

Effect of the Synthetic Method and Support Porosity on the Structure and Performance of Silica-Supported CuBr/Pyridylmethanimine Atom Transfer Radical Polymerization Catalysts. II. Polymerization of Methyl Methacrylate

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ABSTRACT: A systematic study of the effect of the synthesis method and catalyst structure on the atom transfer radical polymerization (ATRP) performance of copper(I) bromide/pyridylmethanimine complexes supported on silica is described. Four different synthetic routes, including multistep-grafting (M1), two-step-grafting (M2), one-pot (M3), and preassembled-complex (M4) methods, have been evaluated on three different silica supports (mesoporous SBA15 with 48- and 100-Å pores and nonporous Cab-O-Sil EH5). The resulting solids have been used for ATRP of methyl methacrylate. The catalysts allow for moderate to poor control of the polymerization, with polydispersity indices (PDIs) ranging from 1.46 to greater than 2. The materials made with the preassembled-complex (M4) and one-pot (M3) approaches are generally more effective than those prepared with a grafting method (M1 and M2) on porous silica, whereas all the methods provide similarly performing catalysts on the nonporous support. Nonporous Cab-O-Sil EH5 is the most effective support because of its small particle size, lack of porosity, and relative compatibility in the reaction media. All the catalysts leach copper into solutions in small amounts. In addition, the catalysts can be effectively recycled, with improved controlled character in recycle runs (PDI \sim 1.2). Control experiments have shown that this improved performance of the used catalysts is likely due to the presence of a soluble Cu(II) complex in the materials that effectively deactivates the growing polymer chain, leading to narrow PDIs and controlled molecular weights. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 42: 1384–1399, 2004

Keywords: atom transfer radical polymerization (ATRP); catalysis; silicas

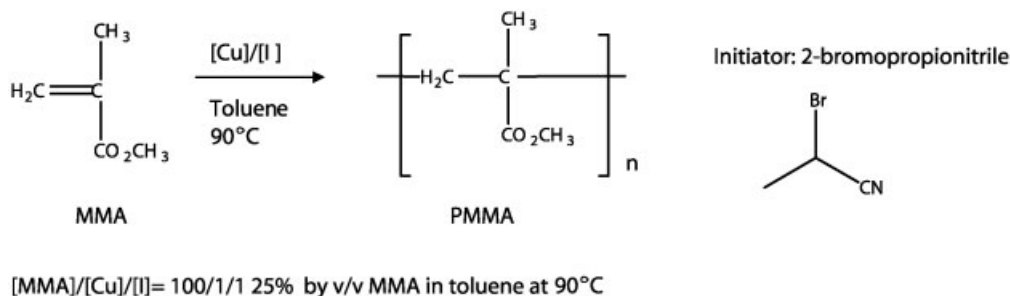
INTRODUCTION

Atom transfer radical polymerization (ATRP) is a subject of intense research because of the possibility of controlling the architecture of the final

polymer product [i.e., the molecular weight, polydispersity index (PDI; or weight-average molecular weight/number-average molecular weight), and end functionality]. Unfortunately, ATRP typically uses one metal/ligand complex to mediate one growing polymer chain to achieve reasonable reaction rates and good polymerization control, and as a result, the final polymer is colored because of the residual metal.^{1,2} Immobilizing the catalyst on a solid support has been an attractive

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Scheme 1

potential solution. However, the immobilized catalysts often do not effectively mediate the polymerization process. This may be attributed to a number of possible reasons, including poor access of the growing radical chain end to deactivating species³ or catalyst heterogeneity.

There are many examples in the literature involving the immobilization of an ATRP metal/ligand complex on various supports,^{3–19} but there are few systematic studies of multiple methods of immobilizing a single type of catalyst. In part 1 of this work, four different synthetic schemes were used to immobilize copper(I) bromide (CuBr)/pyridylmethanimine (PMI) ATRP catalysts on various silica supports, and the resulting solids were characterized in detail.²⁰ Here these new materials are evaluated as catalysts for ATRP of methyl methacrylate (MMA; Scheme 1).

