

Articles

Atom Transfer Radical Polymerization of Methyl Methacrylate Mediated by Copper Bromide–Tetraethyldiethylenetriamine Grafted on Soluble and Recoverable Poly(ethylene-*b*-ethylene glycol) Supports

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ABSTRACT: Polyethylene (PE) and polyethylene-*block*-poly(ethylene glycol) (PE-PEG) grafted with *N,N,N',N'*-tetraethyldiethylenetriamine (TEDETA) were used as soluble and recoverable supports for copper bromide mediated atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA). The PE chain length and poly(ethylene glycol) (PEG) spacer strongly affected the catalytic activity and control of the polymerization. With PE as a catalyst support, the catalytic activity and control of the polymerization were low and decreased as the PE support's chain length increased. The adverse effects of the PE support were minimized by using PEG as spacer to graft the catalyst onto the PE support. The PE₂₅-PEG₄-TEDETA-CuBr and PE₁₆-PEG₁₀-TEDETA-CuBr were found effectively mediated ATRP of MMA. The recycled PE-supported catalysts had low activity because of catalyst side reactions and/or catalyst loss, but the PE₂₅-PEG₄-TEDETA-CuBr retained 90% activity upon recycling and had good control over the polymerization.

Introduction

Atom transfer radical polymerization (ATRP) is of increasing interest because of its versatility for living polymerizations of a wide variety of monomers, producing polymers with well-controlled molecular weights and various architectures.^{1–7} However, its catalyst residue, e.g., CuBr/aliphatic amine complex, deeply colors its final products. Even though highly active catalysts have been developed and thus low catalyst concentrations can be used,⁸ postpurification is still required to remove the catalyst residue from the products.^{9,10}

Supporting catalyst on insoluble particles is a possible solution to this problem. Catalysts immobilized on insoluble particles can be easily separated from the reaction mixture and be recycled and give catalyst-free products.¹¹ However, immobilized catalysts often experience a lack of control over the polymerization. Polydispersities of polymers produced by immobilized catalysts are usually higher than those by homogeneous catalyst systems, and the molecular weights are also higher than predicted (i.e., lower initiator efficiencies).¹¹

Studies on the catalyst supporting spacer effect suggested that the lack of control of ATRP mediated by supported catalysts was caused by the slowed reaction between supported catalysts and propagating radicals due to heterogeneity.^{11f} A well-controlled ATRP is achievable only when generated radicals are deactivated quickly so that the radicals propagate only a few units in each activating/deactivating cycle and remain a low

stationary concentration.¹² Otherwise, the polymerization will proceed like a conventional free radical polymerization.¹²

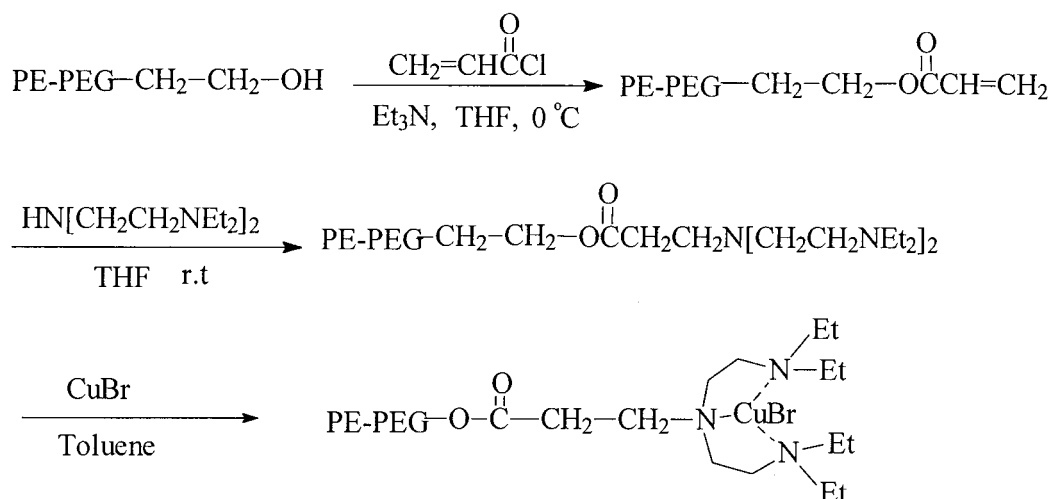
Compared with free catalysts, the accessibility of catalyst molecules bound onto particle surface is substantially reduced. Meanwhile, polymer chains assume coil conformation in solution. The active polymer ends (terminal carbon–halide or radical) may become entrapped inside of coils and thus may experience difficulty in accessing catalytic sites on the surface. These two factors reduce the ability of supported catalysts to deactivate radicals. Therefore, a homogeneous catalyst system is preferred because catalyst molecules can diffuse more freely in solution and thus more effectively regulate polymer chain growth. An ideal catalyst system is that the catalyst is soluble under reaction conditions to achieve a homogeneous reaction but precipitates at workup conditions for catalyst recycling.

Polyethylene (PE) is soluble in toluene at high temperature but insoluble at room temperature. It was used as a soluble recoverable support for small molecule reactions.¹³ Brittain et al.¹⁴ were the first to use PE as a support for ATRP of MMA. However, the PE-supported copper bromide was found to have very low activities even at 100 °C. The molecular weight of produced PMMA was controllable, but the polydispersity was in the range of 1.4–1.5. We found that copper bromide supported to PE through a poly(ethylene glycol) (PEG) spacer gave high activities for the polymerization of methacrylates and styrene, producing polymers with well-controlled molecular weight and low polydispersity.¹⁵ In this work, we investigated the PE support and PEG spacer effects on the MMA polymerization.

