Macromolecules **2006,** *39,* 8603−8608

Synthesis of Well-Defined Homopolymer and Diblock Copolymer Grafted onto Silica Particles by Z-Supported RAFT Polymerization

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Received July 14, 2006; Revised Manuscript Received September 25, 2006

ABSTRACT: Well-defined homopolymer and diblock copolymer were prepared by RAFT polymerization mediated by Z-supported chain transfer agent (CTA) onto silica particles. Silica-supported 3-(methoxycarbonylphenylmethylsulfanylthiocarbonylsulfanyl)propionic acid (Si-MPPA) was used to mediate RAFT polymerization of methyl acrylate, methyl methacrylate, butyl acrylate, and styrene to produce homopolymer grafted silica. The introduction of a free CTA such as MPPA and 2-(2-cyanopropyl) dithiobenzoate (CPDB) in solution during polymerization could significantly improve the control on molecular weight and polydispersity of grafted polymers, and the polymerization in the presence of CPDB was more controlled than that using MPPA. The resultant homopolymer grafted silica was utilized as a macro-CTA to mediate chain extension polymerization, and a series of diblock copolymer grafted silica hybrids were prepared. Aminolysis of the polymers allowed the recovery of the polymeric chains showing 100% chain extension, as illustrated by the complete shift of GPC traces and low polydispersity ($M_w/M_n < 1.2$). This efficient chain extension polymerization confirmed the original macro-CTAs had living homopolymer chains covalently attached to the surface.

Introduction

The surface modification of inorganic particles and synthetic resins with a polymer shell has attracted increasing interest due to their unique properties and potential applications in optics, electronics, engineering, and biosciences.[1−3] In recent years, controlled radical polymerization methods such as nitroxide-mediated polymerization (NMP),[4−8] atom transfer radical polymerization (ATRP),[8−14] and reversible addition−fragmentation chain transfer (RAFT) polymerization[15−31] 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 controlled chain-end functionality. RAFT polymerization has become one of most promising living radical polymerization techniques due to its tolerance to a wide range of reaction conditions, the straightforward setup to result in a block copolymer, and its versatility toward the range of monomers with variable functionality.[32−36] The design of the initial RAFT agent and master of the polymerization mechanism are crucial to synthesize well-defined complex polymeric architectures such as star (co)polymers,[37−43] comb polymers,[44−47] and grafted polymers[15−31] using RAFT polymerization. In general, RAFT polymerization based on solid supports can be performed using both (a) the R-group approach where the chain transfer agent (CTA) is attached to the backbone via the leaving and reinitiating R group and (b) the Z-group approach where the CTA is attached to the backbone via the stabilizing Z group, and both methods have advantages and limitations.[34−36] In the R-group approach, where the solid support is part of the leaving R group, higher molecular weight of grafted polymers and grafting density can be achieved, but the molecular weight distribution may be broadened by the possible chain coupling.[15−17] In the Z-group approach, where the backbone is part of Z group, the RAFT process involves the reaction of linear radical chains with the functional backbone, leading to a monomodal molecular weight distribution and a better-defined grafted polymer, but the grafting density is liable to decrease due to the shielding effect.[37−40] Until now, RAFT polymerization has been successfully used to graft a wide range of polymeric chains onto various solid supports such as functionalized silica particles,[15−19] silicon wafer,[20,46,47] gold nanoparticles,[21,22] CdSe nanoparticles,[23] carbon nanotubes,[24,25] cotton,[26] cellulose,[27,28] and Merrifield resin,[19,29] but reports on Z-supported RAFT polymerization from a solid support are very scarce.[19,27,29] More recently, *S*-methoxycarbonylphenylmethyl dithiobenzoate (MCPDB) was attached to the surface of Merrifield resin and silica particles by our group, and the resultant solid-supported CTAs were successfully used to mediate Z-supported RAFT polymerization of methyl acrylate (MA) by introducing a free MCPDB in solution.[19,29] The Z-group approach based on solid supports is unique to the RAFT system. As all the chains grafted onto silica are attached via the CTA, the process leads to the production of true living polymer chains, as they can be isolated from dead materials by easy procedures such as washing and filtration. The process also enables the straightforward synthesis of pure block copolymers when compared to other living radical polymerization systems. Indeed, simple filtration ensures that the copolymer is not contaminated by homopolymer impurities produced by termination reactions. In this study, the Z-supported RAFT polymerization of various monomers mediated by silica-supported 3-(methoxycarbonylphenylmethylsulfanylthiocarbonylsulfanyl)-propionic acid (Si-MPPA) was investigated, and the macro-CTAs obtained were utilized to mediate chain extension polymerization to prepare well-defined diblock copolymers (Scheme 1). To the best of our knowledge, this is the first report of a free radical polymerization system producing near-perfect living block copolymers.