EXPERIMENTAL

Chemicals

MMA (Aldrich; 99%) and styrene (Sty; Aldrich; 99%) were passed three times through an inhibitor removal column (311332, Aldrich), distilled once under reduced pressure, degassed by three freeze–thaw cycles, and stored under nitrogen at –22 °C. Toluene for polymerization (Acros; 99.8%) was distilled under reduced pressure over sodium/benzophenone, degassed by three freeze–thaw cycles, and stored under nitrogen. 2-Bromopropionitrile (BPN; Aldrich; 97%), chloroform-*d* (CDCl₃; Cambridge Isotope Laboratories, Inc.; 99.8%), methylene chloride-*d*₂ (CD₂Cl₂; Cambridge Isotope Laboratories; 99.8%), and propylamine (Acros; >99%) were dried with 4-Å molecular sieves and stored under nitrogen. BPN was stored in a 0.47 M stock solution in dry toluene under nitrogen. CuBr (Acros; 98%) was

stirred in glacial acetic acid for 5 h, washed with absolute ethanol and anhydrous diethyl ether, dried *in vacuo* for 12 h at room temperature, and stored under nitrogen. Anhydrous methanol (MeOH; Alfa Aesar; >99%), copper(II) bromide (CuBr₂; Aldrich; 99%), and 2-pyridinecarboxaldehyde (PCA; Aldrich; 99%) were used as received and stored under nitrogen. Tetrahydrofuran (THF; Aldrich; HPLC-grade and inhibitor-free, >99%) was used as received as the eluent in gel permeation chromatography (GPC) analysis. Tris[2-(dimethylamino)ethyl]amine (Me₆TREN) was synthesized according to literature procedures,²¹ dried with MgSO₄, and stored under nitrogen in a glove box.

Synthesis of *N*-(*n*-Propyl)-2-pyridylmethanimine (PPMI)

To a 100-mL, round-bottom flask were added 2.28 g of propylamine (0.038 mol), 4.54 g of PCA (.042 mol), and 30 mL of anhydrous MeOH. The reaction solution was stirred at 75 °C for 24 h under argon. The product was isolated by vacuum distillation of the light volatiles (MeOH and PCA) and stored under dry nitrogen in a glove box to yield an orange oil: C₉H₁₂N₂ (**2**; >95% yield, 99% purity).

¹H NMR (CDCl₃, δ): 0.92 (t, 3H, —CH₃), 1.70 (m, 2H, —CH₂CH₂CH₃), 3.60 (t, 2H, —CH₂CH₂CH₃), 7.26 (t, 1H, —CCHCHCHCHN—), 7.69 (t, 1H, —CCHCHCHCHN—), 7.94 (d, 1H, —CCHCHCHCHN—), 8.33 (s, 1H, —CH₂NCH—), 8.60 (d, 1H, —CCHCHCHCHN—).

Characterization

The ¹H NMR measurements were performed with a Mercury Vx 300-MHz instrument. Cu elemental analysis by inductive coupled plasma atomic emis-

sion spectroscopy (ICP-AES) was analyzed by Chemisar Laboratories (Guelph, Canada). The conversion of the monomer was determined with a Shimadzu GC 14-A gas chromatograph equipped with a flame-ionization detector with an HP-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program was as follows: heating from 50 to 140 °C at 30 K/min and heating from 140 to 300 °C at 40 K/min under constant pressure with inlet and detector temperatures kept constant at 330 °C. The molecular weights and molecular weight distributions were determined by GPC with American Polymer Standards columns (10^5 , 10^3 , and 10^2 Å) equipped with a Waters 510 pump and a Waters 410 differential refractometer. THF was used as an eluent at a flow rate of 1 mL/min. Nine linear poly(methyl methacrylate) (PMMA) standards (70,000–2,100,000) were used for the calibration of the MMA polymers.

