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Atom Transfer Radical Polymerization of Methyl Methacrylate by Silica Gel Supported Copper Bromide/Multidentate Amine

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ABSTRACT: A silica gel support system for the copper bromide−hexamethyltriethylenetetramine (HMTETA) complex was successfully developed for the atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) in toluene. The supported complex mediated a living polymerization of MMA, yielding polymers with controlled molecular weights and narrow molecular weight distributions. The MMA concentration had significant influence on the polymerization behavior. At 33% MMA concentration, the polymerization catalyzed by CuBr−HMTETA/silica gel followed typical first-order kinetics with respect to the monomer. But at 50% MMA, the polymerization significantly deviated from the first-order kinetics after the MMA conversion reached 30%. The supported catalysts were recycled for second and third uses. The recycled catalysts remained 80% active in the second use and 50% in the third use relative to their initial activity. The recycled catalysts had even better controllability over the polymerization. The molecular weights of PMMA produced agreed with the predicted values, and the polydispersities were less than 1.2.

Introduction

Living radical polymerization mediated by a metal halide complex, named atom transfer radical polymerization (ATRP), has made significant progress[1] since it was first developed.[2−6] Various systems based on Cu,[1,4,7,8] Ru,[3,9] Fe,[10] Ni,[11−13] and Rh[14] have been developed for ATRP of styrenic, acrylic, and methacrylic monomers. The most important feature of ATRP is its great tolerance to water and other protonic species. In fact, polymerizations were successfully carried out in water.[15,16] This is clearly advantageous over anionic, cationic, and group transfer polymerizations, which are very sensitive to protonic reagents.

ATRP is very useful for synthesizing functional polymers of low molecular weight. For example, polymers with allyl,[17,18] vinyl,[19,20] and hydroxyl groups [21−23] were readily prepared with molecular weights less than 10^5. However, one of the major challenges facing ATRP is its low catalyst efficiency and thus the high catalyst concentration used. In a typical ATRP recipe, the initiator-to-catalyst ratio is usually 1:1, which is one catalyst molecule mediating one polymer chain. The metal halide usually is about 0.1−1% (molar) of the monomer. Residual catalyst in the polymer mixture colors the product. Therefore, additional purification is required to remove the catalyst, usually by passing the polymer solution through silica or alumina gel. This posttreatment is not only time-demanding but also costly due to catalyst waste.

A possible solution to these problems is to support catalyst onto a solid that can be easily removed from the final product and ideally be recycled. Recently, ruthenium(II) catalyst supported onto amine-funtionalized silica gel was successfully used for the heterogeneous ATRP of methyl methacrylate (MMA), which displayed typical living polymerization characteristics.[24]

However, supporting CuBr for heterogeneous ATRP is not very successful. CuBr was supported by a Schiff base ligand to amino-functionalized silica gel and cross-linked polystyrene for styrene and MMA polymerizations. However, the polymerizations by these catalysts showed limited living characters.[25] The polymer molecular weights were significantly higher than predicted, and the polydispersities were high (>1.5).[25] Copper bromide immobilized by multidentate amine-functionalized silica gel did not mediate a living polymerization of MMA, MA, and styrene.[26]

The copper bromide−hexamethyltriethylenetetramine (HMTETA) complex was an excellent catalyst for the ATRP of MMA, (dimethylamino)ethyl methacrylate (DMAEMA), styrene (St), and methyl acrylate (MA).[18,20,27] During the ATRP posttreatment, the catalyst complex was removed by passing the polymer−catalyst mixture solution through silica gel. The blue color from the catalyst complex was retained at the very top layer of the silica gel in the column. This suggested that the copper halide−HMTETA complex strongly adsorbed onto the silica gel. We therefore supported the catalyst complex onto silica gel by simple adsorption for ATRP.[28,29] Compared to grafting methods,[25,26] this adsorption approach is much simpler and does not require special chemicals or tedious procedures.

This paper reports using the silica gel supported CuBr−HMTETA complex for the living polymerization of MMA. The supported catalysts were recycled two to three times with good retention of the catalyst activities. The controllability of the catalyst systems over the polymer molecular weight was even improved after recycling.