Experimental Section

Materials. All solvents, monomers, and other chemicals were purchased from Aldrich at the highest purity available unless otherwise stated. Silica gel particles with particle size of 35−70 μm and a specific surface area of 500 m^2/g were boiled in 20% HCl, washed with distilled water and acetone, and dried under vacuum at 60 °C overnight. 3-(Methoxycarbonylphenylmethyl-

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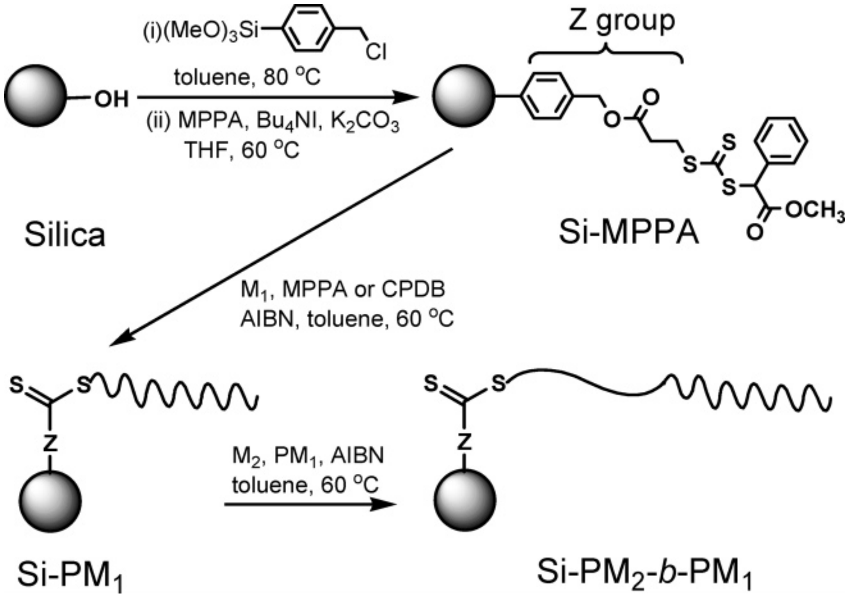
10.1021/ma061586y CCC: $33.50 © 2006 American Chemical Society
Published on Web 11/08/2006

Scheme 1. Synthetic Route to Polymer-Grafted Silica Particles by Z-Supported RAFT Polymerization



sulfanylthiocarbonylsulfanyl)propionic acid (MPPA)[29] and 2-(2-cyanopropyl) dithiobenzoate (CPDB)[32] were synthesized and purified according to literature methods. Methyl acrylate (MA), methyl methacrylate (MMA), butyl acrylate (BA), and styrene (St) were passed through a basic alumina (Brockmann I) column to remove the inhibitor before use. Tetrahydrofuran (THF, Riedel-deHaën, HPLC grade) and toluene were dried over 4 Å molecular sieves. 2,2′-Azobis(isobutyronitrile) (AIBN, 99%, Fisher) was recrystallized twice from ethanol.

Gel Permeation Chromatography (GPC). The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of free and grafted 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 × 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 value in the range of 7 500 000−580 g/mol; other samples were calibrated using PMMA standard samples with M_n value in the range of 1 944 000−1020 g/mol.

^{1}H NMR Spectroscopy. ^{1}H NMR spectra were recorded on a Bruker 400 UltraShield spectrometer at 25 °C using $CDCl_3$ as a solvent.

Elemental Analyses. C, H, and N were determined by combustion followed by chromatographic separation and thermal conductivity detection using a Carlo Erba 1108 elemental analyzer. Chlorine and sulfur analyses were conducted using the Schoniger oxygen flask combustion method followed by the relevant titration.

FT-IR Spectroscopy. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using a single reflection horizontal ATR accessory.

Thermogravimetric Analysis (TGA). TGA was carried out using a TA Instruments TGA 2050 thermogravimetric analyzer from room temperature to 500 °C at a rate of 10 °C/min under a nitrogen atmosphere.

Synthesis of Si-MPPA. Under nitrogen, to a slurry of 20 g of silica in 150 mL of toluene was added 3.50 g (90%, 12.8 mmol) of 4-(chloromethyl)phenyltrimethoxysilane. The reaction mixtures were heated to 80 °C for 15 h. After cooling to room temperature, the benzyl chloride functionalized silica (Si−Cl) was filtered, washed with toluene and diethyl ether, and then dried under vacuum at room temperature. Elemental analysis: Cl, 2.00% (loading of 0.563 mmol/g). FT-IR: 1609 (C═C, Ar ring), 1051 (Si−O), 959, 796, 740 (C−Cl), 695 cm^{-1}.