Polymerization

For the polymerization with the homogeneous CuBr/PPMI catalyst, the following recipe was typical: 100/2/1/1 [MMA]/[PPMI]/[Cu]/[BPN] in 25% (v/v) MMA in toluene. For example, to a 50-mL, round-bottom flask with a sidearm valve, 4.00 g of MMA (0.04 mol, 4.24 mL), 0.12 g of PPMI (0.80 mmol), 0.06 g of CuBr (0.40 mmol), and 0.06 g of BPN (0.40 mmol, 855 μL of the initiator stock solution) were added to 11.03 g of toluene (12.73 mL) under argon. The polymerization vessel was immersed in an oil bath preset to 90 °C. At set time intervals, 0.1-mL aliquots of the polymerization solution were removed via syringe and placed in a vial. The vials were immediately quenched in a dry-ice/acetone bath. Subsequently, 25 μL of a sample was added to 1.5 mL of THF for gas chromatography (GC) analysis. The remaining sample was dried, redissolved in HPLC-grade THF to 8.0 mg/mL, and filtered through a Gelman Acrodisc PTFE filter (0.2 μm) for GPC analysis. The conversion of MMA was followed by GC, and the molecular weights and molecular weight distributions were determined by GPC.

For the polymerization with an immobilized CuBr/PMI catalyst, the following recipe was typical: 100/1/1 [MMA]/[Cu]/[BPN] in 25% (v/v) MMA in toluene. For instance, to a 10-mL Schlenk tube with a sidearm valve, 0.20 g of SBA15(48)–CuBr/PMI-M4 (9.60×10^{-2} mmol of Cu, 0.48 mmol of Cu/g of catalyst), 0.96 g of MMA (9.60 mmol), and

205 μL of an initiator stock solution of BPN (9.60×10^{-2} mmol) were added to 2.65 g of toluene under argon. The polymerization vessel was immersed in an oil bath preset to 90 °C. Samples were taken at preset times and quenched with the previously described procedure. The kinetic analysis and polymer characterization were carried out in a manner similar to that described for the homogeneous polymerization. After the polymerization, the catalysts were recovered from the remaining polymerization solution by sedimentation [SBA15(48) and SBA15(100)] or centrifugation (Cab-O-Sil EH5). The polymers were then precipitated in 50 mL of hexane and were recovered and dried as white powders. The dried polymers were analyzed for trace amounts of copper.

Catalyst Recycling

For the polymerization with the immobilized CuBr/PMI catalyst when catalyst recycling was planned, the following recipe was typical: 100/1/1 [MMA]/[Cu]/[BPN] in 25% (v/v) MMA in toluene. For example, to a 15-mL pressure tube reactor, 0.25 g of SBA15(100)–CuBr/PMI-M4 (9.76×10^{-2} mmol of Cu, 0.48 mmol of Cu/g of catalyst), 0.976 g of MMA (9.76 mmol), and 209 μL of an initiator stock solution of BPN (9.76×10^{-2} mmol) were added to 2.70 g of toluene under argon or nitrogen. A 25- μL sample was taken immediately after mixing and before the start of the polymerization to establish the reference conversion point at time zero. The polymerization vessel was immersed in an oil bath preset to 90 °C for a set time. The polymerization vessel was cooled by immersion in a dry-ice/acetone bath and retransferred into a glove box. A 25- μL sample was taken after the polymerization to determine the final conversion by GC. The polymerization solution was transferred into a 20-mL scintillation vial and filled with toluene (under nitrogen) for catalyst recovery. The vial was then centrifuged for 20 min at 3000 rpm. After centrifugation, the vial containing a lower solid catalyst layer and an upper liquid polymerization solution layer was transferred back into the glove box, and the supernatant toluene/polymerization solution was decanted. Fresh toluene was again added to the used catalyst for the first wash. The vial was shaken vigorously to disperse the catalysts from the bottom of the vial. The wash and centrifugation procedure was repeated twice. After the second wash, the toluene was decanted, the catalyst was returned to the 15-mL pressure tube in the

glove box, and the appropriate amounts of fresh MMA, toluene, and BPN were added (in approximately the same concentrations used for the first polymerization run). The polymerization vessel was reimmersed in an oil bath preset at 90 °C for a set time. The final conversion was determined as previously described. The polymers (first use, second use, etc.) were precipitated from the aforementioned supernatant toluene/polymer solution by addition to 50 mL of hexane. The polymer was recovered and dried. The polymer's molecular weight and molecular weight distribution were determined by GPC. The dried polymers were analyzed for trace amounts of copper.

