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Effect of Ligand Spacer on Silica Gel Supported Atom Transfer Radical Polymerization of Methyl Methacrylate

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ABSTRACT: Silica gels grafted with tetraethyldiethylenetriamine (TEDETA) and di(2-picolyl)amine (DiPA) via poly(ethylene glycol) (PEG) spacers of different chain lengths were synthesized and used as CuBr support for the atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA). The spacer length strongly affected the polymerization rate and polymer molecular weight control. Catalyzed by CuBr immobilized on the silica gel, the MMA polymerization rate increased with spacer length in the order of $PEG_1 < PEG_{10} < PEG_3$ (the subscript is the number of the EG units). Copper bromide supported via three-unit PEG (SG-PEG_3-TEDETA and SG-PEG_3-DiPA) controlled the MMA polymerization best, producing PMMA with controlled molecular weights (initiator efficiency ca. 75%) and low polydispersities ($M_w/M_n \sim 1.2-1.4$). The recycled catalysts had activities similar to the fresh ones at the late stage of polymerization with improved initiator efficiencies. The PMMA-*block*-poly(2-(*N*,*N*-dimethylamino)ethyl methacrylate) with well-controlled molecular weight and low polydispersity was also synthesized by this support system.

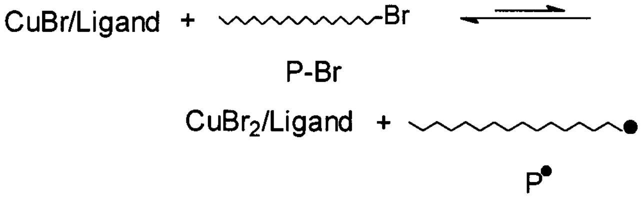
Introduction

Atom transfer radical polymerization (ATRP) is a transition-metal-mediated living radical polymerization of vinyl monomers.[1−9] It is versatile for a wide range of monomers, producing polymers with well-controlled molecular weights and low polydispersities, as well as various functionalities.[10−13] It is also a very useful approach for synthesizing novel polymer architectures such as star polymers,[14−17] polymer brushes,[18] nanoparticle hybrids,[19] and polymer monolayers.[20]

Given the advantages of ATRP, the catalyst residue in the final product remains problematic. Catalyst residue deeply colors the product. For example, poly(2-(*N*,*N*-dimethylamino)ethyl methacrylate) (polyDMAEMA) precipitated in petroleum ether from ATRP solution of DMAEMA catalyzed by CuBr−hexamethyltriethylenetetramine was deep green. The residual catalyst can be removed from the product by passing the solution through a column of silica gel or reprecipitation into aqueous NH_4Cl.[21] Matyjaszewski [22] also reported using ion-exchange resins with acid groups to remove copper complexes. Nevertheless, this postpurification is not only time-demanding but also costly. Catalyst supporting,[23,24] fluorous biphase,[25] and ionic liquid [26] have thus been developed to reduce the catalyst residue and to reuse the catalyst.

Supported catalyst is useful in atom transfer radical addition and continuous membrane process.[27] Catalyst supporting onto insoluble particles is of special importance for ATRP because it not only can reuse the catalyst and obtain catalyst-free products but also is useful for continuous ATRP.[28] Continuous ATRP is of great interest because it avoids the laborious catalyst recycling step in supported batch process and can continuously produce polymers with molecular weight adjustable by simply changing the monomer flow rate. The continuous ATRP of MMA was carried out in a column reactor packed with silica gel supported CuBr−hexamethyltriethylenetetramine.[28] The activity of this reactor was stable for more than 100 h but decreased gradually afterward. This activity reduction resulted from the loss of the catalyst by continuous washing out of the reactor since the catalyst was physically adsorbed on the silica gel surface and the accumulation of Cu(II) species as a result of persistent radicals. Therefore, one way to slow the activity reduction of the continuous reactor is using catalyst that is immobilized on particle surface via covalent bonds so that the catalyst will not be washed out of the reactor. However, to date, covalently supported systems for ATRP were not very successful. Copper halide supported on silica gel/cross-linked polystyrene particles via alkylpyridylmethanimine for methyl methacrylate polymerization did not control the polymer molecular weight satisfactorily.[29] CuBr immobilized on multidentate amine-functionalized silica gel and cross-linked polystyrene particles did not catalyze living polymerizations of styrene, methyl acrylates, and methacrylate.[30]

We believe that the lack of controllability of immobilized catalysts in ATRP may be caused by the diffusion limitation of the catalysts. ATRP is based on a reversible activation/fast-deactivation process of radicals (eq 1).[1] It is critical for a good ATRP that the generated radicals be deactivated quickly to prevent side reactions; otherwise, the ATRP will behave like a conventional free radical polymerization. In a homogeneous catalyst system, the small molecules of catalyst can diffuse freely in solution and thus effectively



