Macromol. Symp. **2007**, 248, 94–103 DOI: 10.1002/masy.200750210

# Synthesis of Poly(methyl acrylate) Grafted onto Silica Particles by Z-supported RAFT Polymerization

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**Summary:** RAFT polymerization of methyl acrylate (MA) mediated by silica-supported 3-(methoxycarbonyl-phenyl-methylsulfanylthiocarbonylsulfanyl) propionic acid (Si-MPPA) and 3-(benzylsulfanylthiocarbonylsulfanyl) propionic acid (Si-BSPA) was investigated. The molecular weight and polydispersity of grafted polymeric chains and the grafted chain transfer agent (CTA) efficiency ($G_e$) were strongly dependent on the types and loading of Si-CTAs and free CTA used in solution. Under similar reaction conditions, the graft polymerization mediated by Si-MPPA was better controlled than that using Si-BSPA. The introduction of a free CTA in solution during Si-MPPA mediated polymerization could significantly decrease the polydispersity of free and grafted polymeric chains and enhance the grafted CTA efficiency, and longer polymeric chains could be grafted onto silica support when Si-MPPA with a higher CTA loading was used to mediate the polymerization. In all cases, the RAFT polymerization using 2-(2-cyanopropyl) dithiobenzoate (CPDB) as a free CTA could afford well-defined grafted PMA and significantly increased $G_e$ value, while the polymerization rate was also decreased.

**Keywords:** graft polymerization; kinetics; poly(methyl acrylate); RAFT polymerization; silica

## Introduction

Reversible addition-fragmentation chain transfer (RAFT) polymerization has become one of the most promising living radical polymerization techniques, due to its tolerance to a wide range of reaction conditions, the straight-forward setup to yield block copolymers, and its versatility towards the range of monomers with variable functionality.[1–5] Meanwhile, the surface modification of inorganic particles and synthetic resins with polymeric chains are of great interest due to their unique properties and potential applications.[6–8] Recently, RAFT graft polymerization has attracted increasing attention due to its ability to afford well-defined polymers with controlled molecular weight, low polydispersity and controlled chain-end functionality,[9–24] and a wide range of polymeric chains have been successfully grafted onto various solid supports using this technique. In general, RAFT graft 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.[3–5] In Z-supported RAFT polymerization, the shielding effect results in relatively low grafting density, but it can produce well-defined grafted polymers with unimodal molecular weight distribution and enable the synthesis of functional block copolymers.[16, 25–28] Until now, reports on Z-supported RAFT polymerization from a solid support are scarce.[14–18]

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In our previous study, silica-supported 3-(methoxycarbonyl-phenyl-methylsulfanylthio carbonylsulfanyl)propionic acid (Si-MPPA) with a MPPA loading of 0.322 mmol/g was synthesized and applied to RAFT polymerization of methyl acrylate (MA), methyl methacrylate, butyl acrylate and styrene to produce well-defined homopolymer grafted onto silica particles.[16] 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. To investigate the effects of types and loading of Si-CTA on graft polymerization, Si-MPPA with a lower MPPA loading and silica supported 3-(benzylsulfanylthiocarbonylsulfanyl)propionic acid (Si-BSPA) were also synthesized in this study, and the RAFT graft polymerization of MA mediated by various Si-CTAs was investigated in detail.

## Experimental Part

### Materials

All solvents, monomers, and other chemicals were of analytical grade. Silica gel particles with particle size of 35–70 μm and a specific surface area of 500 $m^2$/g were purchased from Aldrich. The benzylchloride functionalized silica (Si–Cl, with a loading of 0.563 mmol/g) and Si-MPPA1 (with a loading of 0.322 mmol/g) were synthesized following previously published methods.[14,16] 3-(Methoxycarbonyl-phenyl-methylsulfanylthiocarbonylsulfanyl) propionic acid (MPPA),[14] 3-(benzylsulfanylthiocarbonylsulfanyl)propionic acid (BSPA)[25] and 2-(2-cyanopropyl) dithiobenzoate (CPDB)[1] were synthesized and purified according to literature methods. MA was passed through a basic alumina (Brockmann I) column to remove the inhibitor before use. Tetrahydrofuran (THF) and toluene were dried over 4 Å molecular sieves. 2,2′-Azobisisobutyronitrile (AIBN, Fisher) was recrystallized twice from ethanol.