To a round flask was added 15 g (8.45 mmol) of Si−Cl, 2.76 g (20.0 mmol) of potassium carbonate, 5.00 g (15.2 mmol) of MPPA, and 250 mL of THF under nitrogen. After stirring at room temperature for 30 min, 5.90 g (98%, 15.7 mmol) of tetra-*n*-butylammonium iodide was added to the flask. The mixtures were stirred at 60 °C for 18 h and then cooled to room temperature. The MPPA-grafted silica particles (Si-MPPA) were filtered and washed with THF, THF/water (1:1) mixture, distilled water, acetone, toluene, and acetone, respectively. After drying under vacuum, 16.3 g of deep yellow solid was obtained. Elemental analysis: S, 3.10% (loading of 0.322 mmol/g, 57.2% substitution). FT-IR: 1722 (C═O), 1603 (C═C), 1556, 1456, 1380 (CH_3), 1040 (broad, Si−O, C−O, C═S), 794, 697 cm^{-1}.

RAFT Polymerization of Vinyl Monomers Mediated by Si-MPPA. In a typical run (see run 1 of Table 2), Si-MPPA (0.400 g, 129 μmol), toluene (2.80 mL), MPPA (42.6 mg, 129 μmol), MA (2.78 g, 32.3 mmol), and AIBN (98.0 mg of toluene solution with concentration of 21.6 mg/g, 12.9 μmol) were added to a Schlenk tube. 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 21 h, and then the polymerization was quenched by putting the tube into ice water. A small amount of polymerization solution (typically 0.1−0.2 mL) was drawn to do GPC analysis and measure the monomer conversion in solution by ^{1}H NMR, and then the polymer-grafted silica was filtered, washed with toluene and THF, and dried under vacuum. GPC analyses: cleaved grafted PMA, $M_n = 9800$, $M_w/M_n = 1.18$; free PMA, $M_n = 23\,500$, $M_w/M_n = 1.15$. The monomer conversion (C% = 97.2%) and weight grafting ratio ($G_r\% = 25.9\%$) of polymeric chains were determined by the approach described as follows.

The polymerization solution was drawn and dissolved into $CDCl_3$ to check ^{1}H NMR, and the conversion in solution ($C_{m,f}$) was determined by comparing the integrated areas of characteristic signals of monomer and polymer ($C_{MA,f} = (I_{3.5-3.9} - I_{5.7-6.5})/I_{3.5-3.9}$, $C_{MMA,f} = I_{3.59}/I_{3.5-3.8}$, $C_{BA,f} = 1 - (2I_{5.7-6.5})/(3I_{3.8-4.3})$, $C_{St,f} = (2I_{1.0-2.2})/(3I_{5.1-5.9} + 2I_{1.0-2.2})$). The weight ($G_r$) and molar ($G_p$) grafting ratios of polymeric chains on solid surface were determined by TGA using the following equations.[14,18]

$$G_r = \frac{W\%_{Si-polymer}}{100 - W\%_{Si-polymer}} - \frac{W\%_{Si-MPPA}}{100 - W\%_{Si-MPPA}} \tag{1}$$

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

where $W\%_{Si-polymer}$ and $W\%_{Si-MPPA}$ are the percent weight loss

Table 1. RAFT Polymerization of MA Mediated by Si-MPPA in Toluene at 60 °C[a]

run	$[\mathrm{MA}]_0/[\text{Si-MPPA}]_0$	C (%)	$M_n(\mathrm{th})$[b]	$M_{n,\mathrm{GPC}}(\mathrm{g})$[c]	$M_w/M_n(\mathrm{g})$[c]	$M_{n,\mathrm{GPC}}(\mathrm{f})$[d]	$M_w/M_n(\mathrm{f})$[d]	G_r (%)[e]	G_P (μmol/g)[e]	G_e (%)[f]
1	150	63.1	4400	3870	1.14	6550	1.12	19.6	50.6	15.7
2	250	64.6	7280	7680	1.18	14000	1.16	24.5	31.9	9.91
3	400	79.9	14100	10700	1.23	27000	1.20	22.4	20.9	6.49
4	600	83.9	22000	12500	1.20	48600	1.14	20.5	16.4	5.09