Experimental Section

Materials. MMA (Aldrich, 99.9%) was distilled under vacuum and stored at −15 °C before use. 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA, 99%), CuBr (99.999%), and methyl α-bromophenylacetate (MBP, 97%) were used as received from Aldrich. Toluene was distilled from CaH_2. Silica gel was supplied by SiliCycle Inc. (230−400 mesh,

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average pore diameter of 60 Å). It was boiled in deionized water for 5 h, air-dried, and then vacuum-dried.

Measurements. a. Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{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 residual $CHCl_3$ signal at 7.23 ppm as an internal reference.

b. Molecular Weight Measurements. Number- and weight-average molecular weights (M_n and M_w, respectively) were determined by gel permeation chromatography (GPC: SHK polystyrene gel column; flow rate: 1.0 mL/min) relative to polystyrene using THF−2% (v/v) triethylamine as solvent at 25 °C with RI detector. Data were recorded and manipulated using the Waters Millennium software package.

Polymerizations. A typical polymerization process was as follows (e.g., data in Figure 11): 27.8 mg (0.193 mmol) of CuBr and 278 mg of silica gel were added to a Schlenk flask. The flask was degassed by five vacuum−nitrogen cycles. 3.86 g (38.6 mmol) of degassed MMA, 7.6 g of degassed toluene, and 44.4 mg (0.193 mmol) of HMTETA were added to the flask, and the mixture was bubbled with nitrogen for 5 min with stirring. The mixture became blue upon the ligand addition. The blue silica particles quickly settled to the bottom of the flask, and the upper solution layer became colorless once the stirring stopped. 61.2 μL (0.386 mmol) of degassed initiator (MBP) was then introduced dropwise to the flask with stirring. The blue particles turned green. The flask was then immersed into a 90 °C oil bath with sufficient stirring. At different time intervals, a 0.2−0.5 mL solution mixture was withdrawn from the flask with a nitrogen-purged syringe. The mixture was diluted with $CDCl_3$. The conversion was estimated from the ^{1}H NMR intensity ratio of OCH_3 signals from the polymer (3.60 ppm) and monomer (3.75 ppm).

Catalyst Recycle (Data in Figure 11). Upon completion of the polymerization, the flask was lifted from the oil bath and left still for an hour. The upper layer solution was carefully removed using cannula and nitrogen pressure. The remaining solid in the flask was washed twice with degassed toluene (20 mL) under nitrogen. Then the same amounts of the degassed MMA, toluene, and initiator, as in the first polymerization run, were charged to the flask. The polymerization procedure was repeated.

Results and Discussion

When silica gel was added to the copper bromide−HMTETA complex−MMA−toluene solution, it immediately became blue. Without stirring, the blue particles quickly settled to the bottom of the flask, and the upper layer solution became colorless. This indicated that the catalyst complex was adsorbed onto the silica gel. Although we do not know the exact adsorption mechanism, we believe that the highly polar CuBr−HMTETA complex has a high affinity for the −OH groups on the surface of the silica gel particles.

The blue particles immediately turned green upon adding the initiator. The mixture gradually became viscous at 90 °C. Figure 1 shows the MMA polymerization results with and without silica gel. The polymerizations proceeded at almost the same polymerization rate with and without silica gel. Both the $\ln([M]_0/[M])$ vs time plots are linear, indicating first-order kinetics with respect to monomer and the constant radical concentrations throughout the polymerizations. This demonstrates that the MMA polymerization proceeds without detectable termination. The HMTETA/CuBr molar ratio had a minor effect on the polymerization. Doubling the ligand content slightly accelerated the polymerization.