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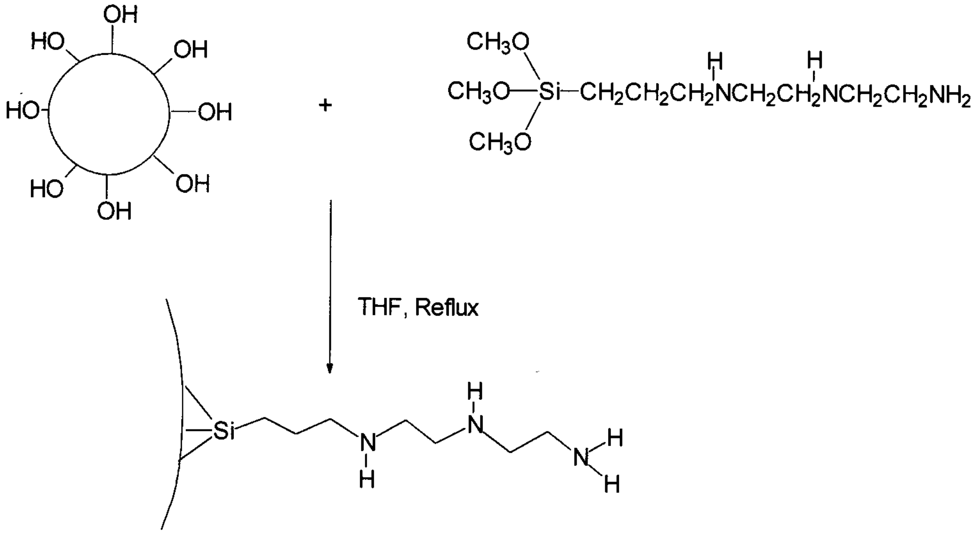
Scheme 1. Grafting Diethylenetriamine onto Silica Gel



regulate the polymer chain growth. However, after the catalyst molecules are covalently bound to large (relative to small molecules) insoluble particles, the mobility of these molecules is substantially reduced, and thus the deactivation reaction (reverse reaction in eq 1) may become slower, resulting in a less controlled ATRP.

We thus propose that the supporting spacer, through which the catalyst is attached to the particle, might affect the mobility of the catalyst. A short spacer provides the catalyst very limited mobility, while a long and flexible spacer renders the catalyst more freedom. However, a too long spacer may form coils surrounding the catalytic site and thus impede the access of the catalyst to the polymer ends for reaction (steric effect). Consequently, the spacer length may strongly affect the catalyst activity and its control of ATRP. This paper investigates the spacer effect by using silica gels grafted with tetraethyldiethylenetriamine (TEDETA) or di(2-picolyl)amine (DiPA) via poly(ethylene glycol) (PEG) spacers of different lengths for MMA polymerizations.

Experimental Section

Methyl methacrylate (99.9%, MMA) and 2-(*N*,*N*-dimethylamino)ethyl methacrylate (99.9%, DMAEMA) from Aldrich were distilled under vacuum and stored at −15 °C. *N*,*N*,*N*′,*N*′-Tetraethyldiethylenetriamine (TEDETA, 90%), di(2-picolyl)-amine (DiPA, 97%), CuBr (99.99%), methyl α-bromophenylacetate (MBP, 99%), N^1-[3-(trimethoxylsilyl)propyl]diethylenetriamine (92%), phenyl ether (99%), poly(ethylene glycol) diacrylates (M_n = 258, 575), and ethylene glycol diacrylates (90%), also from Aldrich, were used as received. Silica gel with 100−200 mesh and an average pore diameter of 60 Å was supplied by SiliCycle Inc.

Synthesis of Diethylenetriamine-Functionalized Silica Gel. The attachment of diethylenetriamine onto silica gel surface was based on the reaction of silicon alkoxides with silanol groups on the particle surface (Scheme 1). Hydrophilic silica gel was dried in a vacuum at 60 °C for 3 days. Silica gel (10 g), N^1-[3-(trimethoxylsilyl)propyl]diethylenetriamine (5 g), and THF (50 mL) were charged to a flask. The mixture was refluxed for 48 h. The silica gel was separated from the solution by centrifugation and washed six times with THF. It was finally dried at 50 °C under vacuum for 24 h. The conversion of N^1-[3-(trimethoxylsilyl)propyl]diethylenetriamine was 8.8%. IR of modified silica gel: 3433 cm^{-1}(Si−OH, NH), 2975 cm^{-1}, 1733 cm^{-1}, 1567 cm^{-1}, 1032 cm^{-1}. The amount of diethylenetriamine grafted onto silica gel was determined by thermogravimetric analysis (TGA) and elemental analysis. The calculated diethylenetriamine loading was 4.24% (w/w).

Ligand Grafting: Grafting Tetraethyldiethylenetriamine (TEDETA) or Di(2-picolyl)amine (DiPA) onto Silica Gel. TEDETA or DiPA was grafted onto silica gel via poly(ethylene glycol) spacer by sequential Michael reactions of acrylates with primary or secondary amines, as shown in Scheme 2. Diethylenetriamine-functionalized silica gel (10 g) was gradually added to poly(ethylene glycol) diacrylates (M_n = 258, 30 g) with sufficient stirring. The mixture was stirred for 48 h at room temperature. It was then diluted with THF to 100 mL and centrifuged. The silica gel was washed with THF (60 mL) six times to remove the adsorbed PEG. About 0.2 g of the silica gel was taken out and dried in a vacuum for analysis. The left silica gel was stirred with 20 mL of TEDETA for 48 h at room temperature. The silica gel was separated by centrifugation and washed with THF seven times. Finally, the silica gel was air-dried and then vacuum-dried at 40 °C for 24 h. DiPA functionalized silica gel supports were prepared by the same procedure. FTIR of silica gel grafted with TEDETA: 3440, 2959, 2923, 2808, 1736, 1457, 1377, and 1108 cm^{-1}. IR of silica gel grafted with DiPA: 2959, 2926, 1735, 1596, 1109, and 797 cm^{-1}. The nitrogen contents in the particles were determined by thermogravimetric analysis (TGA) and elemental analysis. The TEDETA or DiPA contents in the particles were then calculated from the difference in nitrogen contents after and before the ligand grafting reaction. The ligand contents on the silica gels with different spacers are shown in Table 1.

