, 38.9, 21.3, 13.3. IR (cm^{-1}): 3062, 3036, 3010, 2961, 2931, 2871, 1745, 1600, 1583, 1494, 1482, 1454, 1433, 1398, 1378, 1331, 1301, 1285, 1206, 1187, 1150, 1088, 1065, 1047, 1029, 998, 969, 923, 896, 855, 829, 817, 797, 785, 757, 731, 697. Anal. calcd for $C_{13}H_{16}O_2S_3$: C, 51.97%; H, 5.37%; S, 32.02%. Found: C, 51.92%; H, 5.38%; S, 32.00%. ESI-MS: $m/z = 301.0386$ $[M + H]^+$, theoretical value $= 301.0385$ (calcd for $C_{13}H_{17}O_2S_3$).

Synthesis of Silica Supported Chain Transfer Agents (FSi-CTAs). To a 500 mL three-necked flask was added 8.0 g of fumed silica and 250 mL of toluene, and a small amount of water in the system was removed by azeotropic distillation. After cooling to ambient temperature, 8.41 g (20 mmol) of MPTT in 50 mL of dry toluene was added into the flask under nitrogen. The reaction mixtures were heated to 100 °C to react overnight and then maintained at 120 °C for another 3 h. The crude product was cooled down, filtered off, washed with dichloromethane, and extracted with dichloromethane overnight using Soxhlet extractor. After drying at 60 °C under vacuum overnight, 8.64 g of MPTT grafted fumed silica particles (FSi-MPTT1) were obtained as deep yellow solid products. The filtrate was collected and concentrated, and 6.72 g of MPTT was recycled and used further for the synthesis of FSi-MPTT with different CTA loadings. Other fumed silica particles coated with MPTT or BTPT except FSi-MPTT3 were synthesized and purified according to a similar approach, and CTA loadings on solid supports could be adjusted by the control of reaction time and weight ratio of CTAs to fumed silica. As a comparison, FSi-MPPT3 was synthesized using fumed silica and reused MPTT as raw materials but was only purified by washing with toluene, THF, and acetone a few times.

FSi-MPTT1: elemental analysis: C, 10.3%; H, 1.40%; S, 5.65% (loading of 0.587 mmol of CTA per g of solid). IR (cm^{-1}): 1735 (C═O), 1623 (broad), 1456, 1436, 1031 (broad, Si−O, C−O, and C═S), 801, 729, 695.

FSi-MPTT2: C, 5.84%; H, 0.98%; S, 2.26% (CTA loading: 0.235 mmol/g).

FSi-MPTT3: C, 4.40%; H, 0.85%; S, 1.31% (CTA loading: 0.136 mmol/g).

FSi-BTPT1: C, 6.81%; H, 1.32%; S, 3.51% (CTA loading: 0.365 mmol/g). IR (cm^{-1}): 1629 (broad), 1496, 1454, 1031 (broad, Si−O, C−O, and C═S), 799, 699.

FSi-BTPT2: C, 3.80%; H, 0.85%; S, 1.95% (CTA loading: 0.203 mmol/g).

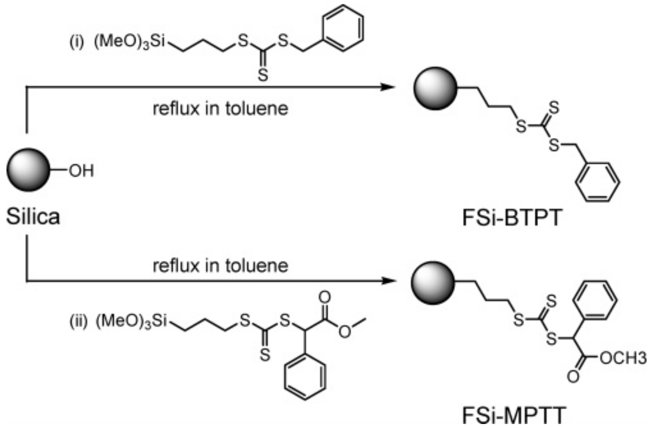
RAFT Polymerization Mediated by FSi-CTAs. In a typical run, FSi-MPTT1 (0.204 g, 120 μmol), MPPT (36.1 mg, 120 μmol), MA (3.10 g, 36.0 mmol), and AIBN (3.94 mg, 24.0 μmol) were added to a Schlenk tube, and toluene was added dropwise until the total volume was 12.0 mL. After adding a magnetic stirring bar, the tube was subjected to three freeze−pump−thaw cycles to remove oxygen. The tube was placed into an oil bath preheated to 60 °C for 18 h and then the polymerization was quenched by putting the tube into an ice−water bath. The residual monomer was removed by evaporation, and monomer conversion was determined to be 84.6% by gravimetry. The free polymer was isolated from polymer coated fumed silica by extracting the resultant mixtures with dichloromethane in a Soxhlet apparatus overnight. The filtrate was subjected to GPC analysis, and the fumed silica carrying surface bound polymer was dried under vacuum before aminolysis and TGA measurements. GPC analyses: cleaved grafted PMA, $M_n(g) = 12\,800$, PDI(g) = 1.18; free PMA, $M_n(f) = 19\,400$, PDI(f) = 1.12. The weight ($G_r = 37.8\%$) and molar ($G_p = 29.5$ μmol/g) grafting ratio of polymeric chains on solid surface was determined by TGA using the following equations,[4,7] where G_r and G_p mean the mass and molar ratio of grafted polymer to solid support, $W\%_{FSi-polymer}$ and $W\%_{FSi-CTA}$ are the percent weight loss between room temperature and 500 °C corresponding to the decomposition of polymer grafted fumed silica (FSi-polymer) and FSi-CTA, and $M_{n,GPC}(g)$ is the apparent molecular weight of grafted polymer determined by GPC

$$G_r = \frac{W\%_{FSi-polymer}}{100 - W\%_{FSi-polymer}} - \frac{W\%_{FSi-CTA}}{100 - W\%_{FSi-CTA}} \qquad (1)$$

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

General Procedure for Cleaving the Grafted Polymers.[48] To a glass tube was added 100 mg of PMA grafted fumed silica, 5 mL of THF, and one drop of a dilute aqueous solution of $Na_2S_2O_4$. The solution was degassed with nitrogen for 5−10 min, and then 0.1 mL of degassed *n*-hexylamine was injected into the mixture. After stirring at ambient temperature overnight, the solution was filtered off, and the recovered PMA was subjected to GPC analysis. Other grafted polymeric chains were cleaved according to a similar procedure.