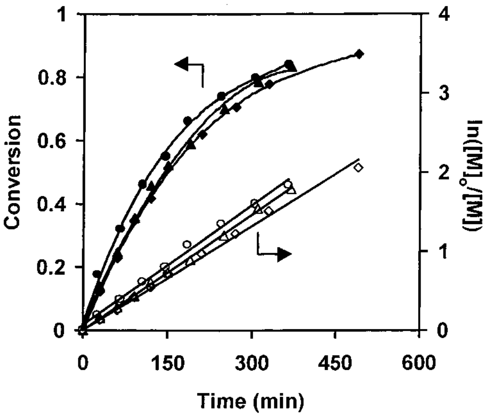

Figure 1. Polymerization of MMA catalyzed by CuBr−HMTETA with and without silica gel; 90 °C, toluene/MMA = 2 (w/w), and [MMA]/[CuBr]/[initiator] = 100:1:1:1 (molar). [HMTETA]/[CuBr] = 1, no silica gel (▲, △); [HMTETA]/[CuBr] = 1, silica gel/CuBr = 2 (w/w) (♦, ◇); [HMTETA]/[CuBr] = 2, silica gel/CuBr = 2 (w/w) (●, ○).

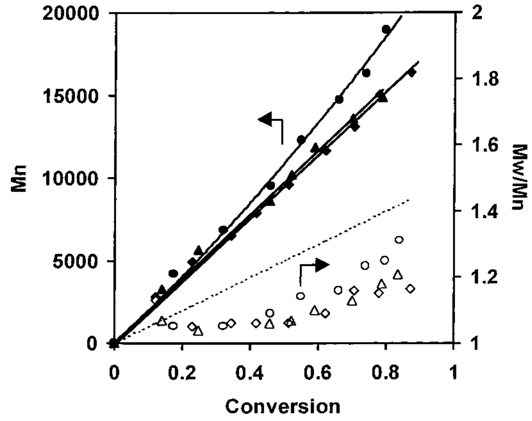

Figure 2. PMMA molecular weight and polydispersity as a function of conversion in the MMA polymerization with and without silica gel. Same experimental conditions as in Figure 1. [HMTETA]/[CuBr] = 1, no silica gel (▲, △); [HMTETA]/[CuBr] = 1 (molar), silica gel/CuBr = 2 (w/w) (♦, ◇); [HMTETA]/[CuBr] (molar) = 2, silica gel/CuBr = 2 (w/w) (●, ○).

Figure 2 shows the molecular weight and molecular weight distribution as a function of conversion. With or without silica gel, the molecular weight distributions of the resulting PMMA were all very narrow with polydispersities below 1.1 at the early stage. The polydispersities increased slightly with conversion, but most remained lower than 1.3. These polydispersities were much lower than those with ruthenium catalysts supported on amine-modified silica gel.[24] The PMMA molecular weights in Figure 2 increased linearly with conversion. This clearly demonstrates that the polymerization mediated by silica gel supported CuBr−HMTETA proceeds without detectable transfer reactions.

However, the PMMA molecular weights were much higher than predicated. The calculated initiator efficiencies ($M_{n,calc}/M_{n,GPC}$) were about 0.5 throughout the polymerization. Since the initiator efficiencies were also low in the unsupported polymerization, the low initiator efficiency was evidently not caused by the silica gel support. Increasing the ligand/CuBr ratio to 2 did not improve the initiator efficiency.

Since the plots of $\ln([M]_0/[M])$ vs time in Figure 1 are linear and the radical concentrations remained constant throughout the polymerization, the low initiator efficiencies must therefore be caused by the consumption of some initiators at the very beginning of the polym-

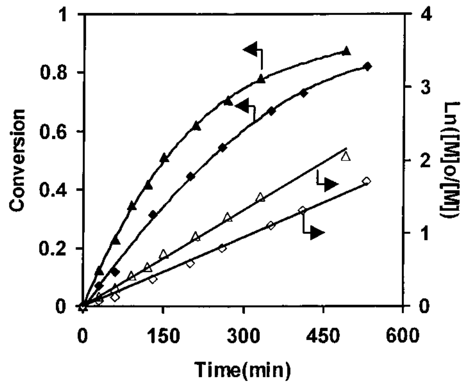

Figure 3. Polymerization of MMA with different CuBr/MBP ratios catalyzed by CuBr−HMTETA/2-silica gel, 90 °C, toluene/MMA = 2 (w/w), [MMA]/[initiator] = 100:1 (molar), and silica gel/CuBr = 2 (w/w); [HMTETA]/[CuBr]/[I] = 1:1:1 (molar) (▲, △); 0.5:0.5:1 (♦, ◇).