Polymerization. A typical polymerization procedure was as follows: CuBr (10 mg, 0.0694 mmol), SG-PEG$_3$-TEDETA (1.04 g, containing TEDETA 0.0694 mmol), and phenyl ether (4.5 g) were added to a Schlenk flask and degassed by five vacuum−nitrogen cycles. Degassed methyl methacrylate (0.69 g, 6.9 mmol) was then added to the flask by a nitrogen-purged syringe. The mixture was stirred at room temperature for 20 min. A slightly blue suspension with a colorless solution was obtained. The degassed initiator (MBP, 7.3 μL, 0.046 mmol) was dropwise added to the flask with stirring. The blue suspension turned to bright green. The flask was subsequently heated to 60 °C in an oil bath. At different time intervals, ca. 0.05 mL of the solution/catalyst mixture was withdrawn with a nitrogen-purged syringe. The solution was diluted with CDCl$_3$. The conversion was measured with ^{1}H NMR by the ratio of the OCH_3 signal intensity in polymer (3.60 ppm) and monomer (3.75 ppm) (see Figure 1). The molecular weight and polydispersity of the polymer were measured by GPC (see Figure 3).

Catalyst Reuse. After the polymerization was complete, the flask was lifted from the oil bath and centrifuged. The supernatant was carefully removed with cannula by nitrogen. The leftover bright green solid in the flask was washed three times with 10 mL of degassed phenyl ether under nitrogen.

Scheme 2. Immobilizing Ligand onto Silica Gel via Polyethylene Glycol Spacer

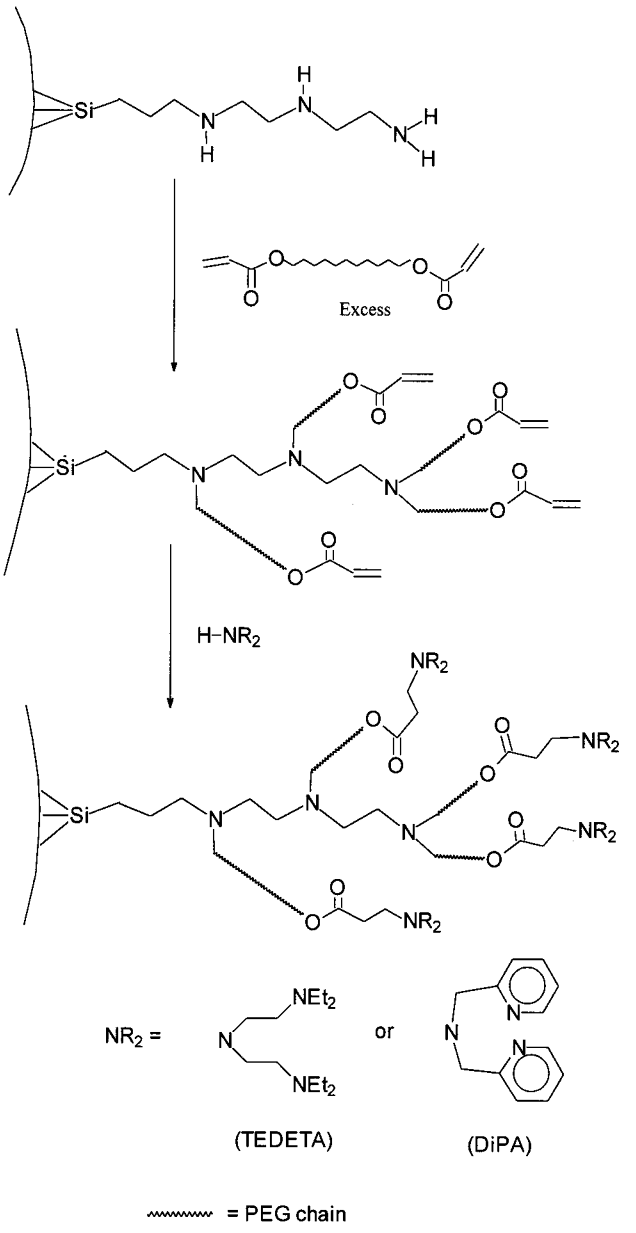


Table 1. TEDETA or DiPA Contents in Synthesized Silica Gel Supports

support name	PEG spacer units	ligand	ligand % (w/w)
SG-PEG$_1$-TEDETA	1	TEDETA	3.0
SG-PEG$_3$-TEDETA	3	TEDETA	1.43
SG-PEG$_{10}$-TEDETA	10	TEDETA	1.32
SG-PEG$_1$-DiPA	1	DiPA	2.97
SG-PEG$_3$-DiPA	3	DiPA	2.35
SG-PEG$_{10}$-DiPA	10	DiPA	1.1

The same amounts of degassed MMA, phenyl ether, and initiator as in the first run were added to the flask and reheated to 60 °C. The same procedure as in the first run was repeated (see Figure 7).