Scheme 1. Synthetic Route to Fumed Silica Supported CTAs



Results and Discussion

Preparation of BTPT and MPTT Grafted Fumed Silica. In this study, fumed silica with a particle size of 7 nm and a specific surface area of 390 m^2/g was chosen as solid support, and functional fumed silica grafted with different CTA loadings was prepared to investigate the influence of loadings on polymerization. To this end, the RAFT-silane coupling agent with a high reactivity was synthesized and directly attached to the surface of fumed silica by a coupling reaction (Scheme 1). Two kinds of trimethoxysilane-containing CTAs− (*S*-benzyl *S*′-trimethoxysilylpropyltrithiocarbonate (BTPT) and *S*-methoxycarbonylphenylmethyl *S*′-trimethoxysilylpropyltrithiocarbonate (MPTT)) were synthesized by a multistep synthesis. First, 3-(mercaptopropyl)trimethoxysilane was reacted with sodium methoxide in dry methanol, followed by the addition of excessive carbon disulfide at ambient temperature. After stirring for 5 h, benzyl bromide or methyl α-bromophenylacetate was then added to the solution to form the target CTA. The reaction was almost quantitatively conducted in methanol at room temperature, and the purity of the crude products obtained was higher than 95%, as is evident from TLC and ^{1}H NMR analysis. Because of the potential instability of the trimethoxysilyl group and the serious absorption onto the silica gel column during purification, the resultant RAFT-silane agents were used without further purification. BTPT and MPTT were then grafted onto the surface of fumed silica by refluxing the mixtures of CTA and fumed silica in toluene. The excessive reactive CTAs were recycled by filtration and concentration, and impurities could be efficiently isolated from fumed silica supported CTAs (FSi-CTAs) by extraction with dichloromethane overnight using a Soxhlet extractor. When the mixtures were washed using organic solvents such as toluene, THF, and acetone, not all the impurities could be fully removed, as is evident from the production of star polymers in solution during FSi-MPTT3-mediated graft polymerization as discussed later. TGA, FT-IR, and elemental analysis (EA) confirmed that chain transfer agents were successfully immobilized to the surface of fumed silica. In addition, it was found that the CTA loadings on fumed silica could be adjusted by control over reaction time and weight ratio of CTAs to solid supports. The elemental analyses revealed that CTA loadings of various FSi-CTAs (mmol of CTA per g of solid)

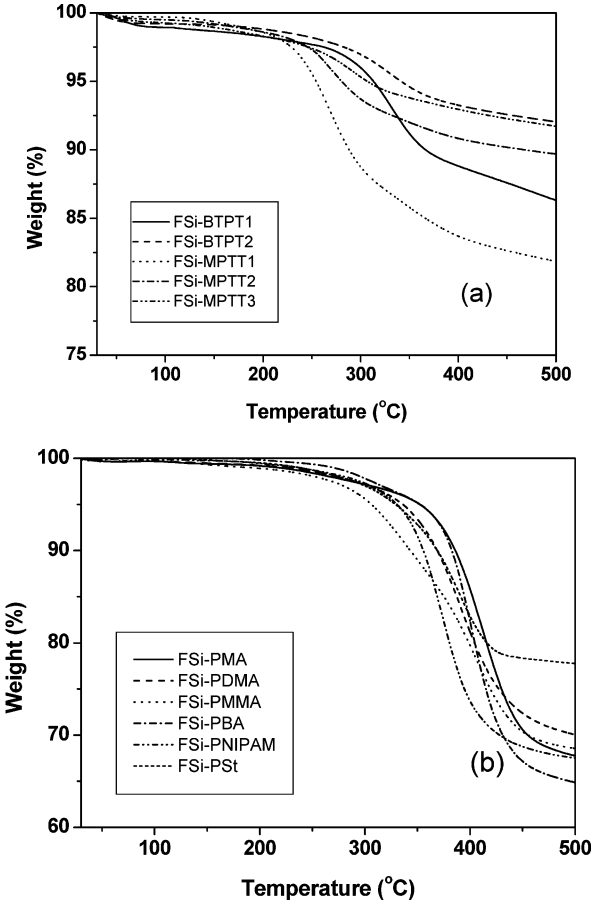


Figure 1. TGA curves of FSi-CTAs (a) and silica-polymer hybrids (b).

were 0.587 (FSi-MPTT1), 0.235 (FSi-MPTT2), 0.136 (FSi-MPTT3), 0.365 (FSi-BTPT1), and 0.203 (FSi-BTPT2), which were comparable to the results estimated by TGA using weight losses ranging from 100 to 500 °C (Figure 1a).