[a] Polymerization conditions: $[\text{Si-MPPA}]_0:[\mathrm{MPPA}]_0:[\mathrm{AIBN}]_0 = 1:1:0.1$, $[\mathrm{MA}]_0 = 3.0$ mol/L, 60 °C, 18 h. [b] $M_n(\mathrm{th}) = M_{w,\mathrm{MA}} \times C\% \times [\mathrm{M}]_0/(2[\text{Si-MPPA}]_0) + M_{w,\mathrm{MPPA}}$, where $M_{w,\mathrm{MA}}$ and $M_{w,\mathrm{MPPA}}$ are molecular weights of MA and MPPA. [c] Molecular weight and polydispersity of grafted PMA determined by GPC using PMMA standards. [d] Molecular weight and polydispersity of free PMA produced in solution. [e] Weight (G_r) and molar (G_P) grafting ratio of PMA grafted onto silica particles determined by TGA using the following equations:[14,18] $G_r = W\%_{\text{Si}-\text{polymer}}/(100 - W\%_{\text{Si}-\text{polymer}}) - W\%_{\text{Si}-\text{MPPA}}/(100 - W\%_{\text{Si}-\text{MPPA}})$, $G_P = G_r/M_{n,\mathrm{GPC}}(\mathrm{g})$, where $W\%_{\text{Si}-\text{polymer}}$ and $W\%_{\text{Si}-\text{MPPA}}$ are the percent weight loss between room temperature and 500 °C corresponding to the decomposition of polymer-grafted silica (Si-polymer) and Si-MPPA. [f] Apparent grafted CTA efficiency, $G_e = G_P/G_{\text{Si}-\text{MPPA}}$, where $G_{\text{Si}-\text{MPPA}} = 0.322$ mmol/g.

between room temperature and 500 °C corresponding to the decomposition of polymer-grafted silica (Si−polymer) and Si−MPPA, and $M_{n,\mathrm{GPC}}(\mathrm{g})$ is the molecular weight of grafted polymer determined by GPC. On the basis of $C_{m,f}$ and G_r, the total monomer conversion for RAFT polymerization was determined by eq 3, and W_{Si} is calculated from $W_{\mathrm{Si}} = W_{\text{Si}-\text{MPPA}}(100 - W\%_{\text{Si}-\text{MPPA}})/100$, where W_m, W_{Si}, and $W_{\text{Si}-\text{MPPA}}$ are the original weights of monomer, silica gel, and Si-MPPA, respectively.

$$C = \frac{(W_m - W_{\mathrm{Si}}G_r)C_{m,f} + W_{\mathrm{Si}}G_r}{W_m} \tag{3}$$

In a comparative experiment without using MPPA, the polymerization ($[\mathrm{MA}]_0:[\text{Si-MPPA}]_0:[\mathrm{AIBN}]_0 = 250:1:0.1$) was conducted in 50 vol % of toluene at 60 °C for 21 h, and monomer conversion and $G_r\%$ were determined to be 98.4% and 19.4%. Grafted PMA, $M_n = 18\,400$, $M_w/M_n = 1.85$; free PMA, $M_n = 109000$, $M_w/M_n = 1.96$.

Chain Extension Polymerization To Synthesize Diblock Copolymer−Silica Hybrids. In a typical experiment (run 1 of Table 3), Si-PMA (0.200 g, 8.24 μmol), toluene (1.70 mL), PMA (144 mg, 33.0 μmol), BA (1.59 g, 12.4 mmol), and AIBN (53.8 mg of toluene solution with concentration of 21.6 mg/g, 7.08 μmol) 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 8 h. After polymerization, the samples were treated according to a method similar to the previously described RAFT polymerization of MA. The monomer conversion and weight grafting ratio of block copolymer chains were determined to be 47.2% and 27.0%, respectively. GPC analyses showed that the degrafted PMA-*b*-PBA diblock copolymer had molecular weight of 13 500 and polydispersity of 1.16, and free PMA-*b*-PBA produced in solution had molecular weight of 29 600 and polydispersity of 1.25.

In a comparative experiment without using free PMA, the chain extension polymerization ($[\mathrm{BA}]_0:[\text{Si-PMA}]_0 = 300:1$, $[\mathrm{BA}]_0 = 3.5$ mol/L, $[\mathrm{AIBN}]_0 = 2.0$ mmol/L) was conducted in toluene at 60 °C for 8 h, and monomer conversion and $G_r\%$ were determined to be 52.4% and 15.3%. Grafted polymer, $M_n = 16\,200$, $M_w/M_n = 2.00$; free polymer, $M_n = 50\,800$, $M_w/M_n = 2.37$.

Aminolysis To Cleave the Grafted Polymeric Chains. In a typical experiment, to a glass tube were added 100 mg of PMA-grafted silica particles, 5 mL of THF, and 2−3 drops of dilute aqueous solution of $\mathrm{Na_2S_2O_4}$.[48] The solution was degassed with nitrogen for 10 min, and 0.1 mL of *n*-hexylamine was added. The aminolysis was conducted at room temperature overnight. The solution was filtered, and the filtrate was evaporated to remove the volatiles. The cleaved PMA was subjected to GPC analysis. Other grafted homopolymer and block copolymer were degrafted according to a similar procedure.