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Scheme 1. Supporting CuBr onto Poly(ethylene-*b*-ethylene glycol) or Polyethylene via Tetraethyldiethylenetriamine (TEDETA)



Experimental Section

Materials. Methyl methacrylate (99.9%, MMA) and 2-(*N,N*-dimethylamino)ethyl methacrylate (99.9%, DMAEMA) from Aldrich were distilled under vacuum and stored at $-15\text{ }^{\circ}\text{C}$. *N,N,N',N'*-Tetraethyldiethylenetriamine (TEDETA, 90%), CuBr (99.99%), and methyl α -bromophenylacetate (MBP, 99%), also from Aldrich, were used as received. Toluene was distilled. Polyethylene-*block*-poly(ethylene glycol) ($\text{CH}_3(\text{CH}_2\text{CH}_2)_x(\text{OCH}_2\text{CH}_2)_y\text{OH}$) with molecular weight of 875 (21% w/w of ethylene units) and 920 (50% ethylene units) and α -hydroxypolyethylene ($\text{CH}_3(\text{CH}_2\text{CH}_2)_m\text{OH}$) with molecular weight of 700 and 460, also from Aldrich, were characterized by proton NMR (^1H NMR 300 MHz in d_8 -toluene $80\text{ }^{\circ}\text{C}$), and the results were agreeable with the reported values from Aldrich. They are designated as PE₂₅-PEG₄-OH, PE₁₆-PEG₁₀-OH, PE₂₅-OH, and PE₁₆-OH (subscripts are the numbers of monomer units).

Supporting TEDETA onto PE. The catalyst supporting procedure is shown in Scheme 1. Polyethylene-*block*-poly(ethylene glycol) (PE₂₅-PEG₄-OH, PE₁₆-PEG₁₀-OH), or α -hydroxypolyethylene (PE₁₆-OH, PE₂₅-OH) were end-capped with an acryloyl group by the reaction of terminal hydroxyl group with acryloyl chloride. The Michael reaction of the acryloyl group with tetraethyldiethylenetriamine (TEDETA) attached the ligand onto the support. A typical procedure is as follows:

PE₂₅-PEG₄-OH (20 g, 0.0228 mol) was dissolved in toluene (200 mL) at $90\text{ }^{\circ}\text{C}$ under a nitrogen atmosphere. The solution was cooled slowly to room temperature. Precipitated PE₂₅-PEG₄-OH was centrifuged. The solid was dispersed in 200 mL of THF-Et₃N (5/1 in v/v) at ambient temperature. Acryloyl chloride (3.6 mL, 0.0442 mol) diluted in 10 mL of THF was dropwise added to this mixture. The mixture was stirred for overnight and then centrifuged. The solid was washed successively seven times with THF, 10 times with water (to wash out formed Et₃N $\cdot$ HCl salt), and twice with THF. The solid was then dispersed in 25 mL of TEDETA and stirred for 48 h (Michael reaction) at ambient temperature. The solid was separated by centrifugation, washed with THF 10 times, and dried under vacuum at $30\text{ }^{\circ}\text{C}$. ^1H NMR in deuterated toluene ($80\text{ }^{\circ}\text{C}$, 300 MHz): $\text{CH}_3(\text{CH}_2-\text{CH}_2)_x(\text{OCH}_2\text{CH}_2)_y\text{CH}_2\text{CH}_2\text{OC(O)-CH}_2\text{CH}_2\text{N}^+[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2]_2$ (PE₂₅-PEG₄-TEDETA) 1.3 ppm (CH_2 in PE segments), 3.65 ppm (CH_2 in PEG segment), 4.2 ppm (COOCH_2), 2.7 ppm (OC(O)CH_2), 2.5 ppm (NCH_2), 1.0 ppm (NCH_2CH_3), 0.87 ppm (CH_3 at the PE end). The intensity ratio is 108:21.1:2.69:2.67:13.1:9.1:4.0. 42% of PE₂₅-PEG₄-OH ends was capped with TEDETA ligand. A similar method was used to synthesize other ligands: PE₁₆-PEG₁₀-TEDETA (22.8% capped); PE₁₆-TEDETA (23.6% capped); PE₂₅-TEDETA (13.7% capped). A low temperature was required for this capping reaction to prevent side reactions. The incomplete capping was due to the limited solubility of PE in the solution at the temperature. To examine the possible effects of the uncapped

PE on polymerization, parallel experiments were carried out with and without additional PE₂₅, and no difference in the results was observed.

Polymerization. In a typical polymerization run, CuBr (0.011 g, 0.0764 mmol), PE₂₅-PEG₄-TEDETA (0.3 g), and toluene (5 g) were charged to a Schlenk flask and degassed with several vacuum/nitrogen cycles. The degassed MMA (1.0 g) was then introduced by syringe and stirred. After the PE₂₅-PEG₄-TEDETA support was thoroughly dispersed, degassed methyl α -bromophenylacetate (12 μL , 0.0757 mmol) was dropwise added to the mixture with stirring. The slightly yellow solution immediately turned green. The mixture was further stirred at room temperature for 30 min. Then the flask was immersed in an oil bath ($80\text{ }^{\circ}\text{C}$) for polymerization. The polymerization solution (0.05–0.1 mL) was withdrawn at different time intervals to analyze the conversion (by NMR) and molecular weight (GPC).