RAFT Graft Polymerization of Various Monomers. As for graft polymerization via the RAFT approach, reports on the effects of CTA loadings on polymerization are very scarce.[9−11] One goal of this study was to investigate the effects of types and loadings of FSi-CTAs on RAFT graft polymerization. To better control the graft polymerization, *S*-benzyl *S*′-propyltrithiocarbonate (BPTT) and *S*-methoxycarbonylphenylmethyl *S*′-propyltrithiocarbonate (MPPT) were synthesized according to procedures similar to RAFT-silane agents and introduced into the RAFT polymerization systems as free CTAs. The fumed silica supported chain transfer agents (FSi-CTA*n* (CTA = BTPT or MPTT, $n = 1$ or 2)) were then used to mediate RAFT polymerization of vinyl monomers such as methyl acrylate (MA), butyl acrylate (BA), *N*,*N*-dimethylacrylamide (DMA), *N*-isopropylacrylamide (NIPAM), methyl methacrylate (MMA), and styrene (St) in toluene at 60 °C. After polymerization, the polymer grafted fumed silica was isolated from free polymers by extraction, and the weight grafting ratio (G_r) was determined by TGA using eq 1 (see Experimental Procedures). The grafted polymer was recovered by aminolysis using *n*-hexylamine in THF at room temperature overnight, and a small amount of aqueous sodium bisulfite was used during aminolysis to avoid the oxidative coupling of the thiol end group.[48] The apparent molar grafting ratio (G_p) of polymeric chains on solid supports was calculated from the equation $G_p = G_r/M_n(g)$, where $M_n(g)$ is the number-average molecular weight of grafted polymer determined by GPC. Various polymeric chains could be efficiently grafted onto the surface of fumed silica, as is evident from TGA and FT-IR analyses. Figure 1b shows the typical TGA curves of FSi-polymer hybrids prepared by FSi-BTPT2-mediated RAFT polymerization. As can be seen, the weight grafting ratios of polymeric chains were satisfactory in each case, while the thermal properties of the silica-polymer hybrid materials were significantly dependent on the types of polymeric chains grafted onto the surface of the silica particles. In FT-IR spectra of silica-polymer samples (Figure 2), a strong and broad absorption band corresponding to the stretch vibration of Si−O and C−O was noted at 1020−1050 cm^{-1}; characteristic absorption bands of C═O stretching were observed at 1730−1732 cm^{-1} (PMA, PBA, and PMMA), 1627 cm^{-1} (PDMA), and 1643 cm^{-1} (PNIPAM); and characteristic peaks of PS appeared at 3060, 3028, 1602, 1494, 1454, 760, and 697 cm^{-1}.

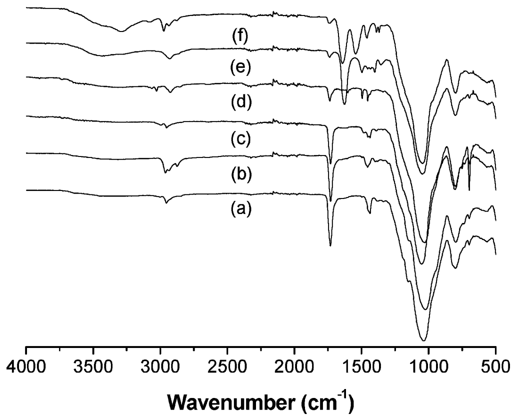


Figure 2. ATR FT-IR spectra of various silica-polymer hybrids: (a) FSi-PMA; (b) FSi-PBA; (c) FSi-PMMA; (d) FSi-PSt; (e) FSi-PDMA; and (f) FSi-PNIPAM.

For when the polymerization ($[M]_0/[\text{FSi-CTA}]_0/[\text{free CTA}]_0/[\text{AIBN}]_0 = 300{:}1{:}1{:}0.2$, $[M]_0 = 3.0$ mol/L, BPTT for FSi−BTPT-mediated polymerization, and MPTT for FSi−MPPT-mediated polymerization) was conducted in toluene at 60 °C for 18 h, the polymerization results are listed in Table 1. It was found that the PDIs of grafted polymers were slightly higher than those of the corresponding free polymers in most cases, perhaps due to unavoidable steric hindrance during graft polymerization. As expected, the molecular weight (M_n) values of the free polymers produced in solution were much higher than those of the grafted polymers due to the shielding effect and slower rate of addition−fragmentation reactions on the surface than in solution. For RAFT graft polymerization of MMA, the resultant free and grafted PMMAs had a relatively high polydispersity since the trithiocarbonates BPTT and MPTT are usually poor RAFT agents for the polymerization of MMA. FSi-BTPT-mediated RAFT polymerization of MMA (runs 17 and 18 in Table 1) could not control M_n and PDI of free and grafted polymers at all, while FSi-MPTT-mediated RAFT polymerization of MMA (runs 19 and 20 in Table 1) was liable to afford partial control over molecular weight and give a satisfactory polydispersity ($1.28 < \text{PDI} < 1.41$), indicating that these types of solid supported CTAs could play an important role in graft polymerization.

For polymerization mediated by FSi-BTPT1 with a higher loading of 0.365 mmol/g in the presence of BPTT (runs 1, 5, 9, 13, and 17 in Table 1), the polydispersity indices of grafted polymers were high ($\text{PDI} > 1.39$) except for polystyrene (run 21 in Table 1, PDI(g) = 1.28), although the PDI values of free polymers were usually low ($\text{PDI} < 1.21$). However, when FSi-BTPT2 with a lower loading of 0.203 mmol/g was used to mediate RAFT graft polymerization of various monomers (runs

Table 1. Polymerization Results for RAFT Graft Polymerization Mediated by FSi-CTA in the Presence of Free CTA (BPTT for FSi-BTPT and MPPT for FSi-MPTT)[a]