Results and Discussion

Si-MPPA was synthesized by a two-step reaction: (i) introduction of the benzyl chloride functionality on the surface by reacting the activated silica particles with 4-(chloromethyl)-phenyltrimethoxysilane; (ii) attaching MPPA to silica surface by coupling reaction between silica-supported benzyl chloride and MPPA catalyzed by tetra-*n*-butylammonium iodine and potassium carbonate. Elemental analysis revealed a loading in active sites of 0.322 mmol of CTA/g of solid, corresponding to a grafting density of 0.388 molecule of CTA/nm^2. Si-MPPA was then used as a CTA to mediate RAFT polymerization of MA, and free MPPA was introduced in the reaction solution to better control the polymerization.[19] When the polymerization ($[\text{Si-MPPA}]_0:[\mathrm{MPPA}]_0:[\mathrm{AIBN}]_0 = 1:1:0.1$, $[\mathrm{MA}]_0 = 3.0$ mol/L) was conducted in toluene at 60 °C for 18 h, the polymerization results are listed in Table 1 where the grafted polymer was recovered by aminolysis using *n*-hexylamine in THF at room temperature overnight.[48] With increasing feed ratio of monomer to Si-MPPA, the molecular weights of free and grafted polymers correspondingly increased. The polydispersity indices remained relatively low ($1.12 < M_w/M_n < 1.23$), indicating a good control over molecular weight during polymerization. In some cases, tailing and/or shoulder were observed in the GPC traces of the free polymeric chains, indicating the existence of some side reactions such as irreversible termination in solution. However, the GPC traces of the grafted polymers only exhibited one monomodal distribution, indicating the absence of the aforementioned side reactions during RAFT graft polymerization on surface (see Supporting Information). In all cases, the molecular weight values of free polymers were much higher than those of the grafted polymers, suggesting faster polymerization rate in solution than that on silica surface. This phenomenon can be ascribed to the increased steric hindrance[37−40] and slower rate of addition−fragmentation reactions on surface than that in solution.[19] In Z-supported RAFT polymerization using a free CTA in solution, there are two types of competitive polymerization reactions, namely, free radical polymerization in solution (including RAFT polymerization and conventional free radical polymerization) and graft polymerization on solid surface (RAFT polymerization). The polymeric chains attached to the support remain in the dormant state, while the growing chain radicals always propagate in solution. Therefore, the introduction of a free CTA can efficiently slow down the propagation of free chains and favor the addition−fragmentation reactions on solid support. With increasing polymeric chains, the steric crowding of reactive sites by previously attached polymers becomes more and more pronounced and leads to the decreased accessibility of the RAFT group on surface, evident from the decreasing grafted CTA efficiency (we coined $G_p/G_{\text{Si}-\text{CTA}}$ as apparent grafted CTA efficiency G_e, where G_p means the apparent molar grafting ratio of polymeric chains on solid support and $G_{\text{Si}-\text{CTA}}$ means the loading of Si-CTA) with increasing molecular weight of grafted polymers in Table 1.

Polymerization kinetics was investigated to better understand the relationships between molecular weights of free and grafted polymers and conversion. For polymerization using a monomer-to-Si-MPPA feed ratio of 400 in toluene at 60 °C, the apparent kinetic curves are depicted in Figure 1. It was found that the

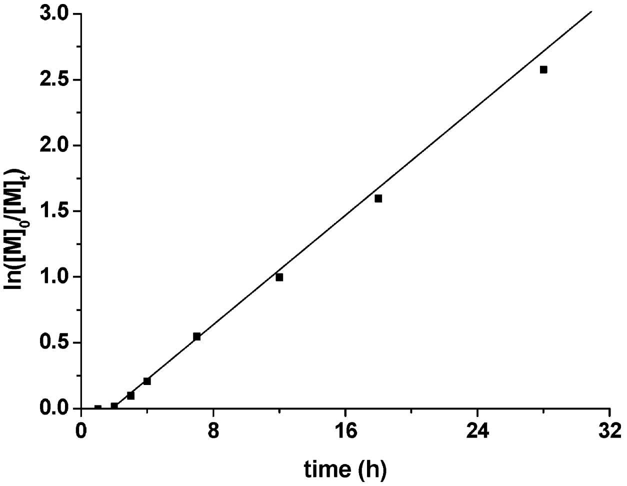


Figure 1. Pseudo-first-order kinetic curves for RAFT polymerization of methyl acrylate (MA) mediated by silica-supported 3-(methoxycarbonylphenylmethylsulfanylthiocarbonylsulfanyl)propionic acid (Si-MPPA). Polymerization conditions: $[MA]_0$:[Si-MPPA]$_0$:$[MPPA]_0$:$[AIBN]_0$ = 400:1:1:0.1, $[MA]_0$ = 3.0 mol/L, in toluene at 60 °C.