### Characterization

The number-average molecular weight ($M_n$) and polydispersity (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 × 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. Samples were calibrated with calibrated with PMMA standard samples with $M_n$ value in the range of 1944000-1020 g/mol. $^1$H NMR spectra were recorded on a Bruker 400 UltraShield spectrometer at 25 °C using $CDCl_3$ as a solvent. Chlorine and 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 Perkin-Elmer Spectrum One FT-IR spectrometer using a single reflection horizontal ATR accessory. 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 Si-CTA

Si-MPPA2 (loading of 0.109 mmol/g) and Si-BSPA (loading of 0.120 mmol/g) were synthesized according to a similar procedure to that of Si-MPPA1 (loading of 0.322 mmol/g).[16] To a round flask was added 15 g (8.45 mmol) of Si–Cl, 1.38 g (10.0 mmol) of potassium carbonate, 2.00 g (6.06 mmol) of MPPA, and 200 mL of THF under nitrogen. After stirring at room temperature for 30 min, 2.90 g (98%, 7.72 mmol) of tetra-n-butyl ammonium iodide was added to the flask. The mixtures were stirred at 60 °C overnight, cooled down, filtered and thoroughly washed with water and organic solvents such as THF and toluene. After drying under vacuum, 15.5 g of Si-MPPA2 was obtained as yellow solid. Elemental analysis: S, 1.05% (loading of 0.109 mmol/g). 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 MA Mediated by Si-CTA

In a typical run (see run 3 of Table 1), Si-MPPA1 (0.400 g, 129 μmol), toluene (2.91 mL), CPDB (28.5 mg, 129 μmol), MA (2.78 g, 32.3 mmol), and AIBN (2.11 mg, 12.9 μmol) were added to a Schlenk tube. The tube was subjected to three freeze-pump-thaw cycles to remove oxygen, and then placed into an oil bath preheated to 60 °C. The polymerization was quenched by putting the tube into ice water after 42 h, and small amount of polymerization solution was drawn to do GPC analysis and measure the monomer conversion in solution by $^1$H NMR. The polymer grafted silica was filtered, washed with toluene and THF, and dried under vacuum until constant weight before TGA measurement. GPC analyses: cleaved grafted PMA, $M_n(g) = 4080$, $PDI(g) = 1.08$; free PMA, $M_n(f) = 4360$, $PDI(f) = 1.15$. The total monomer conversion ($C = 39.6\%$) and weight grafting ratio ($G_r = 16.8\%$) of polymeric chains were determined by equations 1 and 2, where $G_r$ means the mass ratio of grafted polymer to solid support, $W\%_{\text{Si-polymer}}$ and $W\%_{\text{Si-CTA}}$ are the percent weight loss between room temperature and 500 °C corresponding to the decomposition of polymer grafted silica (Si-polymer) and Si-CTA, $W_m$, $W_{Si}$ ($W_{Si} = W_{\text{Si-CTA}}(100 - W\%_{\text{Si-CTA}})/100$) and $W_{\text{Si-CTA}}$ are the original weights of monomer, silica gel and Si-CTA, and $C_{m,f}$ is the conversion in solution determined by $^1$H NMR, respectively.