Catalyst Reuse. After the polymerization completed, the flask was lifted from the oil bath and centrifuged at $0\text{ }^{\circ}\text{C}$. The supernatant was carefully removed by cannula with nitrogen. The leftover green solid in the flask was washed three times with a total of 20 mL degassed toluene under nitrogen. The same amounts of degassed MMA, toluene, and initiator, as in the first run, were added to the flask that was reheated to $80\text{ }^{\circ}\text{C}$. The same procedure as that for the first run was repeated.

Nuclear Magnetic Resonance (NMR) Measurements. Proton (^1H) NMR spectra were recorded on a Bruker ARX-200 or 300 spectrometer at 200 or 300 MHz. ^1H NMR chemical shifts in CDCl_3 were reported downfield from 0.00 ppm using TMS an internal reference.

Molecular Weight Measurements. Number- and weight-average molecular weights (M_n and M_w , respectively) were determined by gel permeation chromatography (columns pore size: 500, 1500, and 10 000 $\text{\AA}$) using THF–2% (v/v) triethylamine as solvent at $25\text{ }^{\circ}\text{C}$ with a RI detector. Narrow polystyrene standards (Polysciences) were used to generate a universal calibration curve ($K_{\text{PS}} = 0.000\ 128$, $\alpha_{\text{PS}} = 0.712$; $K_{\text{PMMA}} = 0.000\ 128$, $\alpha_{\text{PMMA}} = 0.69$). Data were recorded and manipulated using the Windows based Millenium software package.

Catalyst Residue Analysis. After the polymerization was complete, the flask was cooled to 20 or $0\text{ }^{\circ}\text{C}$ and centrifuged at 6000 rpm for 10 min. The precipitate was separated from the solution. The clear solution (0.50 mL) was dissolved in 1.0 mL of $\text{H}_2\text{SO}_4/\text{HNO}_3$ (3/1 in v/v). While the mixture was heated at $100\text{ }^{\circ}\text{C}$, an additional 2.5 mL of $\text{H}_2\text{SO}_4/\text{HNO}_3$ (3/1 in v/v) was gradually added. A clear yellowish solution was finally obtained, and the solution was diluted to 50 mL with deionized water. The copper concentration in the aqueous solution was measured by a Perkin-Elmer Elan 6100 ICP-MS. The copper

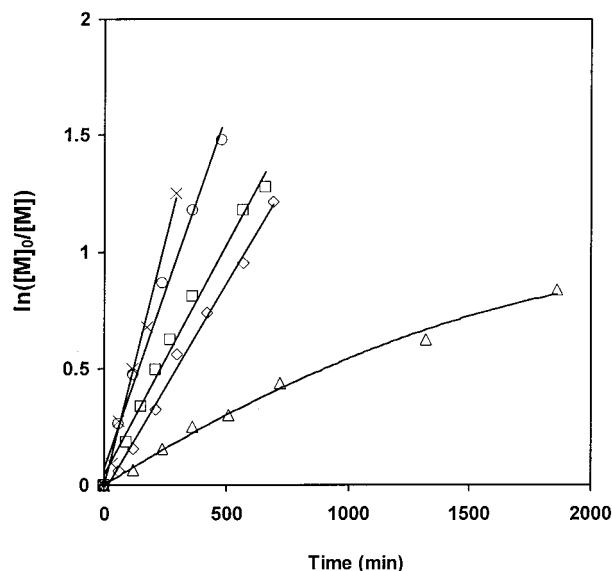


Figure 1. Polymerization of MMA catalyzed by CuBr on different supports. $[\text{CuBr}] = [\text{MBP}] = 0.0115 \text{ mol/L}$, PE-PEG-TEDETA or PE-TEDETA/CuBr = 1.5, $[\text{MMA}] = 1.5 \text{ mol/L}$, 80°C . PE₂-TEDETA (x); PE₁₆-PEG₁₀-TEDETA (○); PE₂₅-PEG₄-TEDETA (□); PE₁₆-TEDETA (◇); PE₂₅-TEDETA (△).

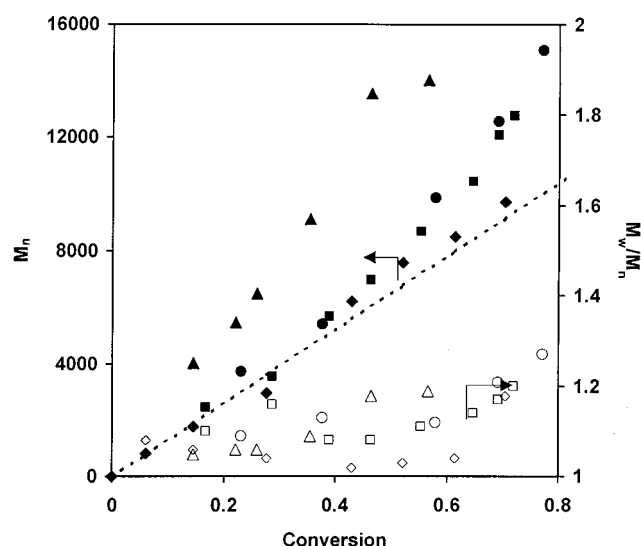


Figure 2. PMMA molecular weight and polydispersity as a function of conversion in the MMA polymerizations catalyzed by CuBr on different supports. See Figure 1 for the experimental conditions. PE₁₆-PEG₁₀-TEDETA (■, □); PE₂₅-PEG₄-TEDETA (●, ○); PE₁₆-TEDETA (◆, ◇); PE₂₅-TEDETA (▲, △); theoretical M_n (---).

concentration in the polymerization solution was then calculated.