Block Copolymerization. CuBr (7.0 mg, 0.0486 mmol), SG-PEG$_3$-TEDETA (730 mg, containing TEDETA 0.0486 mmol), and phenyl ether (3.15 g) were added to a Schlenk flask and degassed as described above. Degassed MMA (0.34 mL, 3.18 mmol) and methyl α-bromophenylacetate (6.3 μL, 0.0397 mmol, MMA/MBP = 80) were added. The mixture was immersed in a 60 °C oil bath for 6 h. A small amount of the mixture (ca. 0.05 mL) was withdrawn to analyze the conversion by ^{1}H NMR spectroscopy (conversion = 75%) and molecular weight by GPC (M_n = 6900, M_w/M_n = 1.22). The flask was connected to vacuum to remove the volatiles. Degassed DMAEMA (DMAEMA/MBP = 80) was charged to the flask and stirred for 10 min. The flask was reheated to 60 °C for 8 h (DMAEMA conversion, 70%; M_n = 14 700, M_w/M_n = 1.46; M_n(theor) = 15 700).

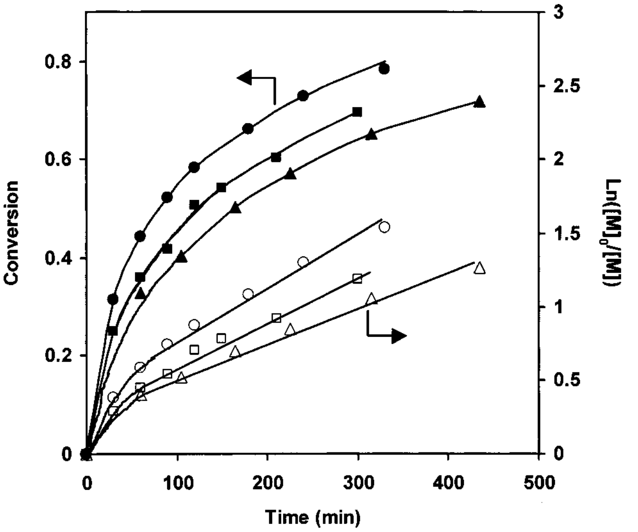


Figure 1. MMA polymerization in phenyl ether catalyzed by CuBr with TEDETA-functionalized silica gel support. [MMA] = 1.38 mol/L, [MBP] = 9.2 × 10^{-3} mol/L, [CuBr] = 1.39 × 10^{-2} mol/L, [TEDETA]/[CuBr] (molar) = 1, 60 °C; Supports: SG-PEG$_1$-TEDETA (▲, △); SG-PEG$_3$-TEDETA (●, ○); SG-PEG$_{10}$-TEDETA (■, □).

Measurements. *Nuclear Magnetic Resonance (NMR) Spectroscopy.* Proton (^{1}H) NMR spectra were recorded on a Bruker ARX-200 spectrometer at 200 MHz. ^{1}H NMR chemical shifts in $CDCl_3$ were reported downfield from 0.00 ppm using TMS as an internal reference.

Molecular Weight Measurements. Number- and weight-average molecular weights (M_n and M_w, respectively) were determined by gel permeation chromatography (pore size: 500, 1500, and 10 000 Å)) using THF−2% (v/v) triethylamine as solvent at a flow rate of 1.0 mL/min at 25 °C with a RI detector. Narrow polystyrene standards (Polysciences) and Mark−Houwink−Sakurada constants were used to generate a universal calibration curve (K_{PS} = 0.000 128, α_{PS} = 0.712; K_{PMMA} = 0.000 128, α_{PMMA} = 0.69 from Polysciences). Data were recorded and manipulated using the Windows based Millennium software package.

Silica Gel Analysis. Thermogravimetric analysis (TGA) was performed on a Netzsch STA-409 high-temperature DTA/TGA under nitrogen at a heating rate of 5 °C/min form room temperature to 800 °C. The elemental analysis was carried out by Guelph Chemical Laboratories Ltd. in Guelph, Ontario, Canada.

Results and Discussion

MMA Polymerization Catalyzed by CuBr Supported on Silica Gel Particles via Different Spacers. Figures 1 and 2 show the MMA polymerizations mediated with CuBr supported on TEDETA or DiPA-modified silica gel via different PEG spacer lengths. The rate constants for MMA polymerizations are summarized in Table 2. The apparent polymerization rate constants k^{app} (i.e., $k_p[R^\bullet]$) increased with the spacer length in the following order: PEG$_1$ < PEG$_{10}$ < PEG$_3$. This may suggest that when CuBr is anchored immediately on the silica gel surface, the catalyst has very limited mobility and therefore less chance to react with the dormant centers (P−Br) (eq 1). However, when the spacer is too long, e.g. with 10 EG units, the PEG coils