run	Si-CTA	M	C%	M_n(th)[b]	M_n(g)[c]	PDI(g)[c]	M_n(f)[d]	PDI(f)[d]	G_r (%)[e]	G_p (μ*mol/g*)[e]
1	FSi-BT PT1	MA	93.3	12300	9200	1.49	22400	1.12	28.3	30.8
2	FSi-BT PT2	MA	91.7	12100	12000	1.25	20700	1.18	39.0	32.5
3	FSi-MP TT1	MA	84.6	11200	12800	1.18	19400	1.12	37.8	29.5
4	FSi-MP TT2	MA	83.7	11100	10500	1.20	18600	1.16	37.4	35.6
5	FSi-BT PT1	BA	94.8	18500	10700	1.45	33200	1.21	37.2	34.8
6	FSi-BT PT2	BA	95.5	18600	12200	1.24	39200	1.15	43.9	36.0
7	FSi-MP TT1	BA	90.9	17800	12400	1.20	32800	1.19	39.3	31.7
8	FSi-MP TT2	BA	89.0	17400	11300	1.18	37000	1.13	41.8	37.0
9	FSi-BT PT1	DMA	98.9	14900	9800	1.39	19400	1.10	28.8	29.4
10	FSi-BT PT2	DMA	99.5	15000	10500	1.18	18200	1.14	33.5	31.9
11	FSi-MP TT1	DMA	98.3	14900	11800	1.14	20200	1.12	33.2	28.1
12	FSi-MP TT2	DMA	97.9	14800	9630	1.15	18000	1.11	35.4	36.8
13	FSi-BT PT1	NIPAM	98.9	17000	10200	1.44	28100	1.17	31.6	31.0
14	FSi-BT PT2	NIPAM	98.5	17000	11800	1.24	27200	1.20	38.5	32.6
15	FSi-MP TT1	NIPAM	94.5	16300	12400	1.22	27000	1.20	33.1	26.7
16	FSi-MP TT2	NIPAM	97.3	16800	10500	1.25	26400	1.22	32.4	30.9
17	FSi-BT PT1	MMA	65.1	10000	22500	1.88	119000	1.82	32.0	14.2
18	FSi-BT PT2	MMA	64.0	9850	21800	1.65	174000	1.63	37.3	17.1
19	FSi-MP TT1	MMA	57.1	8880	9240	1.35	22300	1.41	21.7	23.5
20	FSi-MP TT2	MMA	58.7	9120	8100	1.28	19400	1.37	23.2	28.6
21	FSi-BT PT1	St	28.6	4710	5750	1.28	9620	1.21	17.5	30.4
22	FSi-BT PT2	St	27.0	4460	5800	1.22	9350	1.24	19.4	33.4
23	FSi-MP TT1	St	31.5	5220	6350	1.18	9250	1.11	18.2	28.7
24	FSi-MP TT2	St	26.1	4380	5420	1.20	7770	1.11	18.9	34.9

[a] Polymerization conditions: $[M]_0/[FSi\text{-}CTA]_0/[free\ CTA]_0/[AIBN]_0 = 300{:}1{:}1{:}0.2$, $[M]_0 = 3.0$ mol/L, in toluene at 60 °C for 18 h (runs 1−20) or 48 h (runs 21−24). Loadings of various FSi-CTAs (mmol/g): 0.365 (FSi-BTPT1), 0.203 (FSi-BTPT2), 0.587 (FSi-MPTT1), and 0.235 (FSi-MPTT2). [b] $M_n(th) = M_{w,m} \times C\% \times [M]_0/(2[FSi\text{-}CTA]_0) + M_{w,CTA}$, where $M_{w,m}$ and $M_{w,CTA}$ are molecular weights of monomer and free CTA. [c] Molecular weight and polydispersity of grafted polymers determined by GPC. [d] Molecular weight and polydispersity of free polymers produced in solution. [e] Weight (G_r) and molar (G_p) grafting ratio of polymer grafted onto fumed silica determined by TGA.

2, 6, 10, 14, and 22 in Table 1), both free and grafted polymers had low polydispersities (PDI < 1.25). Furthermore, when FSi−BTPT-mediated graft polymerization of the same monomer was conducted at identical reaction conditions, the monomer conversions were usually close, while slightly longer polymeric chains with a lower polydispersity could be grafted onto the silica surface as FSi-BTPT2 was used as the mediating agent. This phenomenon indicates that CTA loadings on solid supports may significantly affect the graft polymerization due to the potential effects of the CTA surface density on the degree of shielding effect and the rates of polymerization in solution and on the silica surface.

When FSi-MPTT was used to mediate RAFT graft polymerization in the presence of MPPT, the polymerization afforded free and grafted polymers with a low polydispersity (PDI < 1.25), except PMMA samples obtained in runs 19 and 20 (Table 1). When graft polymerizations of the same monomer mediated by FSi-MPTT were conducted at identical conditions, similar conversions and comparable PDI values of polymers were obtained, while FSi-MPTT1 (higher loading of 0.587 mmol/g) mediated polymerization tended to afford slightly longer grafted polymeric chains. This phenomenon also confirmed that the graft polymerization could be affected by CTA loadings.

Theoretically, an intermediate loading of FSi-CTA will favor the Z supported RAFT graft polymerization and afford better-defined grafted polymers and a relatively high grafting density. If the loading is very high, the high concentrations of reactive sites at the surface will increase the shielding effect, and the chain transfer activity at the surface will be strong, which possibly leads to a low grafting efficiency, although the total grafting density of polymeric chains may remain high. On the contrary, a very low loading can significantly decrease the shielding effect and increase the grafting efficiency; however, the low local concentrations of the tethered CTAs may result in the production of nonuniform grafted polymeric chains. From Table 1, it can be seen that the lower loadings of the same FSi-CTA were liable to afford higher molar grafting ratios of polymeric chains on a silica surface. One possible reason for this phenomenon is that the higher surface density of the active sites of FSi-CTAs further prevented the diffusion of monomer and polymeric chain radicals to the reactive sites.[31]

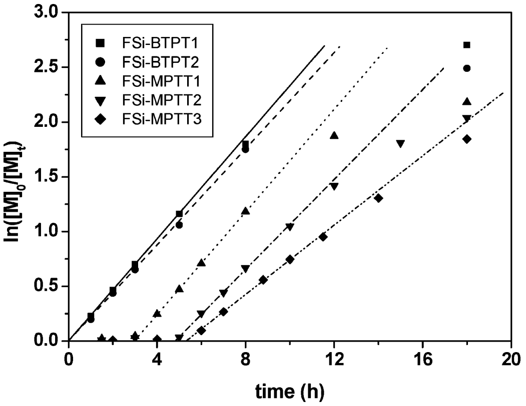


Figure 3. Pseudo-first-order kinetic curves for RAFT graft polymerization of MA mediated by FSi-CTA in the presence of a free CTA (BPTT for FSi-BTPT and MPPT for FSi-MPTT) in toluene at 60 °C. $[M]_0/[FSi\text{-}CTA]_0/[free\ CTA]_0/[AIBN]_0 = 300{:}1{:}1{:}0.2$, $[M]_0 = 3.0$ mol/L. Loadings of various FSi-CTAs (mmol/g): 0.365 (FSi-BTPT1), 0.203 (FSi-BTPT2), 0.587 (FSi-MPTT1), 0.235 (FSi-MPTT2), and 0.136 (FSi-MPTT3).