Results and Discussion

PE Support and PEG Spacer Effect. The MMA polymerization catalyzed by CuBr with PE or PE-*b*-PEG as support is shown in Figures 1 and 2. *N'*-(*n*-Butyloxycarbonyl)-*N,N,N',N''*-tetraethyldiethylenetriamine (PE₂-TEDETA), which has the same structure as other PE-TEDETA but only two ethylene units, was also synthesized from *n*-butyl acrylate and TEDETA in order to compare the effect of PE chain length on the ATRP. All catalysts immobilized on PE-based supports completely dissolved in toluene solution of MMA at 70°C or above, but only part of the catalyst dissolved in the toluene solution of MMA when PE₂-TEDETA was used as lig-

Table 1. Apparent Rate Constant of MMA Polymerization with Different Supports^a

support	PE units	PEG units	$k_p^{\text{app}} (k_p[\text{P}^*]) \times 10^3$
PE ₁₆ -PEG ₁₀	16	10	3.0
PE ₂₅ -PEG ₄	25	4	2.0
PE ₂	2	0	4.2
PE ₁₆	16	0	1.8
PE ₂₅	25	0	0.66

^a See Figure 1 for experimental conditions.

and. Therefore, for PE₂-TEDETA-CuBr catalyzed MMA polymerization, a small amount of γ -butyrolactone was added in order to obtain a homogeneous polymerization. Figure 1 shows that, except for using the PE₂₅-TEDETA-CuBr system, all the polymerizations proceeded at 80°C in a typical first-order kinetics with respect to monomer concentration and constant radical concentration throughout the polymerization. The polymerization with PE₂₅-TEDETA-CuBr was also a first-order reaction in the early stage but started to level off at a medium conversion, indicating a decrease in radical concentration.

The type of support strongly affected catalytic activity, as summarized in Table 1. First, the PE length had very strong effect on the polymerization rate (Table 1). For the catalysts directly supported onto PE via TEDETA (PE₂-TEDETA, PE₁₆-TEDETA, PE₂₅-TEDETA), the catalytic activity substantially decreased as the PE length increased. The apparent polymerization rate constant ($k_p[\text{R}^*]$) was $4.2 \times 10^{-3} \text{ min}^{-1}$ with PE₂-TEDETA, $1.8 \times 10^{-3} \text{ min}^{-1}$ with PE₁₆-TEDETA, and only $0.66 \times 10^{-3} \text{ min}^{-1}$ with PE₂₅-TEDETA as support, respectively. The low activity was also found in the Schiff base-CuBr system when PE with molecular weight of 2000 (71 units) was used as support.¹⁴ Second, this adverse effect of the PE support on the catalytic activity could be minimized by a PEG spacer, as shown in Figure 1 and Table 1. The polymerization rate constants with PE₂₅-PEG₄-TEDETA and PE₁₆-PEG₁₀-TEDETA were 2.0×10^{-3} and $3.0 \times 10^{-3} \text{ min}^{-1}$, compared with $0.66 \times 10^{-3} \text{ min}^{-1}$ using PE₂₅-TEDETA and $1.8 \times 10^{-3} \text{ min}^{-1}$ using PE₁₆-TEDETA as a support.

Figure 2 shows the molecular weight as a function of conversion in the MMA polymerizations mediated by CuBr on different supports. All the PMMA molecular weights increased with conversion. Except for the PE₂₅-TEDETA-CuBr system, the PMMA molecular weights from other systems were very close to the theoretical values. However, those by PE₂₅-TEDETA-CuBr were much higher than predicated with initiator efficiencies ($M_{n,\text{theor}}/M_{n,\text{exp}}$) about 0.50. The polydispersities were less than 1.2 below 70% conversion, similar to those prepared by CuBr complexed with small molecular ligands^{6c} but much lower than those obtained by CuBr supported on insoluble particles.¹¹ When the MMA conversion was higher than 70%, the polydispersity of PMMA increased rapidly with conversion.

Influence of Temperature. Figure 3 shows the MMA polymerizations at different temperatures. The catalytic activity of PE₂₅-TEDETA-CuBr had a strong temperature dependence, while the temperature effect on PE₂₅-PEG₄-TEDETA-CuBr was minor. The initial k_p^{app} value of MMA polymerization by PE₂₅-TEDETA-CuBr increased from 0.65×10^{-3} to $3.8 \times 10^{-3} \text{ min}^{-1}$ as the temperature increased from 80 to 100°C , while that by PE₂₅-PEG₄-TEDETA-CuBr increased only by 50% from 70 to 80°C . Meanwhile, the polymerization with PE₂₅-PEG₄-TEDETA remained a first-order reaction at both 70 and 80°C , but the polymerization with