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

$$C = \frac{(W_m - W_{Si} \times G_r) \times C_{m,f} + W_{Si} \times G_r}{W_m} \tag{2}$$

### 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 $Na_2S_2O_4$.[29] The solution was degassed with nitrogen for 10 min, and 0.1 mL of n-hexylamine was

***Table 1.***

Polymerization results for RAFT graft polymerization of MA mediated by Si-MPPA1 (runs 1–3), Si-MPPA2 (runs 4–6) and Si-BSPA (runs 7-11).[a)]

| Run | Free CTA | $r_f$[b)] | $r_m$[c)] | t (h) | C%[d)] | $M_n$(th)[e)] | $M_n$(g)[f)] | PDI(g)[f)] | $M_n$(f)[g)] | PDI(f)[g)] | $G_r$ (%)[h)] | $G_e$ (%)[i)] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | MPPA | 0 | 250 | 21 | 98.4 | 21500 | 18400 | 1.85 | 109000 | 1.96 | 19.4 | 3.26 |
| 2 | MPPA | 1 | 250 | 21 | 97.2 | 10800 | 9800 | 1.18 | 23500 | 1.15 | 25.9 | 8.20 |
| 3 | CPDB | 1 | 250 | 42 | 39.6 | 4480 | 4080 | 1.08 | 4360 | 1.15 | 16.8 | 12.8 |
| 4 | MPPA | 0 | 250 | 21 | 98.0 | 21400 | 31000 | 2.04 | 128500 | 2.34 | 14.9 | 4.41 |
| 5 | MPPA | 1 | 250 | 21 | 95.8 | 10600 | 4560 | 1.20 | 32400 | 1.18 | 11.5 | 23.1 |
| 6 | CPDB | 1 | 250 | 42 | 35.5 | 4040 | 3500 | 1.12 | 4080 | 1.10 | 11.2 | 29.4 |
| 7 | BSPA | 0 | 250 | 21 | 98.4 | 21500 | 27700 | 2.04 | 46200 | 2.12 | 24.7 | 7.43 |
| 8 | BSPA | 1 | 250 | 21 | 98.0 | 10800 | 9400 | 1.56 | 29800 | 2.24 | 15.5 | 13.8 |
| 9 | BSPA | 1 | 350 | 21 | 97.5 | 15000 | 11300 | 1.84 | 49800 | 1.98 | 19.6 | 14.4 |
| 10 | BSPA | 1 | 500 | 21 | 97.2 | 21200 | 15500 | 1.67 | 69700 | 1.39 | 19.2 | 10.3 |
| 11 | CPDB | 1 | 350 | 24 | 32.0 | 5100 | 4100 | 1.18 | 6050 | 1.20 | 15.2 | 30.9 |

[a)] Polymerization conditions: $[\text{Si-CTA}]_o:[\text{AIBN}]_o = 1:0.1$, in 50 (v%) of toluene at 60 °C.

[b)] Molar ratio of free CTA to Si-CTA.

[c)] Feed ratio of monomer to Si-CTA.

[d)] Total monomer conversion.

[e)] $M_n(th) = M_{w,m} \times C\% \times [M]_o/([\text{Si-CTA}]_o + [\text{free CTA}]_o) + M_{w,CTA}$, where $M_{w,m}$ and $M_{w,CTA}$ are molecular weights of MA and free CTA used in solution.

[f)] Molecular weight and polydispersity of grafted polymers determined by GPC.

[g)] Molecular weight and polydispersity of free polymers produced in solution.

[h)] Weight grafting ratio of PMA grafted silica particles determined by TGA.

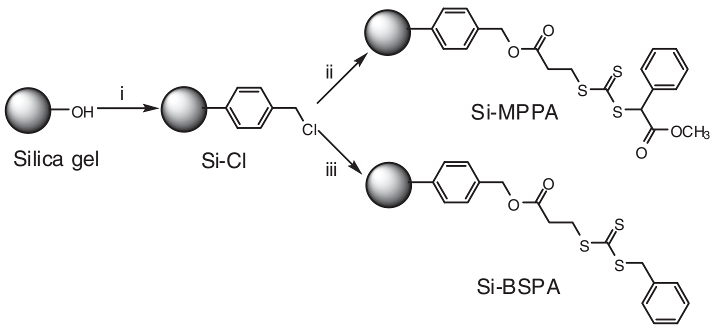
[i)] Apparent grafted CTA efficiency.

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.