RAFT Graft Polymerization of Methyl Acrylate in Toluene: Polymerization Kinetics. To investigate the effects of types and loadings of FSi-CTAs and monomer conversions on graft polymerization, the RAFT graft polymerization of MA was studied in detail. For when the polymerization was conducted in toluene at 60 °C, the apparent kinetic curves are depicted in Figure 3. It was found that pseudo-first-order polymerization kinetics was maintained until high conversion up to 80%. No induction period was noted for FSi-BTPT-mediated polymerization, while an obvious induction period (about 3−5 h) was observed for FSi-MPTT-mediated polym-

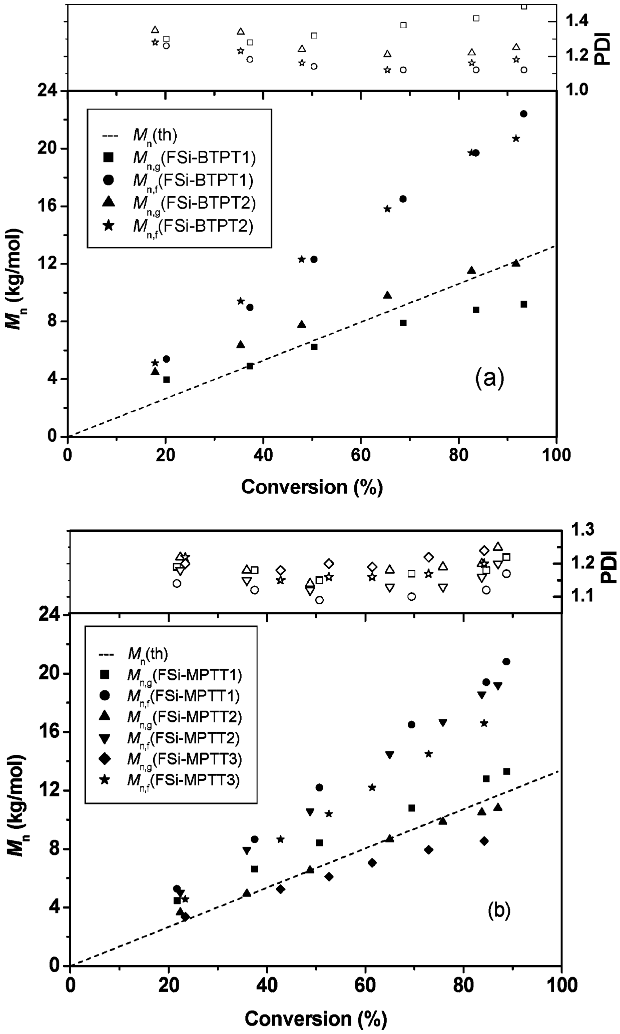


Figure 4. Evolution of molecular weight and polydispersity of free and grafted PMAs with monomer conversion during RAFT graft polymerization. See Figure 3 for polymerization conditions.

erization. The rates of polymerization were slightly increased in the order FSi-BTPT1 > FSi-BTPT2 and FSi-MPTT1 > FSi-MPTT2 > FSi-MPTT3, indicating that higher loadings of same FSi-CTAs were liable to give slightly increased rates of polymerization at identical reaction conditions.

When FSi-BTPTs with different loadings were used to mediate RAFT polymerization in the presence of BPTT, linear evolution of molecular weights of free and grafted polymers with conversion up to 84% was observed (Figure 4a). Free and grafted polymers obtained at low conversions had similar molecular weight values. With increasing conversion, the molecular weights of free polymers were much higher than those of grafted polymers, due to significant shielding effect and lower rates of polymerization on solid surfaces. In all cases, free polymers obtained at similar conversions had very close molecular weights and relatively low polydispersities (PDI = 1.1−1.3). At various conversions, FSi-BTPT1-mediated polymerization could only afford shorter grafted polymeric chains, and their PDIs tended to gradually increase from 1.3 to 1.5; however, FSi-BTPT2-mediated polymerization could give longer polymeric chains with polydispersities ranging between 1.2 and 1.4 grafted onto silica surfaces, indicating that the loadings of FSi-BTPT played an important role in graft polymerization. The former could be ascribed to a significantly increased shielding effect with increasing conversion. At low conversion, rates of addition−fragmentation transfer reactions in solution and on surfaces were quite similar due to the lack of significant shielding effects and much higher concentration of reactive sites at solid surfaces than in solution, resulting in similar chain lengths of free and grafted polymers. With increasing conversion, only polymeric chain radicals with lower molecular weights could reach the surface to conduct the addition−fragmentation chain transfer reaction due to increased steric hindrance, and the polymerization rate at the surface was further slowed down due to the restricted diffusion of monomer and polymeric chain radicals to the reactive sites, leading to a slowly increased molecular weight and broadened polydispersity of grafted polymers. As FSi-BTPT1 with a higher loading was used as a mediating agent, the reversible addition−fragmentation chain transfer reaction at the surface could not be efficiently conducted at high conversion, as is evident from the gradually increased polydispersity and significant tailings in GPC traces of the resultant grafted polymers.