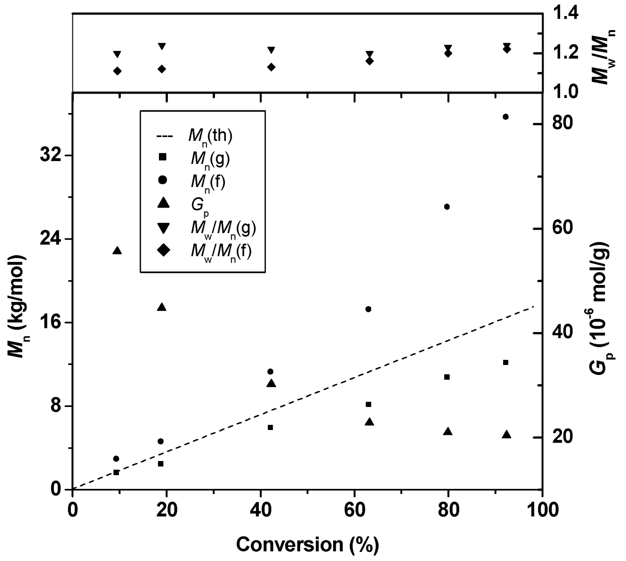


Figure 2. Dependence of molecular weight and polydispersity of free and grafted PMA and G_p on conversion for RAFT polymerization of MA mediated by Si-MPPA in toluene at 60 °C. See Figure 1 for polymerization conditions.

pseudo-first-order polymerization kinetics was maintained until high conversion up to 80%, while an obvious retardation of about 2 h was observed. From the evolution of molecular weight and polydispersity with increasing conversion (Figure 2), it was found that the molecular weights of free and grafted polymers were similar at low conversion but tended to differ with increasing conversion, while the G_p values decreased. This phenomenon can be explained by the increased shielding effect of the grafted polymeric chains with increasing conversion. In Z-supported RAFT graft polymerization, the shielding effect has two consequences: to slow down the polymerization rate at the surface by hindering the diffusion of monomer and polymeric chain radicals to the reactive sites and to prevent the degenerative transfer to polymeric chains with larger molecular weight from the surface during polymerization.[37−40] At low conversions (conversion less than 40%), the shielding effect is not significant, and the concentration of the reactive sites on solid support is much higher than that in solution, resulting in similar rate of addition−fragmentation transfer reactions in solution and on surface. Consequently, the molecular weights of free and grafted polymers obtained at low conversion were similar, and both were close to the theoretically calculated value (M_n(th)). With increasing conversion, the molecular weight of free polymers produced in solution increased drastically due to an increase in termination reactions. On the other hand, the molecular weight of grafted polymers increased slowly due to the decreased polymerization rate resulting from the increased steric hindrance and followed a linear evolution with conversion (Figure 2). Indeed, with increasing conversion, the GPC traces of free and grafted polymers gradually shifted to higher molecular weight sides, indicating the molecular weights could be adjusted by the control of monomer conversion. In all cases, the polydispersity indices of various polymers obtained at different conversions were low (M_w/M_n < 1.24). For RAFT graft polymerization conducted on surface, no star−star (or comb−comb) termination reactions should occur since the solid support never carries a radical,[37−40] as illustrated by the lack of a shoulder in GPC traces of grafted polymers (see Supporting Information). Meanwhile, no obvious tailings were observed in GPC traces, indicating that better-defined grafted polymers without dead polymeric chains were produced on silica surface. For free polymers produced in solution, significant tailings corresponding to dead polymers produced by irreversible termination were usually observed at various conversions, and a shoulder in the high molecular weight side corresponding to radical−radical termination by combination was also noted. The above results showed that better-defined polymers could be synthesized by grafting them onto silica support using Z-supported RAFT polymerization.

The aforementioned analyses indicate less steric hindrance and similar polymerization rates in solution and on surface are crucial to synthesize well-defined free and grafted polymers. Theoretically, the addition−fragmentation transfer reactions are much easier to conduct in solution than on surface due to the increased mobility of linear growing chains resulting from the homogeneous reaction environment and less steric hindrance, so free and grafted polymers with similar molecular weights are difficult to be achieved by Z-supported RAFT polymerization using a same free CTA in solution. However, it is possible to overcome the above limitations if a different CTA is introduced to decrease the polymerization rate in solution. To investigate the possibility to better control the polymerization, a dithiobenzoate-based CTA, 2-(2-cyanopropyl) dithiobenzoate (CPDB),[32] was introduced into the polymerization system. Since the polymerization rate for RAFT polymerization mediated by dithiobenzoates (CPDB) is slower than that using trithiocarbonates (MPPA), it is possible to further decrease the polymerization rate in solution.[35] As a comparison, RAFT polymerization of various monomers such as MA, methyl methacrylate (MMA), butyl acrylate (BA), and styrene (St) in the presence of MPPA was also conducted, and the polymerization results are summarized in Table 2. For polymerization of MA (runs 1 and 2), MMA (runs 4 and 5), and BA (runs 7 and 8) using MPPA as a free CTA, higher conversions were achieved, and the molecular weights of free polymers were much higher than those of the corresponding grafted polymers, as previously described for MA polymerization. For polymerization of St (run 10) using MPPA, the conversion was relatively low (24.8%), the molecular weights of free (M_n = 9710) and grafted (M_n = 7500) polymers were similar, and both were close to the theoretical value (M_n = 8070), indicating that well-defined PSt could be achieved by RAFT polymerization using free MPPA at low conversion.