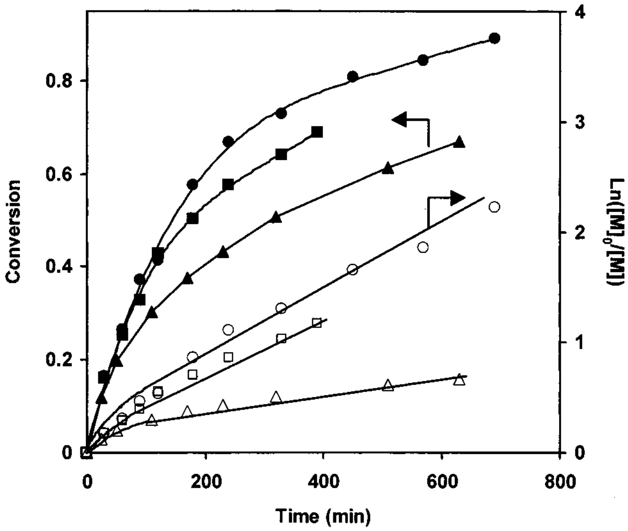


Figure 2. MMA polymerization in phenyl ether catalyzed by CuBr with DiPA-functionalized silica gel support. [MMA] = 1.38 mol/L, [MBP] = 9.2×10^{-3} mol/L, [CuBr] = 1.39×10^{-2} mol/L, [DiPA]/[CuBr] (molar) = 1; 60 °C; Support: SG-PEG$_1$-DiPA (▲, △); SG-PEG$_3$-DiPA (●, ○); SG-PEG$_{10}$-DiPA (■, □).

Table 2. Apparent Rate Constant (k^{app}, $\times 10^{-3}$ min^{-1}) of MMA Polymerization Catalyzed by CuBr Immobilized on Silica Gel with Different Spacer Length[a]

support	$k_p[R^\bullet]$ ($\times 10^{-3}$)	support	$k_p[R^\bullet]$ ($\times 10^{-3}$)
SG-PEG$_1$−TEDETA[b]	2.5	SG-PEG$_1$-DiPA	1.6
SG-PEG$_3$-TEDETA	3.8	SG-PEG$_3$-DiPA	3.0
SG-PEG$_{10}$-TEDETA	3.2	SG-PEG$_{10}$-DiPA	2.7

[a] [MMA] = 1.38 mol/L, [MBP] = 9.2×10^{-3} mol/L, [CuBr] = 1.39×10^{-2} mol/L, [TEDETA] or [DiPA]/[CuBr] (molar) = 1, 60 °C. Solvent: phenyl ether. [b] The subscript is the ethylene glycol unit number.

surrounding the catalytic site may impede the reaction of the catalyst with dormant active center (P−Br). It seems that, of the three spacers, the one with three EG units is optimal for immobilizing CuBr.

The polymerizations in Figures 1 and 2 experienced initial decrease in rate before the $\ln([M]_0/[M])$ vs time curves became linear, which suggests a decrease in the radical concentration in the early stage of polymerization based on $\ln([M]_0/[M]) = k_p[R^\bullet]t$. This decrease was caused by radical termination reactions. At the early stage of the polymerization, the low Cu(II) concentration in the solution favored the forward reaction in eq 1 and thus resulted in a high radical concentration. Consequently, radical side reactions such as termination became significant. These side reactions consumed radicals and generated excess Cu(II) (eq 1). When a certain level of Cu(II) concentration accumulated and the reverse reaction reached an equilibrium with the forward reaction (eq 1), the polymerization proceeded smoothly in a constant radical concentration (i.e., a first-order reaction).

Figures 3 and 4 show the number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the resulting PMMA. The molecular weights of PMMA increased linearly with the conversion, indicating a living process in all cases. The spacer length of the catalyst support affected the initiator efficiency (M_n, theoretical/M_n, experimental) of the polymerization and polydispersity of PMMA. The initiator efficiency was 57% with SG-PEG$_1$-TEDETA, 75% with SG-PEG$_3$-TEDETA, and 70% with SG-PEG$_{10}$-TEDETA. The polydispersity of PMMA was in the range 1.4−1.6 with SG-PEG$_1$-TEDETA, 1.2−1.4 with SG-PEG$_3$-TEDETA, and 1.4−1.5 with SG-PEG$_{10}$-TEDETA. When DiPA was used as ligand, there was little difference in the initiator efficiency, but the polydispersity of PMMA obtained with SG-PEG$_3$-DiPA was clearly the lowest (Figure 4). These results indicate that CuBr immobilized with three units of ethylene glycol regulated the polymerization more effectively. A spacer length longer or shorter than three EG units may slow the deactivation reaction of Cu(II) with an active center (P$^\bullet$) (the reverse reaction in eq 1) and thus decrease the control of the polymerization. This observation agrees with the kinetic data in Figures 1 and 2.

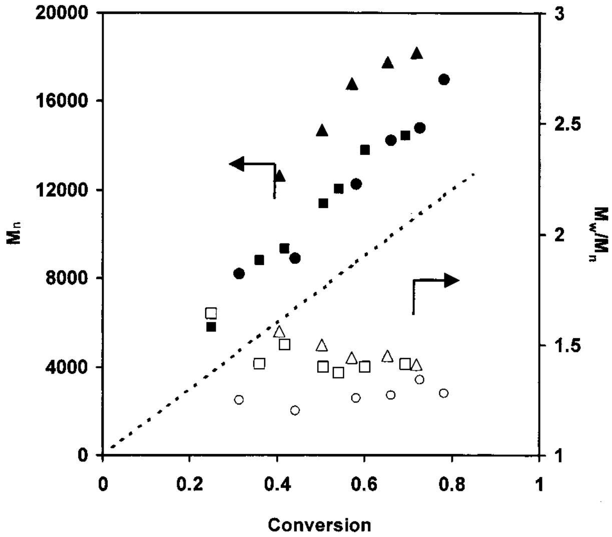


Figure 3. PMMA molecular weight and polydispersity as a function of conversion for MMA polymerizations in phenyl ether with different TEDETA-functionalized supports. See Figure 1 for other experimental conditions. SG-PEG$_1$-TEDETA (▲, △); SG-PEG$_3$-TEDETA (●, ○); SG-PEG$_{10}$-TEDETA (■, □); theoretical M_n (- - -).