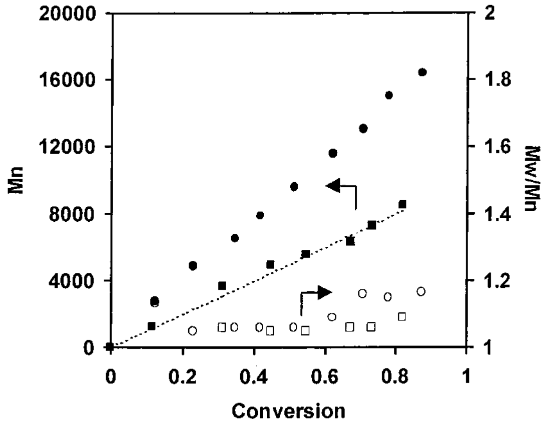

Figure 4. PMMA molecular weight and polydispersity as a function of conversion in the MMA polymerization with different CuBr/initiator ratios catalyzed by CuBr−HMTETA/2-silica gel; 90 °C, toluene/MMA = 2 (w/w), [MMA]/[initiator] = 100:1 (molar), and silica gel/CuBr = 2 (w/w); [HMTETA]/[CuBr]/[I] = 1:1:1 (molar) (●, ○), 0.5:0.5:1 (■, □).

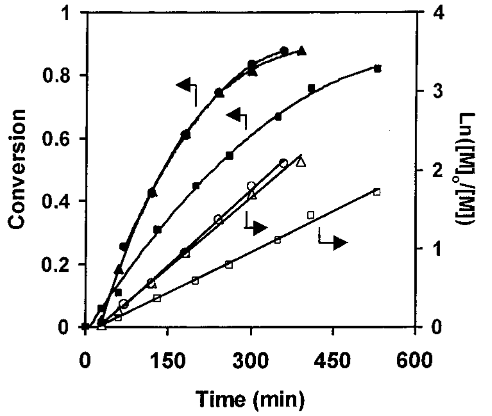

Figure 5. Polymerization of MMA catalyzed by CuBr−HMTETA with different amounts of silica gel; 90 °C, [MMA]/[HMTETA]/[CuBr]/[initiator] = 100:0.5:0.5:1 (molar); toluene/MMA = 2 (w/w); silica gel/CuBr (w/w) = 2 (■, □), 5 (▲, △), and 10 (●, ○).

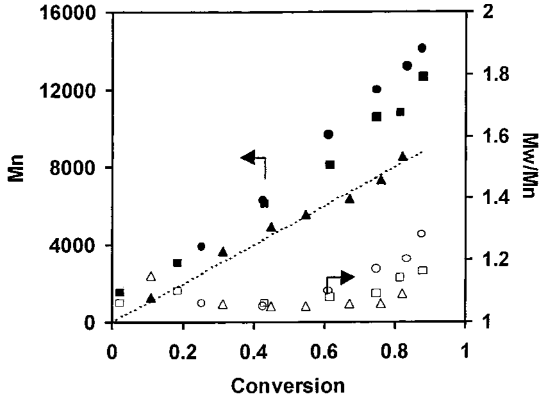

Figure 6. PMMA molecular weight and polydispersity as a function of conversion in the MMA polymerization catalyzed by CuBr−HMTETA in the presence of different amount of silica gel. Same conditions as in Figure 5. Silica gel/CuBr (w/w) = 2 (▲, △), 5 (●, ○), and 10 (■, □).

erization. Therefore, reducing the catalyst concentration may minimize initiator side reactions and thereby increase the initiator efficiency. Figure 3 shows the MMA polymerization with [CuBr]/[I] = 0.5 and 1. The polymerization with [CuBr]/[I] = 0.5 was slower than that with [CuBr]/[I] = 1. The concentration of the propagating centers in the [CuBr]/[I] = 0.5 system calculated from the slope of $\ln([M]_0/[M])$ vs time plot in Figure 3 was about 0.69 of that of [CuBr]/[I] = 1 system. Figure 4 shows PMMA molecular weight and polydispersity versus conversion data with different copper bromide concentrations. Reducing the CuBr level by half produced PMMA with a molecular weight close to the theoretical value. The initiator efficiencies approached 1. The polydispersities of PMMA were around 1.1 throughout the polymerization.