Table 2. RAFT Polymerization of Various Monomers Mediated by Si-MPPA in the Presence of MPPA or CPDB[a]

run	M	free CTA	$[M]_0$/ $[\text{Si-MPPA}]_0$	t (h)	C (%)	$M_n(\text{th})^b$	$M_{n,\text{GPC}}(g)^c$	$M_w/M_n(g)^c$	$M_{n,\text{GPC}}(f)^d$	$M_w/M_n(f)^d$	G_r (%)^e	G_P (μmol/g)^e	G_e (%)^f
1	MA	MPPA	250	6	42.5	4900	4450	1.15	9720	1.13	16.1	36.2	11.2
2	MA	MPPA	250	21	97.2	10800	9800	1.18	23500	1.15	25.9	26.4	8.20
3	MA	CPDB	250	42	39.6	4480	4080	1.08	4360	1.15	16.8	41.2	12.8
4	MMA	MPPA	400	8	40.8	8500	6330	1.22	17800	1.25	19.7	31.1	9.66
5	MMA	MPPA	400	21	84.7	17300	12100	1.20	41300	1.29	30.6	25.3	7.86
6	MMA	CPDB	400	14	43.0	8830	8360	1.13	9620	1.12	28.8	34.4	10.7
7	BA	MPPA	300	5	27.2	5560	4360	1.17	8250	1.15	14.8	33.9	10.5
8	BA	MPPA	300	21	94.5	18500	14800	1.16	23800	1.09	27.2	18.4	5.71
9	BA	CPDB	300	30	25.6	5140	4990	1.15	6050	1.20	20.4	40.9	12.7
10	St	MPPA	600	21	24.8	8080	7500	1.17	9710	1.09	21.7	28.9	8.98
11	St	CPDB	600	45	<1								

[a] Polymerization conditions: $[\text{Si-MPPA}]_0$:$[\text{free CTA}]_0$:$[\text{AIBN}]_0 = 1{:}1{:}0.1$, in 50 vol % of toluene at 60 °C. [b] $M_n(\text{th}) = M_{w,m} \times C\% \times [M]_0/(2[\text{Si-MPPA}]_0) + M_{w,\text{CTA}}$, where $M_{w,m}$ and $M_{w,\text{CTA}}$ are molecular weights of monomer and free CTA used in solution. [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 homopolymer grafted silica particles determined by TGA. [f] Apparent grafted CTA efficiency, $G_e = G_P/G_{\text{Si-MPPA}}$.

Table 3. Chain Extension Polymerization To Synthesize Diblock Copolymers Using Various Macro-CTAs[a]

run	macro-CTA	M	$[M]_0$ (mol/L)	t (h)	C (%)	$M_n(\text{th})^b$	$M_{n,\text{GPC}}(g)^c$	$M_w/M_n(g)^c$	$M_{n,\text{GPC}}(f)^d$	$M_w/M_n(f)^d$	G_r (%)^e	G_P (μmol/g)^e
1	Si-PMA	BA	3.5	8	47.2	22 200	13 500	1.16	29 600	1.25	27.1	20.1
2	Si-PMMA	St	3.0	14	20.5	14 800	11 600	1.15	24 600	1.12	32.2	27.8
3	Si-PMMA	MA	3.8	14	39.2	18 500	15 200	1.10	28 300	1.18	28.4	18.7
4	Si-PBA	MA	3.8	14	30.2	12 800	9 650	1.18	21 200	1.18	30.8	31.9
5	Si-PSt	MA	5.5	8	56.8	22 200	17 500	1.20	39 700	1.17	22.8	13.0

[a] Polymerization conditions: $[M]_0$:$[\text{macro-CTA}]_0$:$[\text{free polymer}]_0 = 1500{:}1{:}4$, $[\text{AIBN}]_0 = 2.0$ mmol/L, in toluene at 60 °C, the macro-CTAs and free polymers used in runs 1−5 were synthesized by runs 3, 6, 6, 9, and 10 of Table 2. [b] $M_n(\text{th}) = M_{w,m} \times C\% \times [M]_0/([\text{macro-CTA}]_0 + [\text{free polymer}]_0) + M_{w,\text{macro-CTA}}$, where $M_{w,m}$ and $M_{w,\text{macro-CTA}}$ are molecular weights of monomer and homopolymer 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. [e] Weight (G_r) and molar (G_P) grafting ratio of block copolymers determined by TGA.