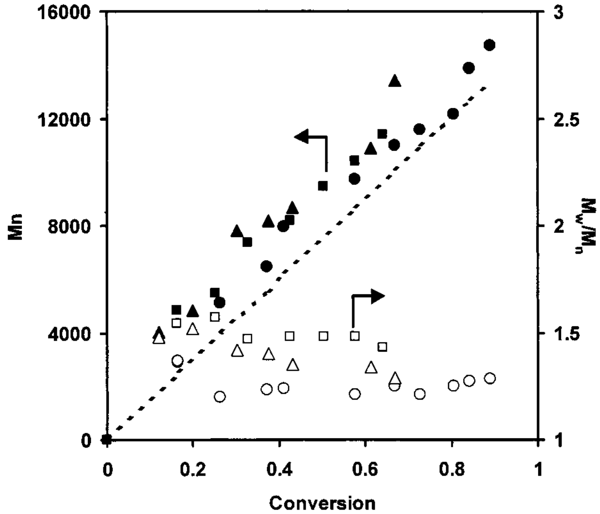


Figure 4. PMMA molecular weight and polydispersity as a function of conversion for MMA polymerizations in phenyl ether with different DiPA-functionalized supports. See Figure 2 for other experimental conditions. SG-PEG$_1$-DiPA (■, □); SG-PEG$_3$-DiPA (●, ○); SG-PEG$_{10}$-DiPA (▲, △); theoretical M_n (- - -).

Our previous work demonstrated that it was necessary to use excess catalyst relative to the initiator to mediate ATRP for catalysts supported with a short

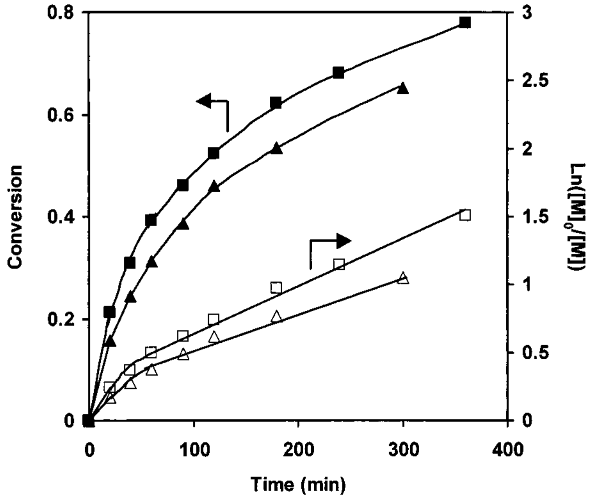


Figure 5. MMA polymerization at CuBr/initiator = 1 in phenyl ether. [MMA] = 1.38 mol/L, [MBP] = 9.2 × 10^{-3} mol/L, [CuBr] = 9.2 × 10^{-3} mol/L; [TEDETA]/[CuBr] (molar) = 1, 60 °C. Support: SG-PEG$_3$-TEDETA (■, □); SG-PEG$_1$-TEDETA (▲, Δ).

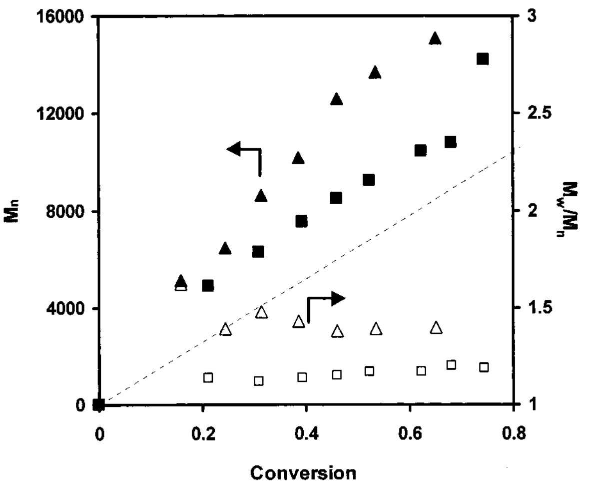


Figure 6. PMMA molecular weight and polydispersity as a function of conversion for the polymerization in phenyl ether at CuBr/MBP = 1. See Figure 5 for other experimental conditions. SG-PEG$_3$-TEDETA (■, □); SG-PEG$_1$-TEDETA (▲, Δ) as support; theoretical M_n (- - -).