Chain Extension

For polymerization with the immobilized CuBr/PMI catalyst when polymer chain extension was planned, the following procedure was followed. The catalyst used in these experiments was pretreated with an initiator to avoid uncontrolled propagation observed when a fresh catalyst was used. In a 15-mL pressure tube reactor, 0.5 g of Cab-O-Sil-CuBr/PMI-M4 was pretreated with 515 μL of a BPN stock solution in 5 g of toluene at 90 °C for 2 h. Afterward, the sealed pressure tube reactor was transferred back into the glove box, and the catalyst was recovered by filtration, washed with copious amounts of toluene, and dried on the vacuum line overnight. The seed or macroinitiator (PMMA-Br) was synthesized with the following polymerization conditions: 100/1/1 [MMA]/[Cu]/[BPN] in 25% (v/v) MMA in toluene for 3 h at 90 °C. For instance, to a 15-mL pressure tube, 0.30 g of pretreated Cab-O-Sil-CuBr/PMI-M4 (14.46×10^{-2} mmol of Cu, 0.48 mmol of Cu/g of catalyst), 1.45 g of MMA (14.47 mmol), and 309 μL of an initiator stock solution of BPN (14.46×10^{-2} mmol) were added to 4.00 g of toluene under nitrogen in the glove box. The polymerization vessel was sealed and immersed in an oil bath preset to 90 °C. The Cab-O-Sil-CuBr/PMI-M4 catalyst was removed from the polymerization solution by centrifugation. The recovered polymerization solution was passed through a pipette silica gel column for the removal of any leached species. The polymer was then precipitated in 50 mL of dry hexanes, recovered by filtration, washed with copious amounts of hexanes, and dried on the vacuum line overnight. The conversion and other attributes of the macroinitiator polymer were characterized as described previously. Chain extension was performed with the

addition of fresh MMA (homopolymer) or fresh Sty (block copolymer) under the following polymerization conditions with fresh pretreated Cab-O-Sil-CuBr/PMI-M4: 300/1/1 [monomer]/[Cu]/[PMMA-Br] in 25% (v/v) monomer in toluene for 24 h at 90 °C. For instance, for MMA, to a 15-mL pressure tube, 0.06 g of pretreated Cab-O-Sil-CuBr/PMI-M4 (2.95×10^{-2} mmol of Cu, 0.48 mmol of Cu/g of catalyst), 0.88 g of MMA (8.8 mmol), and 0.2 g of the PMMA-Br macroinitiator [number-average molecular weight (M_n) = 6800; 2.95×10^{-2} mmol of Br if all chains were living] were added to 3.25 g of toluene under nitrogen in the glove box. The polymerization vessel was sealed and immersed in an oil bath preset to 90 °C. The catalyst was recovered by centrifugation. The polymers were then precipitated in 50 mL of hexane, and the polymers were recovered and dried as white powders. The conversion and characterization of the chain-extended polymer were characterized as described previously.

RESULTS

Homogeneous PPMI/CuBr Polymerizations

The PPMI ligand was synthesized as a homogeneous analogue for comparison with immobilized CuBr/PMI catalysts on silica.²² Figure 1 shows the kinetic results for the homogeneous polymerization. The polymerization had an initial rate of 0.78 mol L⁻¹ h⁻¹ and reached 73% conversion of the monomer after 12 h. The first-order kinetic plot was linear for low conversions, but the plot deviated at higher conversions, likely because of increased chain termination at higher conversion levels. M_n increased linearly with conversion and was slightly higher than the predicted. PDI decreased with conversion, leveling out at approximately 1.13. The linear kinetics and narrow PDI were evidence that the polymerization was controlled. These results are consistent with those reported by Haddleton and coworkers.^{22,23}

Heterogeneous Silica-Immobilized CuBr/PMI Polymerizations

Table 1 summarizes the polymerization results with all the fresh catalysts. In all the experiments, no observable catalyst settling occurred when the polymerization solution was stirred. For CuBr/PMI catalysts immobilized by methods 1–4 (M1–M4) on SBA15 with 48-Å pores, the initial