## Results and Discussion

In this study, two types of silica supported CTAs, Si-MPPA and Si-BSPA, were synthesized by a two-step reaction (Scheme 1): (a) introduction of the benzylchloride functionality on silica surface and (b) attaching MPPA or BSPA to the support by coupling reaction between silica-supported benzylchloride and CTA. The target CTA was successfully attached to silica particles, evident from IR, TGA and elemental analysis. Elemental analysis revealed the loading in active sites of the various Si-CTAs ($G_{\text{Si-CTA}}$) were 0.322 mmol/g (Si-MPPA1), 0.109 mmol/g (Si-MPPA2) and 0.120 mmol/g (Si-BSPA), which was very similar to the value estimated by TGA. TGA analyses of the various Si-CTAs (Figure 1) revealed an amount of physisorbed water around 4%, and the weight loss beyond 120 °C was ascribed to thermal degradation of the grafted CTAs.

RAFT polymerization of MA mediated by different Si-CTAs was conducted in toluene at 60 °C, and the polymerization results are shown in Table 1. It was found that the grafted polymeric chains could be efficiently recovered by aminolysis using n-hexylamine in THF, evident from TGA, IR, GPC and elemental analysis. The weight grafting ratio ($G_r$) of PMA on silica surface was determined by TGA, and the apparent grafted CTA efficiency ($G_e$) was calculated from the equation $G_e = G_r/(G_{\text{Si-CTA}} \cdot M_n(g))$, where $G_e$ is the molar ratio of grafted polymeric chains to the CTA loading on solid support, $G_{\text{Si-CTA}}$ is the loading of CTA grafted onto solid support, and $M_n(g)$ is the molecular weight of grafted PMA determined by GPC. For polymerization mediated by Si-CTA without free CTA in solution (runs 1, 4 and 7 of Table 1), longer polymeric chains could be grafted onto silica particles, but the polydispersity of grafted polymer was very high, and the $G_e$ value was low, suggesting an uncontrolled polymerization system. To better control the polymerization, a free CTA was introduced in the reaction solution. During RAFT polymerization mediated by Si-MPPA in the presence of free MPPA (runs 2 and 5), the polydispersity indices of free and grafted polymers are lowered to less than 1.2, indicating that a better control over the free radical polymerization in solution is obtained by introducing the same CTA in solution. In Z-supported RAFT polymerization, the growing chain radicals always propagate in solution, whilst the polymeric chains attached to the support remain in the dormant state.[14,16] Steric hindrance prevents the addition of the propagating



***Scheme 1.***

Synthetic route to Si-MPPA and Si-BSPA. Reaction conditions: (i) 4-(chloromethyl)phenyltrimethoxysilane, toluene, 80 °C, 15 h; (ii) MPPA, $K_2CO_3$, $Bu_4NI$, THF, 60 °C, 18 h; (iii) BSPA, $K_2CO_3$, $Bu_4NI$, THF, 60 °C, 18 h.

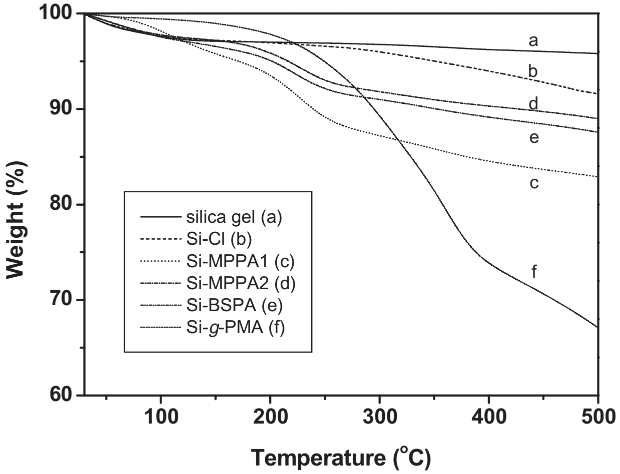


**Figure 1.**
TGA curves of silica gel, Si-Cl, Si-MPPA, Si-BSPA and Si-*g*-PMA.

chains to the Z-supported CTA, thus increasing the number of termination events, and inducing a poor control over molecular weight. Indeed, we observe that the molecular weight values of free polymers were much higher than those of the grafted polymers. Therefore, the introduction of a free CTA should permit to improve the control over polymerization in solution, and favor the addition-fragmentation reactions on solid support.