Effect of Silica Gel. The MMA polymerizations with silica gel to CuBr ratios (w/w) of 2, 5, and 10 are shown in Figure 5. All of the polymerizations were first-order in monomer. However, the polymerization rate doubled as the silica gel/CuBr ratio was increased from 2 to 5 but remained constant when further increased to 10.

Figure 6 shows the dependence of molecular weight and polydispersity of PMMA on the MMA conversion with different silica gel levels. The PMMA molecular weights increased linearly with the conversion in all the runs. With silica gel/CuBr = 2 (w/w), the molecular weights agreed with the theoretical values. However, the molecular weights were higher than predicted at silica gel/CuBr = 5 and 10 (w/w). The deviations increased with conversion. The polydispersities were all lower than 1.15 at the conversion less than 70%. With silica gel/CuBr = 5 and 10 (w/w), the polydispersities increased at higher conversions, corresponding to the molecular weight increase. This was probably caused by insufficient deactivation of the radicals by $CuBr_2$ due to limited diffusion of polymer radicals and silica gel supported catalyst in the viscous media.

Effect of MMA Concentration. To determine the effect of viscosity on the polymerization, MMA was also polymerized using CuBr−HMTETA/2-silica gel at a high monomer concentration, while maintaining monomer/catalyst molar ratio. Figure 7 shows the MMA polymerizations at the two monomer concentrations. Using 33% MMA concentration (toluene/MMA = 2 (w/w)), the polymerization proceeded with a typical first-order monomer kinetics throughout the polymerization. However, at 50% MMA (toluene/MMA = 1 (w/w)), the polymerization followed the first-order kinetics only in the early stage of the reaction but deviated rapidly from the first-order kinetics when conversion was higher than 30%, indicating a rapid increase in the radical concentration based on $\ln([M]_0/[M]) = k_p[R^\bullet]t$ equation. Correspondingly, the molecular weight deviated from the predicted values, and the polydispersity increased (Fig-

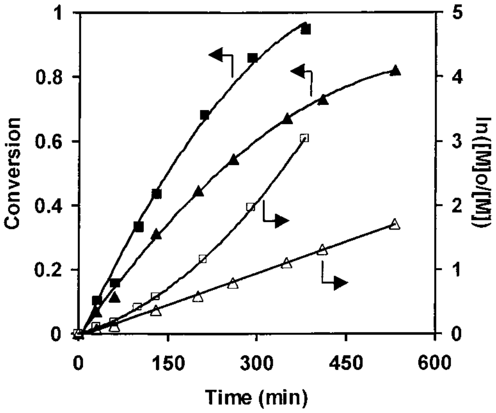

Figure 7. Polymerization of MMA catalyzed by CuBr–HMTETA/2-silica gel with different solvent fractions; 90 °C. Silica gel/CuBr = 2 (w/w); [MMA]/[CuBr]/[HMTETA]/[initiator] = 100:0.5:0.5:1; toluene/MMA (w/w) = 1 (■, □) and 2 (▲, △).