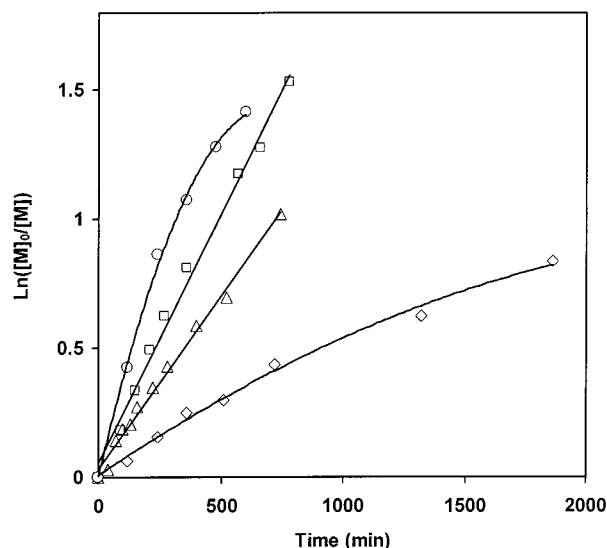


Figure 3. MMA polymerizations at different temperatures catalyzed by CuBr on PE₂₅-PEG₄-TEDETA and PE₂₅-TEDETA. [CuBr] = [MBP] = 0.0115 mol/L, PE₂₅-PEG₄-TEDETA or PE₂₅-TEDETA/CuBr = 1.5, [MMA] = 1.5 mol/L, 80 °C. PE₂₅-PEG₄-TEDETA: 80 °C (□), 70 °C (Δ); PE₂₅-TEDETA: 100 °C (○), 80 °C (◇).

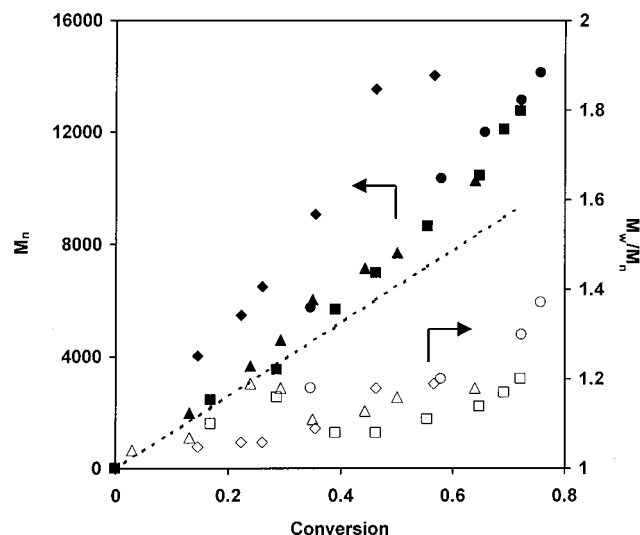


Figure 4. PMMA molecular weight and polydispersity as a function of conversion in MMA polymerizations at different temperatures catalyzed by CuBr on PE₂₅-PEG₄-TEDETA and PE₂₅-TEDETA. See Figure 3 for the experimental conditions. PE₂₅-PEG₄-TEDETA: 80 °C (■, □), 70 °C (▲, Δ); PE₂₅-TEDETA: 100 °C (●, ○), 80 °C (◆, ◇).

PE₂₅-TEDETA-CuBr experienced deviation from the first-order kinetics, i.e., decrease in radical concentration according to the $\ln([M]_0/[M]) = k_p[M^*]t$ equation, when the conversion reached 40%, as observed at 80 °C.

Temperature did not affect the control of the PMMA molecular weight with PE₂₅-PEG₄-TEDETA-CuBr (Figure 4). However, the molecular weights of PMMA prepared by PE₂₅-TEDETA-CuBr at 100 °C were much closer to the theoretical values than those prepared at 80 °C, suggesting that the polymerization with PE₂₅-TEDETA-CuBr at 100 °C had better control of the polymerization than that at 80 °C.

The above results demonstrated that supporting the ATRP catalyst to polyethylene through a PEG spacer resulted in an increased polymerization rate and improved control over polymer chain growth compared

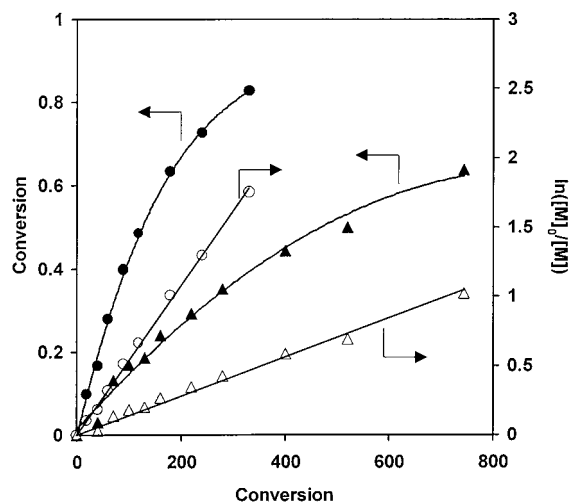


Figure 5. MMA polymerizations in different solvents. [CuBr] = [MBP] = 0.0115 mol/L, PE₂₅-PEG₄-TEDETA/CuBr = 1.5, [MMA] = 1.5 mol/L, 70 °C. Solvent: toluene (▲, Δ), phenyl ether (●, ○).

with grafting the catalyst directly to the PE support. Polyethylene has a high tendency to crystallize and thus dissolves in toluene only at high temperatures, e.g., 100 °C. Even though low molecular weight PE (PE oligomers) can dissolve in toluene at lower temperatures, e.g., 80 °C, its chains may not be extended but compact coils in solvent. The catalyst directly attached on a PE chain may thus be trapped inside the compact PE coil. Consequently, the catalyst could not effectively activate the dormant PMMA chains (P-Br), resulting in a low polymerization rate. The catalysts trapped in the PE coils may also not effectively deactivate the active radicals (P[•]), resulting in radical termination and consequently low initiator efficiency. This was particularly true at 80 °C, as seen in the MMA polymerization catalyzed by PE₂₅-TEDETA-CuBr at 80 °C (Figures 1 and 2). At 100 °C, the PE coils became less compact. The catalyst could access to the dormant/active chain ends easier and therefore could have much higher activity and more effectively regulate the chain growth. As the PMMA chains grew longer, the PMMA chain ends (P-Br) may also be trapped in their own chain coils, imposing diffusion limitations on the accessibility of PMMA chain ends (P-Br) to the catalyst sites and thus reducing the polymerization rate, as observed in the PE₂₅-TEDETA-CuBr system in Figures 1 and 3.