For RAFT polymerization mediated by Si-BSPA (runs 7–10), the polydispersity of free and grafted polymers was very high even if free BSPA was introduced into the solution, suggesting the RAFT graft polymerization was significantly affected by the type of CTA. To further understand this aspect, polymerization kinetics for RAFT polymerization of MA mediated by MPPA and BSPA in toluene at 60 °C was investigated. From the results shown in Figure 2, it can be seen that first order kinetics were maintained until high conversion in both cases, and the polymerization could indeed afford PMA with well-defined molecular weight and low polydispersity ($PDI < 1.2$) at various conversions. As expected from trithiocarbonates, rates of polymerization are similar, and the only difference is in the presence of an induction time (initialization) for the polymerization mediated by MPPA. A potential explanation to the poor control of a RAFT graft polymerization mediated by Si-BSPA is the poor efficiency of the benzyl group as leaving/reinitiating group. Indeed, RAFT polymerization generally shows an initialization period, during which all the CTAs are consumed, before the polymerization starts. However, in the case of polymerizations mediated by Si-BSPA, the monomer conversion increases immediately, suggesting that polymeric chains start their growth despite the fact that some CTAs have not yet reacted. Slow reaction of the CTA with propagating radicals would lead to polymeric chains starting their growth at different times, therefore leading to broader molecular weight distributions. It is however interesting to note that this effect has a dramatic effect on the control over polymerizations from silica particles, but does not seem to affect the control of the polymerization in solution (see Figure 2, PDI's $< 1.2$).

For RAFT polymerization mediated by Si-MPPA, it was found that the polymerization using Si-MPPA2 (lower CTA loading) could only afford low molecular weight of grafted polymer even at high conversion, indicating that the RAFT graft polymerization is also dependant on the loading of grafted CTA on silica surface. For poly-

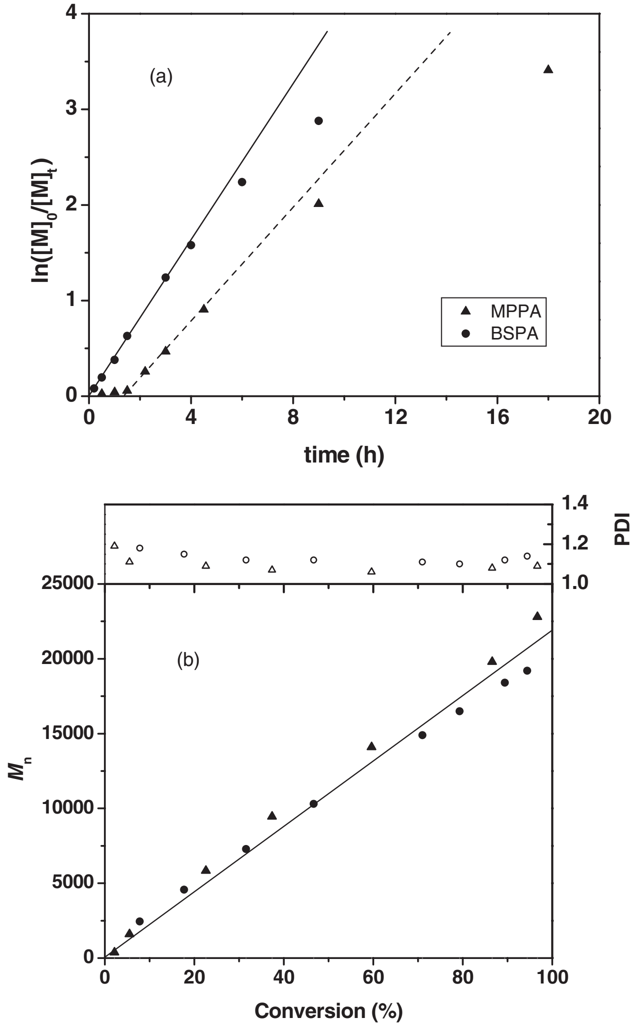


***Figure 2.***
Polymerization kinetic curves (a) and $M_n$ and PDI evolution with conversion (b) for RAFT polymerization of MA mediated by MPPA (triangle) and BSPA (circle): $[MA]_0$:$[CTA]_0$:$[AIBN]_0 = 250:1:0.1$, in 50 (v%) of toluene at 60 °C. The line in b means the theoretical molecular weight.