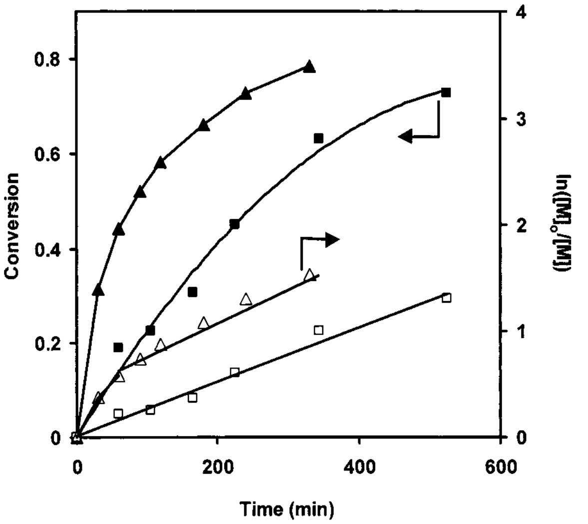


Figure 7. Recycling SG-PEG$_3$-TEDETA supported CuBr for MMA polymerization in phenyl ether. [MMA] = 1.38 mol/L, [MBP] = 9.2 × 10^{-3} mol/L, [CuBr] = 1.39 × 10^{-2} mol/L, [TEDETA]/[CuBr] (molar) = 1, 60 °C; fresh catalyst (▲, Δ); recycled catalyst (■, □).

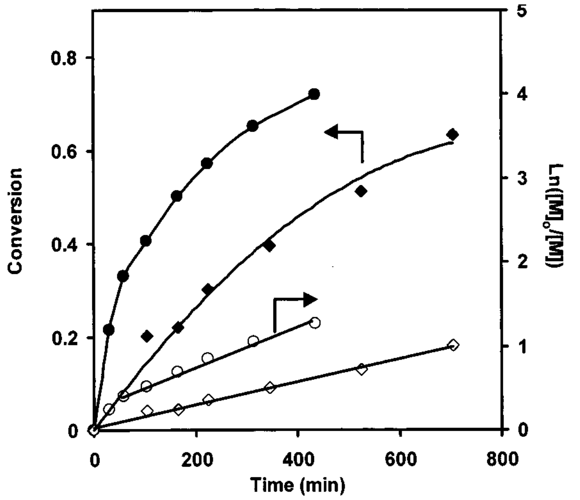


Figure 8. Recycling SG-PEG$_1$-TEDETA supported CuBr for MMA polymerization in phenyl ether. [MMA] = 1.38 mol/L, [MBP] = 9.2 × 10^{-3} mol/L, [CuBr] = 1.39 × 10^{-2} mol/L, [TEDETA]/[CuBr] (molar) = 1, 60 °C; fresh catalyst (●, ○); recycled catalyst (◆, ◇).

spacer, typically CuBr/initiator = 1.5, to achieve a controlled polymerization.[31] However, the CuBr/initiator ratio could be lowered with longer spacers. Figure 5 shows the MMA polymerization at CuBr/initiator = 1 with SG-PEG$_3$-TEDETA or SG-PEG$_1$-TEDETA as support. The kinetic plots were similar to those at CuBr/initiator = 1.5 (Figure 1) with slightly lower polymerization rates. Figure 6 shows the molecular weight and polydispersity as a function of conversion. At CuBr/MBP = 1, the molecular weight development and polydispersity of PMMA obtained were also very similar to those at CuBr/initiator = 1.5 with SG-PEG$_3$-TEDETA and SG-PEG$_1$-TEDETA. These comparisons suggest that with longer spacer the supported catalyst effectively mediates ATRP, and thus extra catalyst is not necessary.

Catalyst Reuse. One of the major objectives of catalyst supporting is recycling the catalyst. A series of catalyst recycling experiments were therefore carried out with SG-PEG$_1$-TEDETA and SG-PEG$_3$-TEDETA as support. The results are shown in Figures 7 and 8. MMA was first polymerized. Upon completion, the catalyst was recycled and washed with degassed phenyl ether. The same amounts of degassed solvent, MMA, and initiator as in the first run were recharged to the recycled catalyst for a second polymerization at 60 °C. Unlike the polymerization with fresh catalyst, the recycled catalysts gave rather smooth lines without the initial decrease in rate. This is presumably due to Cu^{II}Br$_2$ in the recycled catalysts, which equilibrated with CuBr in the first run polymerization. The ln([M]$_0$/[M]) vs time plots were linear throughout the polymerization with the recycled catalysts and parallel to those with the fresh catalysts, indicating that the recycled catalysts had the same catalytic activity as the fresh ones at the late stage of the polymerization.

Figure 9 shows the molecular weight and polydispersity of PMMA as a function of conversion with the fresh and recycled catalysts. In all cases, the molecular weights increased linearly with conversion. Most significantly, the molecular weights of PMMA prepared by the recycled catalysts were much closer to their theoretical values, i.e., higher initiator efficiencies. The