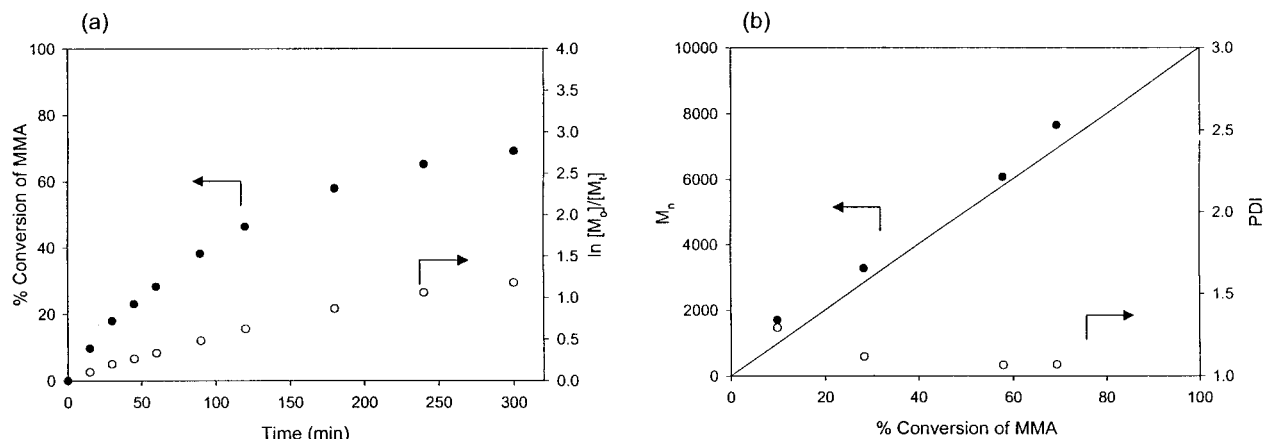


Figure 1. Time evolution of (a) the conversion and (b) the evolution of M_n and PDI with the monomer conversion for homogeneous polymerizations with the CuBr/PPMI catalyst. See the Experimental section for the polymerization conditions.

rate ranged from 0.31 to 0.65 mol L⁻¹ h⁻¹. The final conversions were measured after 24 h. The polymerization proceeded more slowly than the homogeneous polymerization after the first hour (homogeneous, 73% after 12 h; heterogeneous, 67–82% after 24 h). The kinetic plots showed evidence of a large degree of termination based on the nonlinear nature of the first-order kinetic plot and the evolution of M_n with conversion (Fig. 2). Most of the polymerizations were uncontrolled, with PDIs above or approaching 2.0. The polymerization with M3 showed the most control with a PDI of 1.58. Interestingly, M4, an *in situ* metal-

lation method similar to M3, exhibited poor polymerization behavior similar to that of M1 and M2. To verify this observation, we prepared and evaluated new batches of catalyst for SBA15(48)-CuBr/PMI-M3 and SBA15(48)-CuBr/PMI-M4, and we observed consistent polymerization results. In all cases, the polymers had higher molecular weights than predicted and showed only a limited increase in the molecular weight with conversion.

For the catalysts supported on SBA15 with 100-Å pores, the polymerization results for M3 and M4 were comparable to those of CuBr/PMI-immobilized systems reported by Haddleton et

Table 1. MMA Polymerization Results for CuBr/PMI Immobilized on Silica^a

Entry	Materials	Initial Rate (mol/L h)	Time (h)	Conversion (%)	M_n^{Theor}	M_n^{Exp}	PDI	R_{Cu} (ppm)		Leached (%)
								Theoretical ^b	Actual ^c	
1	CuBr/PPMI	0.78	12	73	7,300	7,800	1.13	8,460	—	—
2	SBA(48)-CuBr/PMI-M1	0.31	24	82	8,200	15,400	1.97	7,480	42	0.56
3	SBA(48)-CuBr/PMI-M2	0.54	24	70	7,000	13,600	1.96	8,720	47	0.54
4	SBA(48)-CuBr/PMI-M3	0.62	24	67	6,700	8,700	1.58	9,090	10	0.11
5	SBA(48)-CuBr/PMI-M4	0.65	24	82	8,200	10,300	2.27	7,480	34	0.45
6	SBA(100)-CuBr/PMI-M1	0.04	7	64	6,400	11,000	2.05	9,500	169	1.78
7	SBA(100)-CuBr/PMI-M2	1.05	7	83	8,300	13,900	1.90	7,400	80	1.08
8	SBA(100)-CuBr/PMI-M3	1.17	7	84	8,400	14,200	1.52	7,310	191	2.61
9	SBA(100)-CuBr/PMI-M4	1.26	7	78	7,800	12,100	1.60	7,860	10	0.13
10	Cab-O-Sil-CuBr/PMI-M1	1.39	7	83	8,300	11,200	1.46	7,400	186	2.51
11	Cab-O-Sil-CuBr/PMI-M2	2.05	6	85	8,500	12,200	1.64	7,230	317	4.39
12	Cab-O-Sil-CuBr/PMI-M3	1.87	8	81	8,100	13,600	1.66	7,570	23	0.30
13	Cab-O-Sil-CuBr/PMI-M4	1.68	8	80	8,000	12,500	1.57	7,670	56	0.73