merization mediated by Si-MPPA1 and Si-MPPA2 with different CTA loadings, polymerization kinetics were investigated in order to better understand the relationships between molecular weights and conversion for both free and grafted polymers. When polymerization ($[MA]_0$:[Si-MPPA]$_0$: $[MPPA]_0$: $[AIBN]_0 = 400:1:1:0.1$, $[MA]_0 = 3.0$ mol/L) was conducted in toluene at 60 °C, the apparent kinetic curves are depicted in Figure 3. It was found that the pseudo-first-order polymerization kinetics was maintained until high conversion up to 80%, while a significant induction period was observed in both cases. Figure 4 indicates the evolution of molecular weight and polydispersity with increasing conversion. For polymerization mediated by Si-MPPA1, the molecular weights of free and grafted polymers were similar at low conversion but tended to differ rapidly with increasing conversion. We attribute this behavior to the increased shielding effect with increasing conversion (Figure 4a).

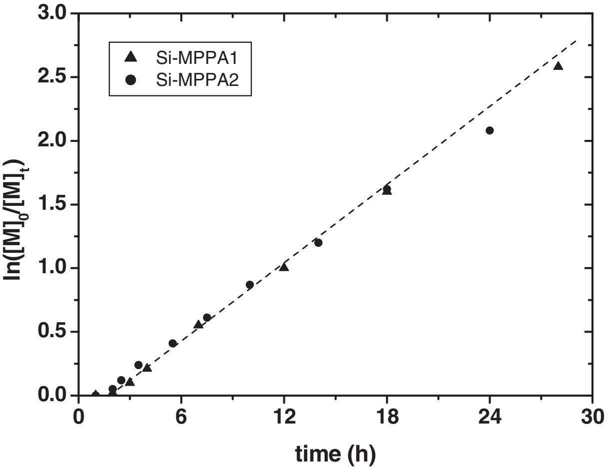


***Figure 3.***
Pseudo-first-order kinetic curves for RAFT polymerization of MA mediated by Si-MPPA in the presence of MPPA. Polymerization conditions: $[MA]_0$:$[Si\text{-}MPPA]_0$:$[MPPA]_0$:$[AIBN]_0 = 400{:}1{:}1{:}0.1$, $[MA]_0 = 3.0$ mol/L, in toluene at 60 °C.

The GPC traces of free and grafted polymers gradually shifted to higher molecular weight sides with increasing time (Figure 5A), indicating the molecular weights could be adjusted by the control of monomer conversion. For polymerization mediated by Si-MPPA2 (Figure 4b), however, only short grafted polymeric chains ($M_n < 5{,}000$ g/mol) could be achieved, and no obvious increase in molecular weight of grafted polymer was observed for monomer conversion higher than 40% (Figure 5B). These results indicate that almost all the reactive sites were hindered from monomer and growing polymeric chain radicals at high conversion. A potential explanation is that most of the CTA functionality at low loading exists in the internal surface of mesopores, and the graft polymerization takes place almost entirely inside the mesopores.[30] As expected, the polydispersity indices of various polymers obtained at different conversions were relatively low ($M_w/M_n < 1.3$), and no obvious shoulders and tailings were observed in the GPC traces of the grafted polymers (Figure 5). This indicates that better-defined polymers without dead polymeric chains could be successfully grafted onto silica support. These results also confirmed the significant effects of loading of Si-CTA on Z-supported RAFT polymerization.