When the catalyst was grafted to the PE support through PEG spacer, the flexible PEG chains rendered the catalyst higher mobility. Therefore, the catalyst not only more efficiently reacted with the P-Br to have higher polymerization rate but also more quickly deactivated the radicals. A similar spacer effect was also found in the PMMA polymerization mediated by silica gel supported catalysts.^{11f}

Solvent Selection. The polymerization catalyzed by PE₂₅-PEG₄-TEDETA-CuBr in different solvents was also investigated. The reaction in the polar solvent (phenyl ether) was faster than in toluene. For example, the k^{app} value in phenyl ether at 70 °C was $5.4 \times 10^{-3} \text{ min}^{-1}$, compared with $1.4 \times 10^{-3} \text{ min}^{-1}$ in toluene (Figure 5). The molecular weights of PMMA prepared in phenyl ether were also agreeable with the predicted (Figure 6). However, the catalyst in phenyl ether was found very difficult to be separated from the solution. The suspended green catalyst behaved like gel and could

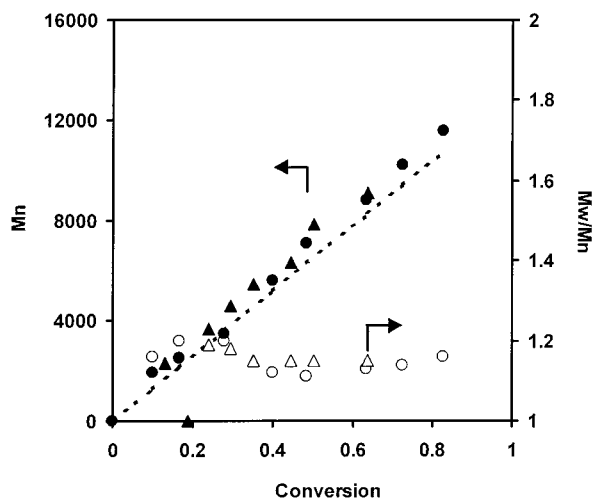


Figure 6. PMMA molecular weight and polydispersity as a function of MMA conversion in MMA polymerizations catalyzed by PE₂₅-PEG₄-TEDETA-CuBr in phenyl ether and toluene. See Figure 5 for the experimental conditions. Solvent: phenyl ether (●, ○); toluene (▲, △).

not be precipitated from the solution even by centrifugation. Toluene is therefore a better solvent in terms of catalyst recycling.

Catalyst Reuse. The recyclability of the catalyst on each support was assessed using the recovered catalyst in a subsequent MMA polymerization. After the polymerization was complete and the solution was cooled to 0 °C, solids precipitated from the solution were recovered by centrifugation. After washed with degassed toluene, the solid was recombined with the monomer, solvent, and initiator, and the mixture was reheated at 80 or 100 °C (for PE₂₅ support system). Figures 7–10 show the MMA polymerization runs with the fresh and recycled catalysts on the four different supports. All the recycled catalysts still mediated a first-order polymerization, but their catalytic activity retention strongly depended on the supports used. The catalytic activity retained 61% of its fresh catalyst for PE₁₆-TEDETA-CuBr, 31% for PE₂₅-TEDETA-CuBr, 67% for PE₁₆-PEG₁₀-TEDETA-CuBr, and 90% for PE₂₅-PEG₄-TEDETA-CuBr.

The activity reduction of the recycled catalysts was also found in other supported catalyst systems for ATRP.¹¹ There were several reasons possibly contributing to this reduction. First, in recycled catalysts there was some CuBr₂ produced in the first run polymerization, which equilibrated with CuBr in the first run. It was demonstrated that a small amount of CuBr₂ could significantly decrease the catalytic activity.¹² This was also found in the silica gel-supported catalysts.¹¹ Second, the loss of catalyst during recycling could also decrease the activity. Third, there might be some side reactions of the catalyst. This was particularly true for the PE₂₅-TEDETA-CuBr system. It was observed that after heating at 100 °C the color of the PE₂₅-TEDETA-CuBr catalyst turned deep brown, in contrast to green at 70 or 80 °C. Therefore, the loss of catalyst during recycling due to high solubility contributed the reduction in catalytic activity of recycled PE₁₆-TEDETA-CuBr and PE₁₆-PEG₁₀-TEDETA-CuBr. The activity reduction of recycled PE₂₅-TEDETA-CuBr was probably mainly caused by side reactions at high temperature rather than catalyst loss. The first recycled PE₂₅-PEG₁₀-TEDETA-CuBr catalyst retained 90% activity of the