^a Polymerization conditions: 100/1/1 [MMA]/[Cu]/[BPN] in 25% (v/v) MMA in toluene at 90°C.

^b It was assumed that all copper on the catalysts leached into the polymer.

^c Determined by elemental analyses (detection limit = 10 ppm).

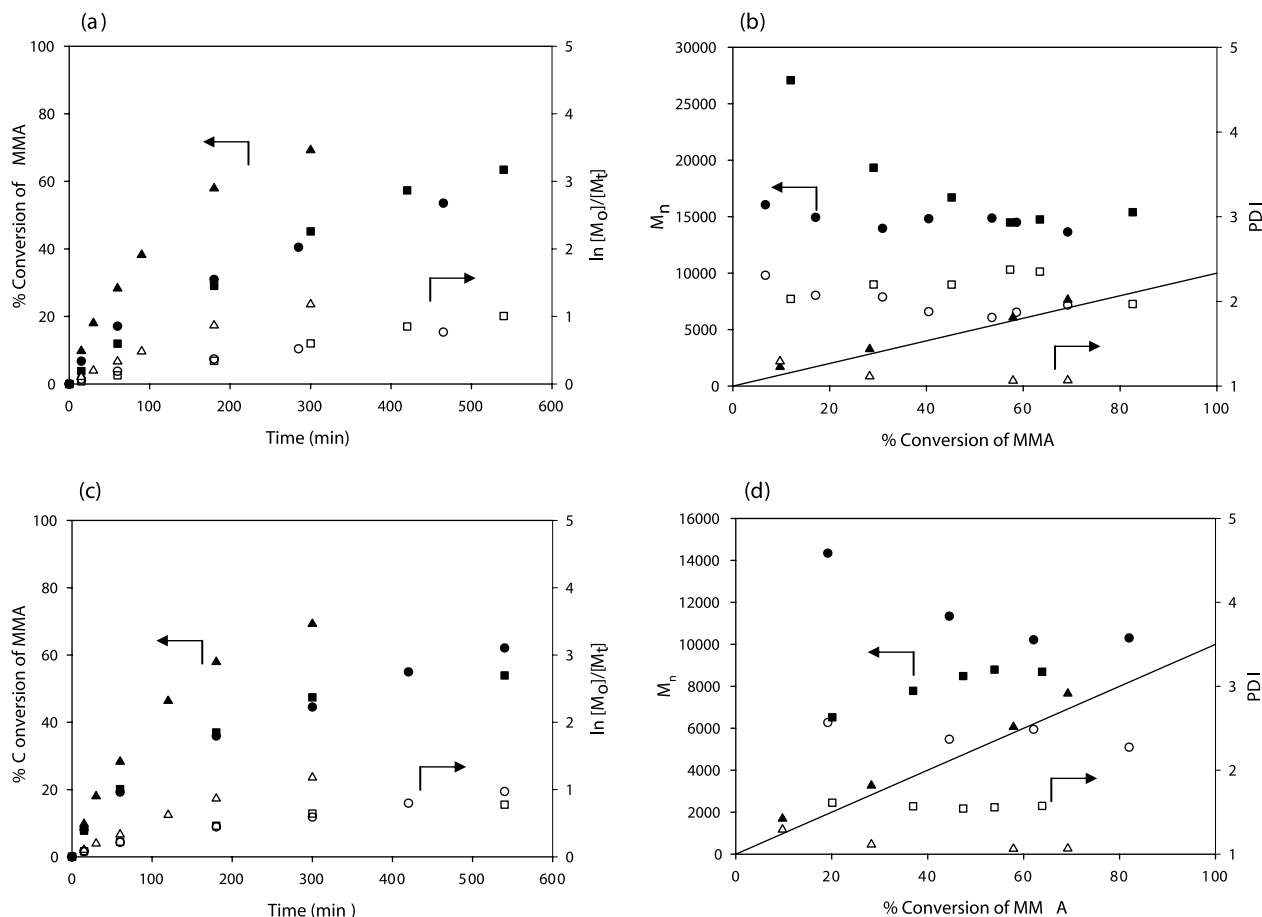


Figure 2. Time evolution of (a,c) the conversion and (b,d) the evolution of M_n and PDI with the monomer conversion for heterogeneous polymerizations with (a,b) (■,□) SBA15(48)-CuBr/PMI-M1 and (●,○) SBA15(48)-CuBr/PMI-M2 and (c,d) (■,□) SBA15(48)-CuBr/PMI-M3 and (●,○) SBA15(48)-CuBr/PMI-M4 catalysts and for homogeneous polymerizations with (a-d) (▲,△) the CuBr/PPMI catalyst. The theoretical M_n values are presented by the diagonal line. See the Experimental section for the polymerization conditions.

al.⁸ and Brittain and coworkers.^{10,11} The initial rate ranged from 0.04 to 1.26 mol L⁻¹ h⁻¹. The final conversions were measured after 7 h. The rate of polymerization was faster than the homogeneous polymerizations for M2, M3, and M4. Figure 3 shows the kinetic plots for the polymerization with CuBr/PMI complexes immobilized on SBA15(100) by M1–M4. The first-order kinetic plots show evidence of chain termination [Fig. 3(a,c)]. The molecular weights were higher than predicted in all cases [Fig. 3(b,d)]. The M1 and M2 catalysts showed poor polymerization control, which was evident from the broad molecular weight distributions. The M4 catalyst followed the theoretical molecular weight line more closely than the M3 catalyst. In Figure 3(d), the evolution

of PDI with the conversion shows that M4 reached its minimum PDI earlier in the polymerization than the other methods. At earlier stages in the polymerization, the PDI was 1.52 for M4 and remained around 1.60, whereas for M3, the PDI was 2.17 and decreased with conversion; this is a more classic profile for a controlled or quasi-controlled system.^{24,25}

For CuBr/PMI catalysts supported on nonporous Cab-O-Sil, the initial rates ranged from 1.39 to 2.05 mol L⁻¹ h⁻¹, they and were generally higher than those of CuBr/PMI catalysts immobilized on SBA15(48 and 100). The final conversions were greater than 80% after 8 h. Figure 4 shows the kinetic plots for polymerizations with CuBr/PMI complexes immobilized on Cab-O-Sil by M1–