For RAFT graft polymerization, less steric hindrance and similar polymerization rates in solution and on surface are crucial to obtain well-defined free and grafted polymers. To improve control of the graft polymerization, a dithiobenzoate-based CTA, CPDB, was introduced into the polymerization system. Since the polymerization rate for RAFT polymerization mediated by dithiobenzoates (CPDB) is retarded when compared to that using trithiocarbonates (MPPA and BSPA), it is possible to further decrease the polymerization rate in solution. The results as listed in Table 1 (runs 3, 6 and 11) indicated that the polymerization rate in solution was efficiently slowed down. In these cases, the molecular weights of free polymers were very close to those of the corresponding grafted polymers, both were similar to the theoretical values, with PDI less than 1.2. Comparing to similar conversions for the polymerizations in presence of free MPPA, for which the molecular weight of free and grafted polymeric chains differ greatly (Figure 4), it is clear that the introduction of CPDB improves control over molecular weight

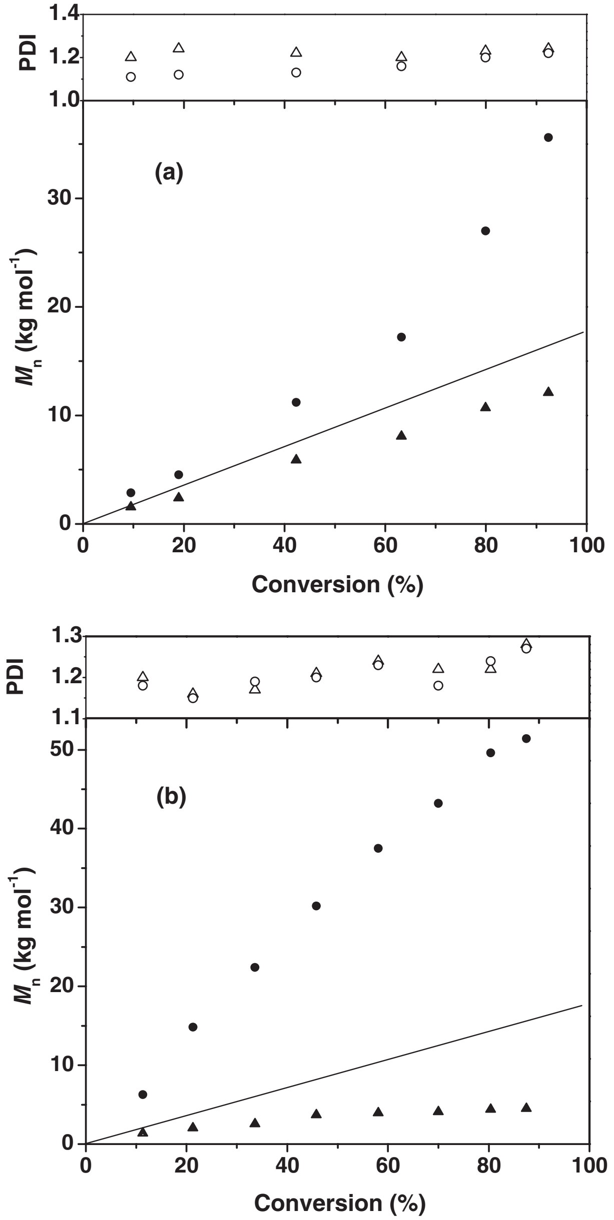


***Figure 4.***

Dependence of $M_n$ and PDI of free (circle) and grafted (triangle) PMAs on conversion for RAFT polymerization of MA mediated by Si-MPPA1 (a) and Si-MPPA2 (b) in the presence of MPPA. See Figure 3 for polymerization conditions.

and PDI. This observation is also supported by a similar study undertaken on different monomers.[16] The above results also demonstrated 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 the same free CTA.