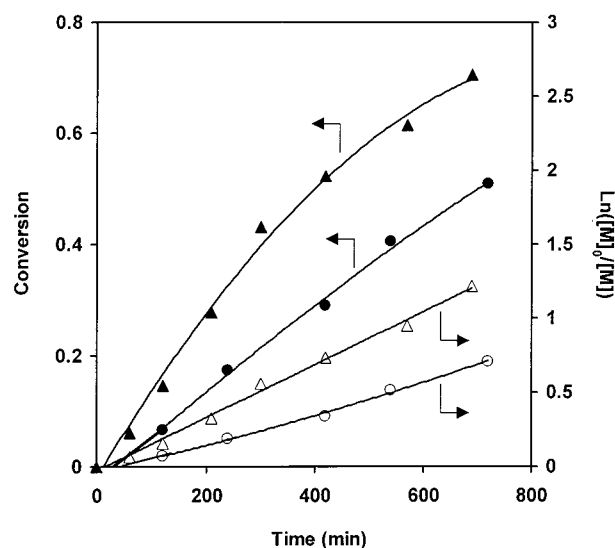


Figure 7. Reuse of PE₁₆-TEDETA-CuBr for the MMA polymerization. [CuBr] = [MBP] = 0.0115 mol/L, PE₁₆-TEDETA/CuBr = 1.5, [MMA] = 1.5 mol/L, 80 °C; First use (▲, △) and second use (●, ○).

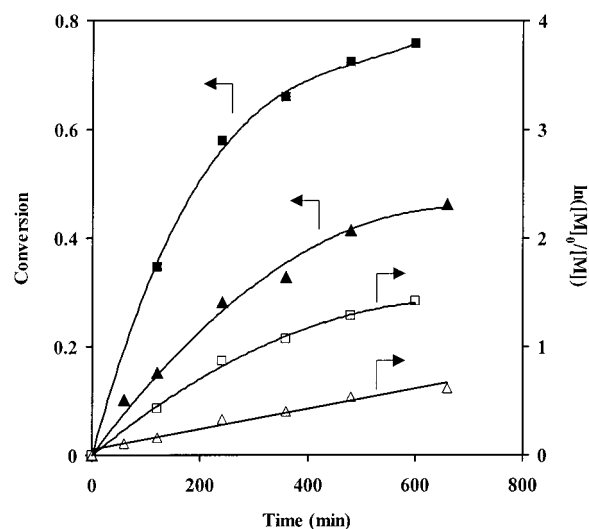


Figure 8. Reuse of PE₂₅-TEDETA-CuBr for the MMA polymerization. [CuBr] = [MBP] = 0.0115 mol/L, PE₂₅-TEDETA/CuBr = 1.5, [MMA] = 1.5 mol/L, 100 °C; First use (■, □) and second use (▲, △).

fresh catalyst (Figure 10), while the second recycled catalyst had almost the same activity as the first recycled catalyst (97% activity).¹⁵ This activity retention was much higher than those of silica gel-supported CuBr.¹¹ The slight decrease in activity upon recycling was mainly caused by the presence of CuBr₂.

Figures 11 and 12 show that the recycled catalysts still had good control over the molecular weight. The molecular weights of PMMA obtained from the recycled catalysts increased linearly with conversion and were closer to theoretical values than those obtained from the fresh catalysts. This improvement in the molecular weight control resulted from CuBr₂ in the recycled catalysts, which equilibrated with CuBr during the first run. The CuBr₂ decreased the radical concentration and thus minimized radical side reactions. The PMMA molecular weights from the first and second recycled PE₂₅-PEG₁₀-TEDETA-CuBr were also very close to the theoretical values (Figure 12).¹⁵ The polydispersities were less than 1.2, similar to those from homogeneous ATRP.^{6c}

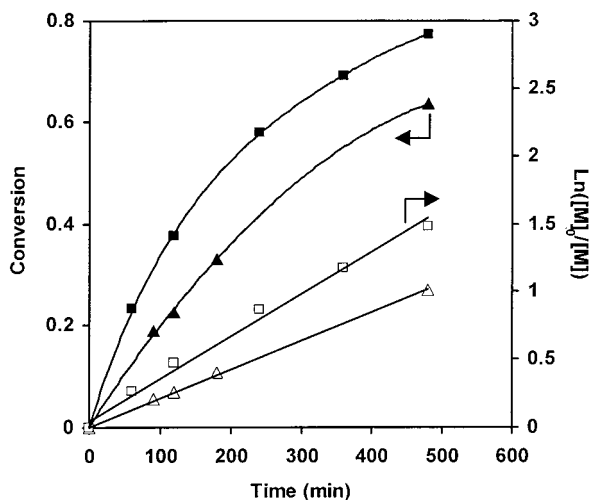


Figure 9. Reuse of PE₁₆-PEG₁₀-TEDETA-CuBr for the MMA polymerization. [CuBr] = [MBP] = 0.0115 mol/L, PE₁₆-PEG₁₀-TEDETA/CuBr = 1.5, [MMA] = 1.5 mol/L, 80 °C; First use (■, □) and second use (▲, △).

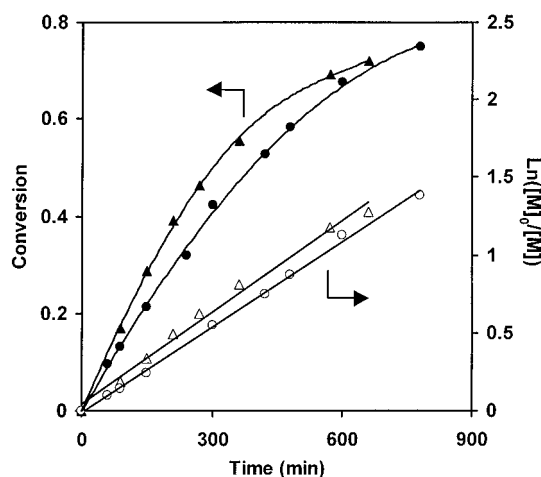


Figure 10. MMA polymerization with fresh and recycled PE₂₅-PEG₄-TEDETA-CuBr catalysts. [CuBr] = [MBP] = 0.0115 mol/L, PE₂₅-PEG₄-TEDETA/CuBr = 1.5, [MMA] = 1.5 mol/L, 80 °C. Fresh catalyst (▲, △), second use catalyst (●, ○).