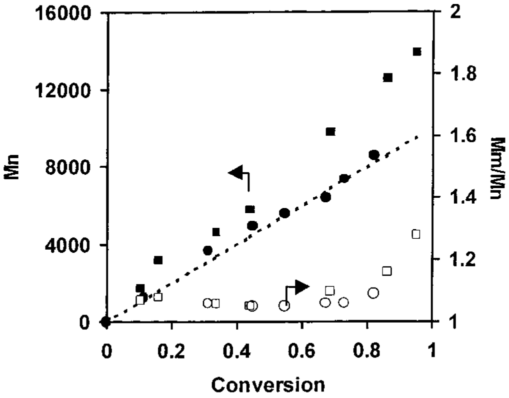

Figure 8. PMMA molecular weight and polydispersity as a function of conversion in the MMA polymerization catalyzed by CuBr–HMTETA/2-silica gel with different solvent fractions. Toluene/MMA (w/w) = 1 (■, □) and 2 (●, ○). Same conditions as in Figure 7.

ure 8). The 50% MMA polymerization media became highly viscous after 30% conversion. This observation suggested that low monomer concentrations should be used for successful ATRP mediated by a supported catalyst system.

Catalyst Recycle. Following the first polymerization run, the catalyst particles were allowed to settle to the bottle of the flask. Then the upper layer solution was removed, and the remaining green particles were washed twice with degassed toluene. The same amounts of fresh toluene, MMA, and initiator as in the first polymerization run were charged to the flask. The system was heated again for a second polymerization cycle.

Figures 9, 10, and 11 show the MMA polymerization with the recycled catalysts. The MMA polymerizations were still first-order kinetics in monomer. All of the first recycled catalysts retained around 80% of their initial activities (k_{app} ratios). The reduced activity may be caused by loss of some supported catalysts when isolating polymer. In addition, side reactions such as radical termination reaction may produce extra $CuBr_2$, which can significantly decrease the polymerization rate even in the presence of a small amount.

After the second use for MMA polymerization, some CuBr–HMTETA/2-silica gel catalyst remained on the surface of the flask, and therefore it could not be recycled again. However, CuBr–HMTETA/5-silica gel and CuBr–HMTETA/10-silica gel catalysts were easily separated from the polymer solution. Therefore, these catalysts could be reused for a third time. Figure 11 shows that the catalyst recycled twice still had reasonable activity, about 65% of the second use and 50% of the fresh. The recycled catalysts maintained excellent control of the polymerization. The M_n values of the PMMA produced by the recycled catalysts also increased linearly with conversion (Figures 12 and 13), very similar to the first run. The molecular weights of PMMA obtained in the second and third run polymerization

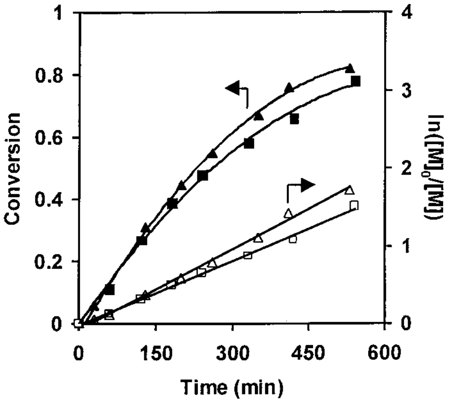

Figure 9. Recycle of CuBr–HMTETA/2-silica gel for the MMA polymerization; 90 °C. Toluene/MMA = 2 (w/w); silica gel/CuBr = 2 (w/w); [MMA]/[CuBr]/[HMTETA]/[initiator] = 100:0.5:0.5:1. First use (▲, △); second use (■, □).

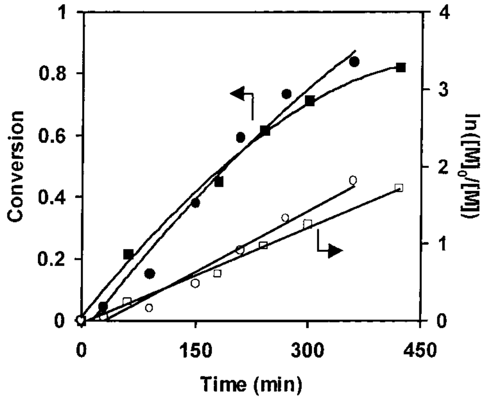

Figure 10. Recycle of CuBr–HMTETA/5-silica gel for the MMA polymerization; 90 °C. Toluene/MMA = 2 (w/w); silica gel/CuBr = 5 (w/w); [MMA]/[CuBr]/[HMTETA]/[initiator] = 100:0.5:0.5:1. First use (●, ○); second use (■, □).