The results in Table 1 also indicated that the apparent grafted CTA efficiency was affected by the types and loading of

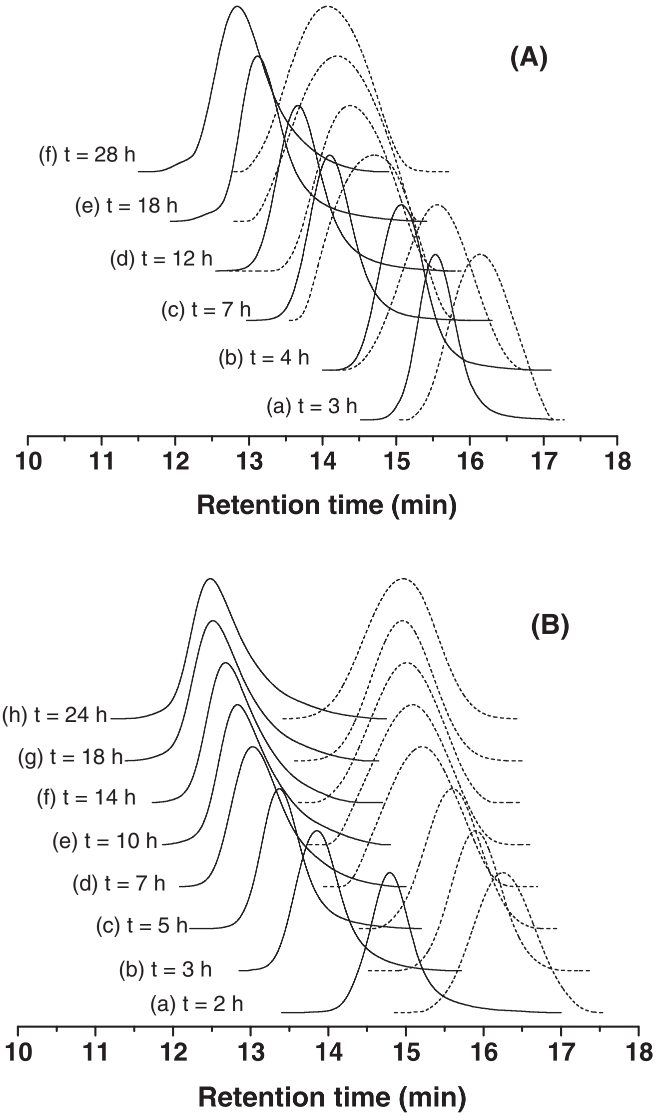


**Figure 5.**
GPC traces of free (solid line) and grafted (dashed line) PMA samples synthesized by RAFT graft polymerization of MA at various times: (A) Si-MPPA1; (B) Si-MPPA2.

Si-CTAs and free CTA in solution. The polymerizations without using a free CTA give low $G_e$ values, maybe due to a poorer control over molecular weights and increased shielding effect resulting from longer propagating polymeric chain radicals. When a free CTA is introduced in the solution, the control over polymerization is improved, and the graft polymerization conducted smoothly, thus favoring the surface graft polymerization and increasing the grafted CTA efficiency. For polymerization mediated by Si-MPPA, higher $G_e$ values are achieved when Si-MPPA2 with a lower CTA loading is used, maybe due to less shielding effect at the early stage of polymerization. In all cases, the graft polymerization using CPDB in reaction system affords very high $G_e$ values, confirming slow propagation of polymeric chain radical in solution favors the graft polymerization and affords more active CTAs on silica surface. The above results indicated that the grafted CTA efficiency depends on the type and loading of Si-CTA, the nature of free CTA used in solution and the grafted polymeric chain length.

## Conclusion

Si-MPPA and Si-BSPA were synthesized and used to mediate the RAFT polymerization of MA. The molecular weight and polydispersity of grafted polymer and the grafted CTA efficiency were affected by the types and loading of Si-CTAs and free CTA in solution. When the same free CTA was introduced into the solution, the polymerization mediated by Si-MPPA was more controlled than that using Si-BSPA. For RAFT polymerization mediated by Si-MPPA, the introduction of a free CTA in solution during polymerization could significantly decrease the polydispersity of free and grafted PMA and enhance the grafted CTA efficiency. Moreover, the RAFT graft polymerization using CPDB as a free CTA afforded well-defined PMA grafted onto silica support and significantly increased $G_e$ value, while the polymerization rate was also decreased.

*Acknowledgements:* Y. L. Zhao acknowledges the financial support from the University of Leeds and EPSRC.

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