As compared with the polymerization using MPPA, the polymerization in the presence of CPDB gave lower conversions even at longer reaction time, confirming that the polymerization rate in solution was efficiently slowed down. For polymerization of MA (run 3), MMA (run 6), and BA (run 9), the molecular weights of free polymers were only slightly higher than those of the corresponding grafted polymers; both were close to the theoretical values, demonstrating that the slow propagation of free chains in solution would favor the addition−fragmentation reactions on solid support and result in similar polymerization rate in solution and on surface, therefore affording better-defined grafted polymers than that using MPPA. For polymerization of St (run 11), no obvious polymerization occurred after 45 h at 60 °C, which may be due to a very slow fragmentation at low reaction temperature. Indeed, the RAFT polymerization of styrene mediated by dithiobenzoate derivatives is known to proceed very slowly at these temperatures.[35] The grafted polymers also exhibited a symmetric monomodal molecular weight distribution, indicating the absence of side reactions during graft polymerization on surface (see Supporting Information, Figure S3). It is also noteworthy that it is possible to obtain a well-controlled PMMA when using a Z-supported trithiocarbonate, while nonsupported trithiocarbonates usually give poor control over MMA polymerization.[35]

Since the Z-group approach based on silica particles permits to isolate polymeric chains with 100% chain-end functionality from dead materials, it is possible to synthesize well-defined block copolymers.[19] In this study, the homopolymer-grafted silica and the corresponding free polymers synthesized in runs 3, 6, 9, and 10 were used to mediate the RAFT chain extension polymerization of a second monomer to synthesize diblock copolymer grafted silica particles. When the polymerization ($[M]_0$:$[\text{macro CTA}]_0$:$[\text{free polymer}]_0 = 1500{:}1{:}4$, $[\text{AIBN}]_0 = 2.0$ mmol/L) was conducted in toluene at 60 °C, the polymerization results are listed in Table 3. From Table 3, it can be seen that the grafted block copolymers possessed molecular weight lower than that of free block copolymers produced in solution. This phenomenon is similar to that observed for the homopolymerization and can be ascribed to the increased shielding effect.[37−40] In GPC traces (Figure 3), free block copolymers usually exhibited tailing and/or shoulder, corresponding to the irreversible termination during polymerization. As a comparison, the GPC traces of grafted homopolymers attached to macro-CTAs are also shown in Figure 3. The GPC traces of grafted block copolymers were completely shifted to higher molecular weight side, no obvious tailing and shoulder was observed, and the polydispersity indices were lower than 1.2, suggesting that well-defined diblock copolymer grafted silica particles were suc-

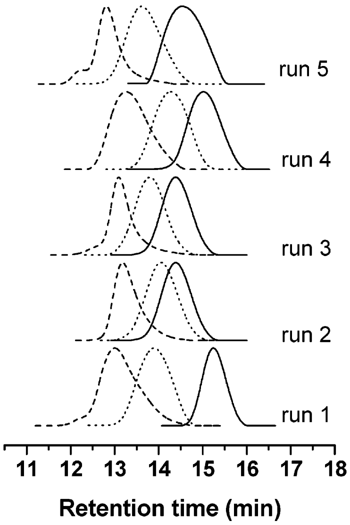


Figure 3. GPC traces of grafted homopolymer (macro-chain transfer agent, solid line) and free (dashed line) and grafted (dotted line) diblock copolymers. The polymerization conditions for various runs are shown in Table 3.

cessfully synthesized by chain extension polymerization in the presence of free polymer. The above results also demonstrated the livingness of the macro-CTAs grafted onto silica particles and quantitative reinitiation efficiency of the macro-CTAs.

Conclusion

A series of well-defined homopolymer and diblock copolymer grafted onto silica particles were successfully achieved in this study. The introduction of a free CTA such as MPPA and CPDB in solution during polymerization could significantly improve the control on molecular weight and polydispersity and enhance the grafting efficiency. The Z-supported RAFT polymerization could afford living polymeric chains attached to the solid surface, evident from the highly efficient chain extension polymerization to produce well-defined diblock copolymers. This technique can be extended to enable the synthesis of a variety of functional pure block copolymers, since RAFT polymerization tolerates a wide range of functionalities.

Acknowledgment. The financial support from University of Leeds is gratefully acknowledged.

Supporting Information Available: GPC traces of free and grafted polymers and TGA curves of Si-MPPA and polymer grafted silica particles. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Publication. This article was published ASAP on November 8, 2006. The title of the article has been amended. The correct version was published on November 17, 2006.

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MA061586Y

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