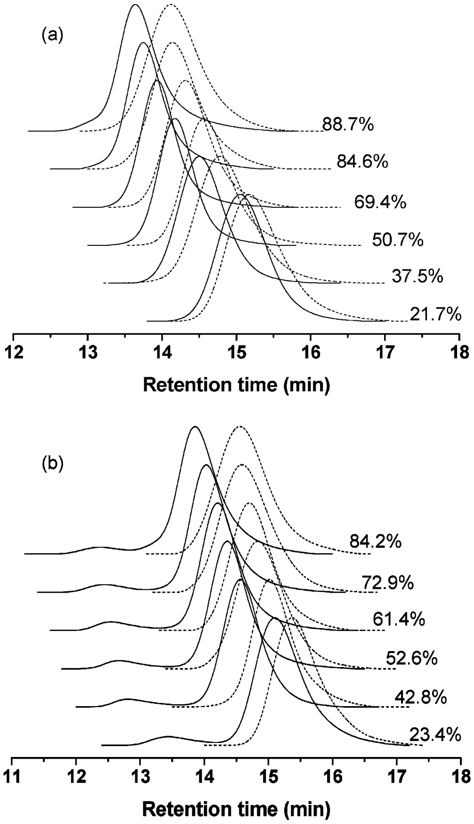


Figure 5. GPC traces of free (solid line) and grafted (dashed line) PMAs obtained by RAFT graft polymerization mediated by FSi-MPTT1 (a) and FSi-MPTT3 (b) at various conversions.

Figure 4b shows the dependence of molecular weight and polydispersity of free and grafted polymers on monomer conversion during RAFT graft polymerization of MA mediated by FSi-MPTT in the presence of MPPT. As expected, the molecular weights of free and grafted polymers linearly increased with an increase in monomer conversion, and the molecular weights of free polymers obtained at high conversions were much higher than those of grafted polymers. It was noted that the molecular weights of free and grafted polymers obtained by FSi-MPTT-mediated graft polymerization at identical conditions tended to increase in the order FSi-MPTT1 > FSi-MPTT2 > FSi-MPTT3, while the PDIs were relatively low (PDI < 1.3) in all cases. These results suggest that higher loadings of FSi-MPTT were liable to afford longer polymeric chains grafted onto silica surfaces.

Table 2. Molecular Weight and Polydispersity of Free PMA Samples Obtained via RAFT Graft Polymerization of MA Mediated by FSi-MPTT3 (0.136 mmol/g) in the Presence of Free MPPT in Toluene at 60 °C[a]

run	*t* (h)	C%	M_n(th)	M_n(f_1)	PDI(f_1)	M_w(f_1)	M_n(f_2)	PDI(f_2)	M_w(f_2)	M_w(f_2)/M_w(f_1)
1	7	23.4	3320	4560	1.22	3780	26 200	1.10	29 100	7.70
2	8.8	42.8	5830	8660	1.15	6250	48 900	1.10	49 400	7.90
3	10	52.6	7090	10400	1.16	7310	58 200	1.09	56 200	7.69
4	11.5	61.4	8230	12200	1.16	8800	68 800	1.09	66 400	7.55
5	14	72.9	10100	14500	1.17	10400	80 000	1.08	75 200	7.23
6	18	84.2	11200	16600	1.20	12400	89 200	1.06	88 700	7.15

[a] Polymerization conditions: $[M]_0/[\text{FSi-MPTT3}]_0/[\text{MPPT}]_0/[\text{AIBN}]_0 = 300{:}1{:}1{:}0.2$, $[M]_0 = 3.0$ mol/L, where f_1 means linear PMA and f_2 means star PMA, M_n is number-average molecular weight determined by GPC, and M_w is number-average molecular weight determined by GPC-LS.

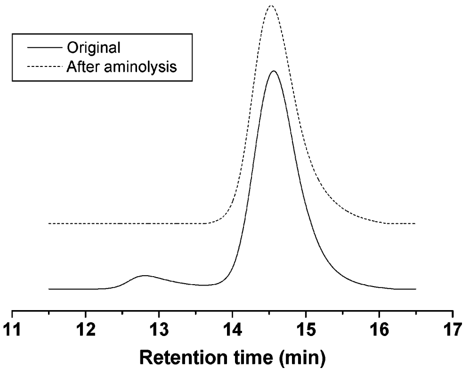
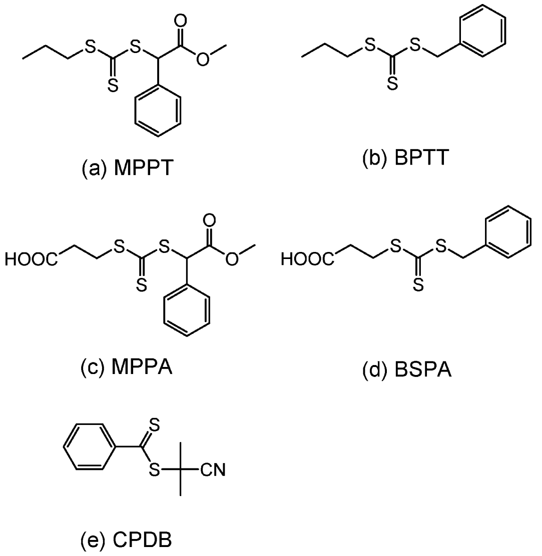


Figure 6. GPC traces of free PMA before and after aminolysis, where the original PMA sample was obtained by FSi-MPTT3-mediated RAFT graft polymerization in the presence of MPPT.