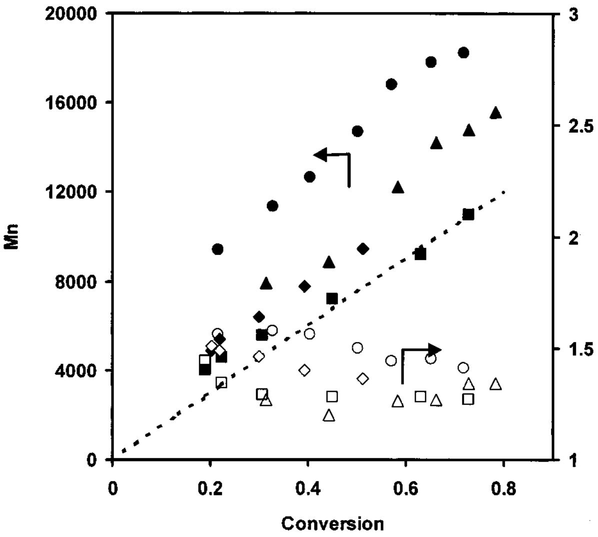


Figure 9. PMMA molecular weight and polydispersity as a function of conversion for the polymerizations with fresh and recycled catalysts on different supports. See Figures 7 and 8 for experimental conditions. SG-PEG$_3$-TEDETA: fresh catalyst (▲, △); recycled catalyst (■, □); SG-PEG$_1$-TEDETA: fresh catalyst (●, ○); recycled catalyst (◆, ◇); theoretical M_n (- - -).

Table 3. DMAEMA Polymerization Catalyzed by CuBr Supported on SG-PEG$_3$-TEDETA[a]

time (min)	conv	Ln([M]$_0$/[M])	M_n(GPC)	M_n(theor)	M_w/M_n
20	0.27	0.31	8 370	5 525	1.21
50	0.44	0.58	10 900	9 016	1.24
80	0.56	0.82	13 700	11 402	1.23
110	0.69	1.16	15 500	14 027	1.31
170	0.75	1.37	16 600	15 209	1.28

[a] [DMAEMA] = 1.38 mol/L, [MBP] = 9.2 × 10^{-3} mol/L, [CuBr] = 1.39 × 10^{-2} mol/L, [TEDETA]/[CuBr] (molar) = 1, 60 °C. Solvent: phenyl ether.

initiator efficiency was ca. 100% for the recycled CuBr/SG-PEG$_3$-TEDETA and 78% for the recycled CuBr/SG-PEG$_1$-TEDETA, compared to 75% and 57% respectively for their corresponding fresh catalysts. These results indicate that the recycled catalysts had improved ability to regulate chain growth. The improvement in the initiator efficiency presumably resulted from Cu(II) in the recycled catalysts, which suppressed the radical termination by lowering the radical concentration (eq 1).

Block Copolymerization of MMA with 2-(*N*,*N*-Dimethylamino)ethyl Methacrylate (DMAEMA). The ability of the silica gel supported CuBr to mediate block copolymerization was examined by block copolymerizing DMAEMA from PMMA using reinitiation method. The DMAEMA polymerization by CuBr/SG-PEG$_3$-TEDETA was investigated first. Table 3 shows the DMAEMA polymerization with the CuBr/SG-PEG$_3$-TEDETA. Similar to the MMA polymerization, the DMAEMA polymerization was also a first-order reaction but was much faster than the MMA polymerization. This is consistent with the higher ATRP polymerization rate in more polar media.[32,33] The molecular weights of poly(DMAEMA) were very close to the predicted values with low polydispersities(1.2−1.4).

MMA (MMA/MBP = 80) was first polymerized using CuBr/SG-PEG$_3$-TEDETA for 6 h, yielding macroinitiator of PMMA with M_n = 6900 and M_w/M_n = 1.22 ($M_{n,theor}$ = 6000) with 75% conversion. The unreacted MMA was removed by vacuum. DMAEMA was then added, and the mixture was reheated to 60 °C for 8 h. A block copolymer of P(MMA-*b*-DMAEMA) was isolated with 70% DMAEMA conversion. The resulting polymer had M_n of 14 700 ($M_{n,theor}$ = 15 700) and polydispersity of 1.46 (Figure 10). This demonstrates that this silica gel supported CuBr is good for block copolymerization.

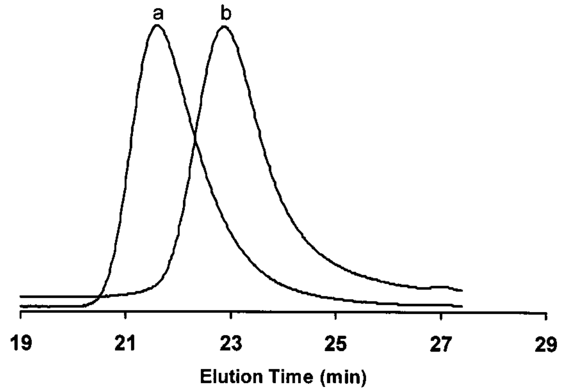


Figure 10. GPC traces of (a) poly(MMA-*b*-DMAEMA) block copolymer and (b) PMMA macroinitiator. [MBP] = 9.2 ×10^{-3} mol/L, [CuBr] = 1.39 × 10^{-2} mol/L, [TEDETA]/[CuBr] (molar) = 1, 60 °C; MMA/MBP (molar) = 80; DMAEMA/MBP (molar) = 80.

Conclusion

The spacer between the catalyst and its support strongly affected the polymerization rate and control over the molecular weight and polydispersity of the resulting polymers. Of the three spacers used in this paper, the optimum spacer length was about three units of ethylene glycol since the supported catalyst had the highest reaction rate and the best control over the molecular weight of PMMA. The recycled catalyst on these supports retained much of its activity and improved the initiator efficiencies.

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