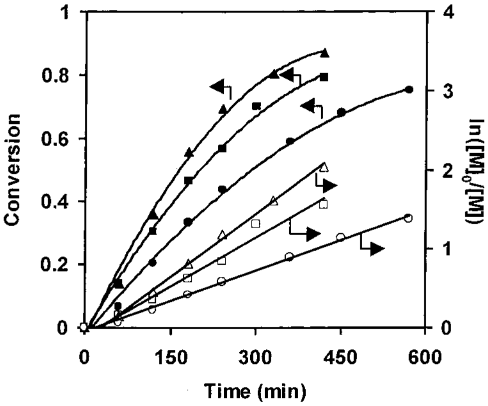

Figure 11. Recycle of CuBr–HMTETA/10-silica gel for the MMA polymerization; 90 °C. Toluene/MMA = 2 (w/w), silica gel/CuBr = 10 (w/w), [MMA]/[CuBr]/[HMTETA]/[initiator] = 100:0.5:0.5:1. First use (▲, △), second use (■, □), and third use (●, ○).

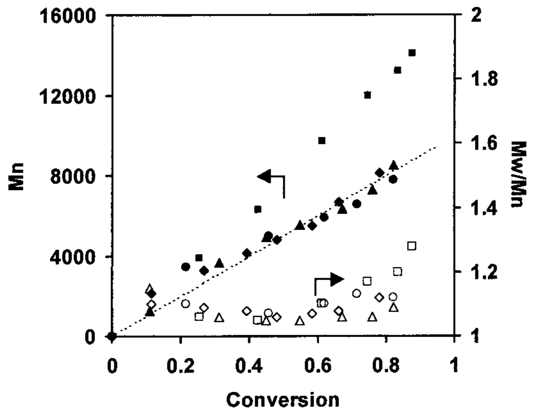

Figure 12. PMMA molecular weight and polydispersity as a function of conversion in the MMA polymerization catalyzed by CuBr−HMTETA/2-silica gel and CuBr−HMTETA/5-silica gel. CuBr−HMTETA/2-silica gel: first use (▲, △), second use (♦, ◇); CuBr−HMTETA/5-silica gel: first use (■, □), second use (●, ○). Same conditions as in Figures 9 and 10, respectively.

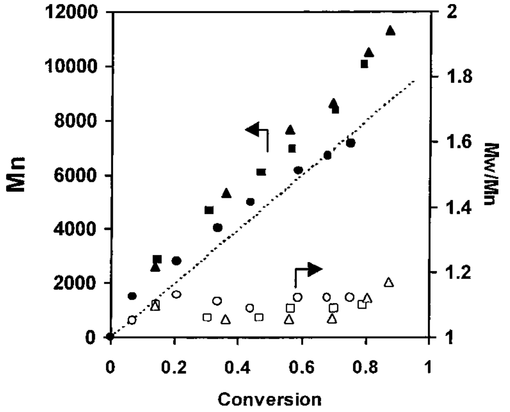

Figure 13. PMMA molecular weight and polydispersity as a function of conversion in the MMA polymerization catalyzed by CuBr−HMTETA/10-silica gel. First use (▲, △), second use (■, □), and third use (●, ○). Same conditions as in Figure 11.

were actually much closer to the theoretical values than those in the first run. The polydispersities of PMMA were still very low. These results indicated that the recycled catalysts still effectively mediated the polymerization in a living manner.

Conclusion

This paper presents a simple but very efficient method to prepare supported catalyst for ATRP of MMA. CuBr−HMTETA adsorbed on silica gel was demonstrated to be an efficient catalyst for ATRP of MMA, yielding polymers with well-controlled molecular weight and very low polydispersity. The supported catalyst was recycled for subsequent MMA polymerizations and retained 80% activity in the second use and 50% activity in the third use. The recycled catalysts had improved control over the molecular weight of PMMA. The molecular weights of PMMA prepared by the recycled catalysts were closer to the theoretical values with narrower polydispersities.

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