Scheme 2. Chemical Structures of Various Free CTAs Used in RAFT Graft Polymerization



(a) MPPT (b) BPTT (c) MPPA (d) BSPA (e) CPDB

As a comparison, the GPC traces of free and grafted PMAs obtained by FSi-MPTT1 (a) and FSi-MPTT3 (b) mediated RAFT graft polymerization are shown in Figure 5. In Figure 5a, the GPC traces of various polymers gradually shifted to the high molecular weight side with increasing conversion, and no significant shoulders and tailings were observed except that a shoulder in the high molecular weight side corresponding to radical−radical termination by combination was noted for free polymers obtained at 88.7% conversion. In Figure 5b, however, a shoulder in the high molecular weight side (about 5% calculated from the peak areas of free polymers) was observed in GPC traces of free PMAs obtained by FSi-MPTT3-mediated polymerization at various conversions, which gradually shifted to the higher molecular weight side with increasing conversions. Noting that the shoulder peak could not be ascribed to polymers produced by coupling reactions, two kinds of free polymers (f_1, linear PMA and f_2, higher M_n fraction) were analyzed by conventional GPC and GPC-MALLS with THF as an eluent, and the results are shown in Table 2. As can be seen, the molecular weight values of linear PMAs estimated by conventional GPC were significantly higher than those determined by GPC-LS, and the latter were very close to the theoretical values, which can be ascribed to different hydrodynamic volumes of PMA and PMMA samples. The PDIs obtained were less than 1.22, corresponding to the nature of controlled polymerization. The molecular weight ratios of f_2 to f_1 ranged between 7 and 8, suggesting that the high molecular weight fraction was a star polymer with an average arm number of 7−8. The star polymer was presumably originated from the silsesquioxane cage-based multifunctional CTA, which maybe produced during the refluxing reaction of fumed silica and MPTT in toluene at high temperature and absorbed on the surface of fumed silica. The free polymers were then subjected to aminolysis, and the GPC traces of free polymer samples (run 2 in Table 2) before and after aminolysis are shown in Figure 6. After aminolysis, the signal corresponding to the star polymer wholly disappeared, and only one unimodal distribution was observed in GPC traces. The aminolyzed PMA ($M_n = 8840$, PDI = 1.13) and the original linear PMA sample ($M_n = 8660$, PDI = 1.15) had similar molecular weight and polydispersity, suggesting that the star polymer was also formed by RAFT polymerization via Z-group approach in which the arm could be efficiently cleaved from the core by aminolysis. Other free PMA samples were also subjected to aminolysis, and the results were quite similar, confirming that the arm length of the star polymer was almost uniform. To wholly remove the impurities, FSi-MPTT3 was extracted with dichloromethane overnight using a Soxhlet extractor, and the resultant FSi-MPTT3′ had a loading of 0.0964 mmol/g as determined by elemental analysis. FSi-MPTT3′ was then used to mediate RAFT graft polymerization of MA at identical conditions, and the polymerization for 15 h gave a conversion of 81.8%. As expected, only one monomodal distribution was observed in GPC traces of free ($M_n = 16\,300$, PDI = 1.19) and grafted ($M_n = 8480$, PDI = 1.25) polymers obtained. The previous results demonstrated that the washing method using organic solvents could not efficiently remove the impurities such as multifunctional CTAs absorbed on the surface of fumed silica.

Effects of Free CTAs and Reaction Media on Graft Polymerization. Until now, most of the solid-based graft polymerization was conducted either solvent-free or in a good solvent of polymer chains, while polymerization performed in poor solvents was very scarce. Recently, Guo et al. reported the synthesis of PMMA brushes grafted onto single-walled carbon nanotubes by in situ free radical polymerization in methanol or a methanol/water mixture and found that the grafting ratio of the polymer chains was significantly enhanced as compared to that in toluene, indicating the potential effects of reaction media on graft polymerization.[46] One the other hand, less steric hindrance and similar polymerization rates in solution

Table 3. RAFT Graft Polymerization of MA Mediated by FSi-CTAs in the Presence of Various Free CTAs in Toluene (T) and Methanol (M)[a]

run	FSi-CTA	free CTA	solvent	C%	M_n(th)	M_n(g)	PDI(g)	M_n(f)	PDI(f)	G_r (%)	G_p (*μmol/g*)
1	FSi-M PTT1	MPPT	T	84.6	11200	12800	1.18	19400	1.12	37.8	29.5
2	FSi-M PTT1	BPTT	T	91.4	12000	7880	1.32	16400	1.20	27.1	34.4
3	FSi-M PTT1	MPPA	T	85.0	11300	11200	1.16	17800	1.16	31.6	28.2
4	FSi-M PTT1	BSPA	T	90.5	12000	8070	1.39	19200	1.28	28.4	35.2
5	FSi-M PTT1	CPDB	T	48.5	6480	7280	1.16	9130	1.19	36.8	50.5
6	FSi-M PTT1	MPPT	M	81.2	10800	13200	1.14	23100	1.15	49.5	37.5
7	FSi-M PTT1	BPTT	M	86.3	11400	10600	1.22	23600	1.17	42.8	40.4
8	FSi-M PTT1	MPPA	M	82.1	10900	12500	1.15	20900	1.18	48.7	39.0
9	FSi-M PTT1	BSPA	M	86.1	11400	9920	1.28	23700	1.19	42.6	42.9
10	FSi-M PTT1	CPDB	M	31.2	4250	5360	1.12	6770	1.14	31.2	58.2
11	FSi-B TPT1	MPPT	T	89.8	11900	10900	1.22	21700	1.17	33.9	31.1
12	FSi-B TPT1	BPTT	T	93.3	12300	9200	1.49	22400	1.12	28.3	30.8
13	FSi-B TPT1	MPPA	T	86.7	11500	9550	1.21	19100	1.17	30.7	32.1
14	FSi-B TPT1	BSPA	T	91.9	12100	8360	1.52	22200	1.19	26.1	31.2
15	FSi-B TPT1	CPDB	T	45.5	6100	6830	1.16	8420	1.13	33.3	48.8
16	FSi-B TPT1	MPPT	M	84.8	11300	11200	1.18	23100	1.12	48.3	43.1
17	FSi-B TPT1	BPTT	M	87.4	11500	10500	1.28	23800	1.14	47.6	45.3
18	FSi-B TPT1	MPPA	M	81.9	10900	9720	1.15	20400	1.13	43.2	44.4
19	FSi-B TPT1	BSPA	M	85.5	11300	8870	1.26	22900	1.18	40.8	46.0
20	FSi-B TPT1	CPDB	M	34.6	4690	5840	1.12	7350	1.09	34.2	58.6
21	FSi-B TPT2	CPDB	T	39.8	5360	5510	1.12	6720	1.13	26.2	47.5
22	FSi-M PTT2	CPDB	T	33.1	4490	5240	1.16	5820	1.11	25.4	48.5