Copper Residue. After the polymerization was complete, the catalyst was separated at 20 or 0 °C. The clear polymerization solution was dissolved in a concentrated H₂SO₄/HNO₃ (3/1 in v/v) solution. The copper concentration in the aqueous solution was measured by ICP-MS. The calculated copper concentration in the polymerization solution isolated at 0 °C was 12.6 ppm with PE₂₅-PEG₄-TEDETA-CuBr as catalyst, 33.4 ppm with PE₁₆-PEG₁₀-TEDETA-CuBr, 8.3 ppm with PE₂₅-TEDETA-CuBr, and 21.3 ppm with PE₁₆-TEDETA-CuBr, equivalent to 0.77%, 2.0%, 0.51%, and 1.3%, respectively, of the catalyst initially charged. This indicates that PE₂₅-PEG₄-TEDETA-CuBr and PE₂₅-TEDETA-CuBr had very low solubility in the polymerization solution, while those of PE₁₆-PEG₁₀-TEDETA-CuBr and PE₁₆-TEDETA-CuBr were higher. These results agreed with those of catalyst recycling. The catalysts had higher solubility at higher temperature. For example, the copper concentrations in the polymerization solution isolated at 20 °C were 21.6 and 18.0 ppm with PE₂₅-PEG₄-TEDETA-CuBr and PE₂₅-TEDETA-CuBr as catalyst, respectively.

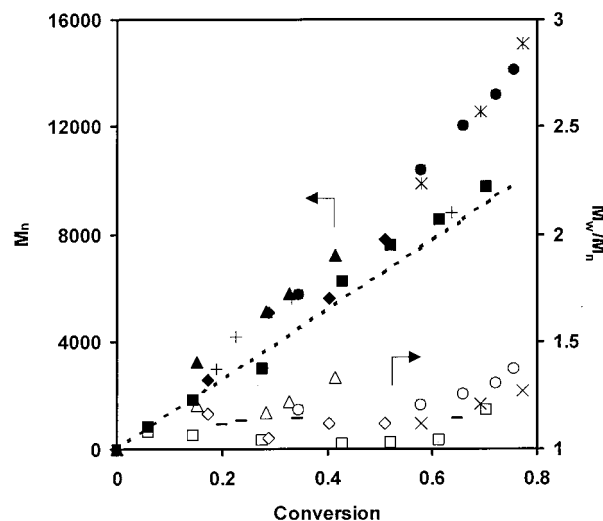


Figure 11. PMMA molecular weight and polydispersity as a function of MMA conversion catalyzed by fresh and recycled catalysts. See Figures 7–9 for the experimental conditions. PE₁₆-TEDETA-CuBr: first use (■, □); second use (◆, ◇). PE₂₅-TEDETA-CuBr: first use (●, ○), second use (▲, △). PE₁₆-PEG₁₀-TEDETA-CuBr: first use (*, ×); second use (+, -); theoretical M_n (---).

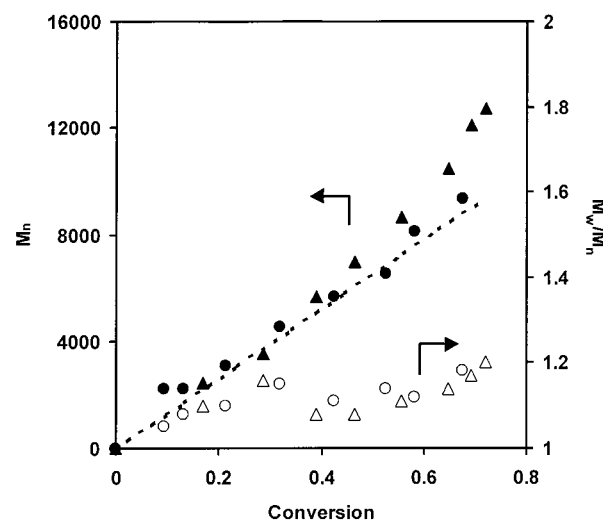


Figure 12. Molecular weight and polydispersity of PMMA as a function of conversion in MMA polymerization with fresh and recycled catalysts. Fresh catalyst (▲, △), recycled catalyst (●, ○), theoretical M_n (---). See Figure 10 for the experimental conditions.

Conclusion

Polyethylene could be used as soluble and recoverable support for ATRP of MMA, but the chain length of the polyethylene support strongly affected the catalytic activity and the control of polymerization. Long PE chain decreased not only the catalytic activity but also the control of polymerization. Using polyethylene-*block*-poly(ethylene glycol) (PE-PEG) as support, i.e., grafting the catalyst onto the PE support through a PEG spacer, effectively minimized the adverse effects of the PE support. The catalyst on PE-PEG support had higher catalytic activity and better control over molecular weight than that on the PE support. The recycled catalysts on the PE support had low catalytic activity retention because of catalyst side reactions or loss of catalyst. PE₂₅-PEG₄ was found to be a good soluble and recoverable support for CuBr, on which the catalyst gave

high activity retention and maintained good control over polymer molecular weight upon recycling.

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