[a] Polymerization conditions: $[M]_0/[FSi\text{-}CTA]_0/[free\ CTA]_0/[AIBN]_0 = 300:1:1:0.2$, $[M]_0 = 3.0$ mol/L, at 60 °C for 42 h (free CTA = CPDB) or 18 h (other free CTAs).

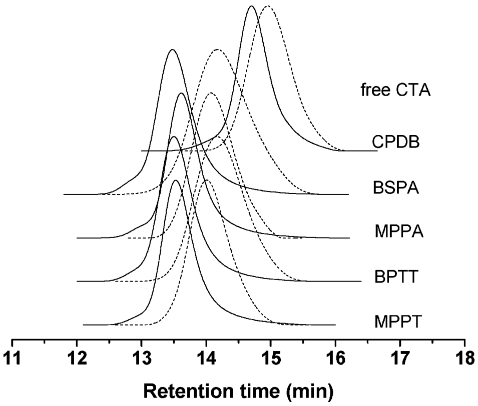


Figure 7. GPC traces of free (solid line) and grafted (dashed line) PMAs obtained by RAFT graft polymerization mediated by FSi-MPTT1 in the presence of various free CTAs in methanol. See Table 3 for detailed reaction conditions.

and on surfaces are crucial to synthesize free and grafted polymers with similar molecular weights via graft polymerization, so choosing a suitable free CTA in solution is necessary to obtain well-defined grafted polymers. To investigate the effects of various free CTAs and reaction media on polymerization, FSi-MPTT1 and FSi-BTPT1 were chosen as the mediating agents to perform RAFT polymerization of MA in toluene or methanol, and MPPT, BPTT, MPPA, BSPA, and 2-(2-cyanopropyl) dithiobenzoate (CPDB) were introduced into the solution as free CTAs (Scheme 2).

For when the graft polymerization using various free CTAs and reaction media was conducted at 60 °C, the results are shown in Table 3. When RAFT polymerization was performed at identical conditions, the total conversion in toluene was slightly higher than that in methanol, which can be ascribed to the homogeneous reaction in toluene and heterogeneous reaction in methanol. As compared to samples prepared in toluene, the free PMA samples obtained in methanol had higher molecular weights, although the PDIs in both cases were similar. When RAFT polymerization is conducted in a good solvent such as toluene, some side reactions such as radical−radical coupling and disproportionation terminations can be avoided under optimal conditions even at high conversion. When methanol was used as a solvent, a polymer−polymer interaction is favored over a polymer−solvent interaction, so the living polymeric radicals are expelled from the solvent and tend to form polymer globules or be close to the surface of fumed silica.[46] The side reactions were correspondingly increased due to increased local concentrations of monomer and free radicals (which is similar to that in dispersion polymerization), as is evident from the significant shoulders and tailings in GPC traces of polymers (Figure 7). Meanwhile, the grafted polymers prepared in methanol possessed higher molecular weights and lower PDIs than those obtained in toluene, and no significant shoulders and tailings were observed from GPC traces of the cleaved PMA samples. This observation follows early work by Odian and others, who studied the effect of solvents on graft polymerization and observed that poor solvents for the grafted polymeric chains lead to faster polymerization rates and higher grafting ratios, when compared to polymerizations undertaken in good solvents, as a result of a Trommsdorff-type effect.[49,50] Since methanol is a poor solvent for poly(methyl acrylate), the growing polymeric chains become relatively immobilized, as a result of which their rate of collision with other growing chains is decreased, and consequently, termination is reduced. These results confirm that for RAFT as well, graft polymerization in a poor solvent could afford grafted polymers with a higher molecular weight and lower polydispersity and increased grafting density.

For polymerization conducted in the same solvent, the polymerization using free CTAs with the same R-group and similar Z-group such as MPPT and MPPA tended to give a similar polymerization rate and comparable molar grafting ratio. As compared to the polymerization using free CTAs of BPTT and BSPA, the polymerization using MPPT and MPPA as free CTAs could afford lower polydispersity indices of PMAs (PDI < 1.22), longer grafted polymeric chains, and lower molar grafting ratios, indicating that the graft polymerization could be significantly affected by types of free CTAs used in solution. As expected, the introduction of a dithiobenzoate-based CTA such as CPDB in toluene could afford free and grafted polymers with much closer M_n values due to a significantly decreased polymerization rate in solution, which was in good agreement with the results in RAFT graft polymerization mediated by flash silica supported CTAs.[9,10] The previous results show that well-defined polymeric chains can be grafted onto fumed silica particles via the RAFT process using suitable free CTAs and reaction media.

Conclusion

It was demonstrated that Z supported RAFT graft polymerization could yield well-defined polymer grafted fumed silica under suitable conditions. The CTA loadings, types of free CTAs, and reaction media played important roles during graft polymerization. Under optimized conditions, well-defined polymeric chains with a low polydispersity and chain lengths similar to those of free polymers could be grafted onto the surface of fumed silica, and the grafting ratios were relatively high, as is evident from GPC, FT-IR, and TGA analyses. The graft polymerization of methyl acrylate in inhomogeneous media such as methanol could afford longer grafted chain lengths and significantly increased grafting density due to the heterophase reaction environment and smaller shielding effect.

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