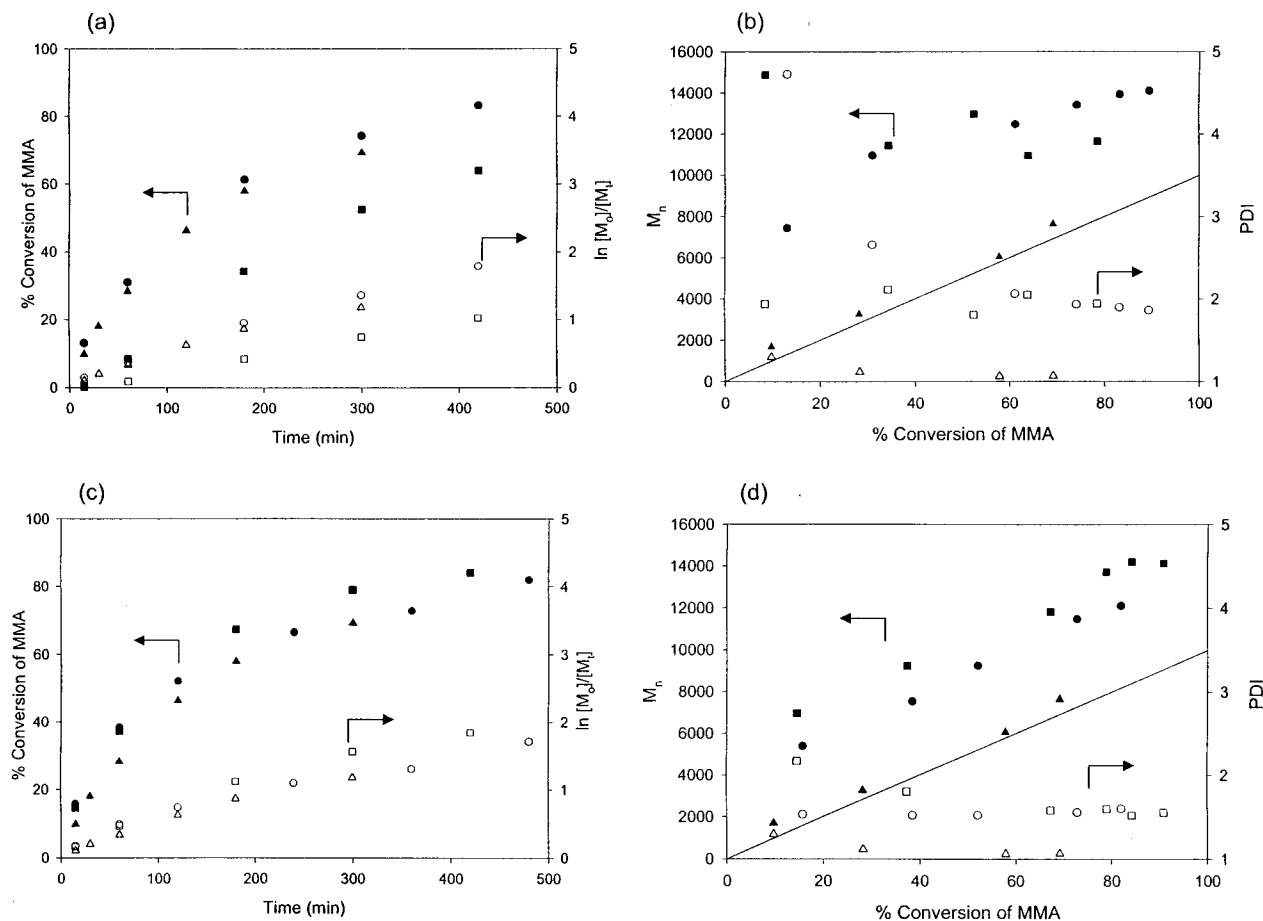


Figure 3. Time evolution of (a,c) the conversion and (b,d) the evolution of M_n and PDI with the monomer conversion for heterogeneous polymerizations with (a,b) SBA15(100)-CuBr/PMI-M1 and (c,d) SBA15(100)-CuBr/PMI-M2 and (c,d) SBA15(100)-CuBr/PMI-M3 and (a-d) the CuBr/PPMI catalyst. The theoretical M_n values are presented by the diagonal line. See the Experimental section for the polymerization conditions.

M4. The first-order kinetic plot shows evidence of some chain termination [Fig. 4(a,c)], especially at higher conversions. The plots of the molecular weight with the conversion were linear [Fig. 4(b,d)] and relatively parallel with the theoretical line, although the molecular weights were always higher than predicted. This observation is common for supported ATRP catalysts and can result from poor deactivation of the growing chain at the outset of the polymerization.^{3-5,8-19} All the catalysts exhibited some degree of control over the polymerizations, with PDIs ranging from 1.46 to 1.66 for the final polymer. The M1 catalyst and M2 catalyst behaved similarly kinetically. Likewise, catalyst M3 and catalyst M4 behaved alike, with both exhibiting fair-to-moderate control throughout the polymerization.

DISCUSSION

Effect of the Immobilization Method

According to the aforementioned polymerization results, the synthetic method used has a pronounced influence on the catalyst structure and performance. For the porous SBA15 supports, catalysts prepared by M1 and M2 were clearly ineffective. The observed kinetics displayed signs of significant chain termination, and the PDIs of the polymers produced by these catalysts were very broad, approaching 2 on both porous supports. In contrast, catalysts prepared with M3 displayed better performance, giving polymers with relatively narrow molecular weight distributions near 1.5. Interestingly, catalysts prepared with M4

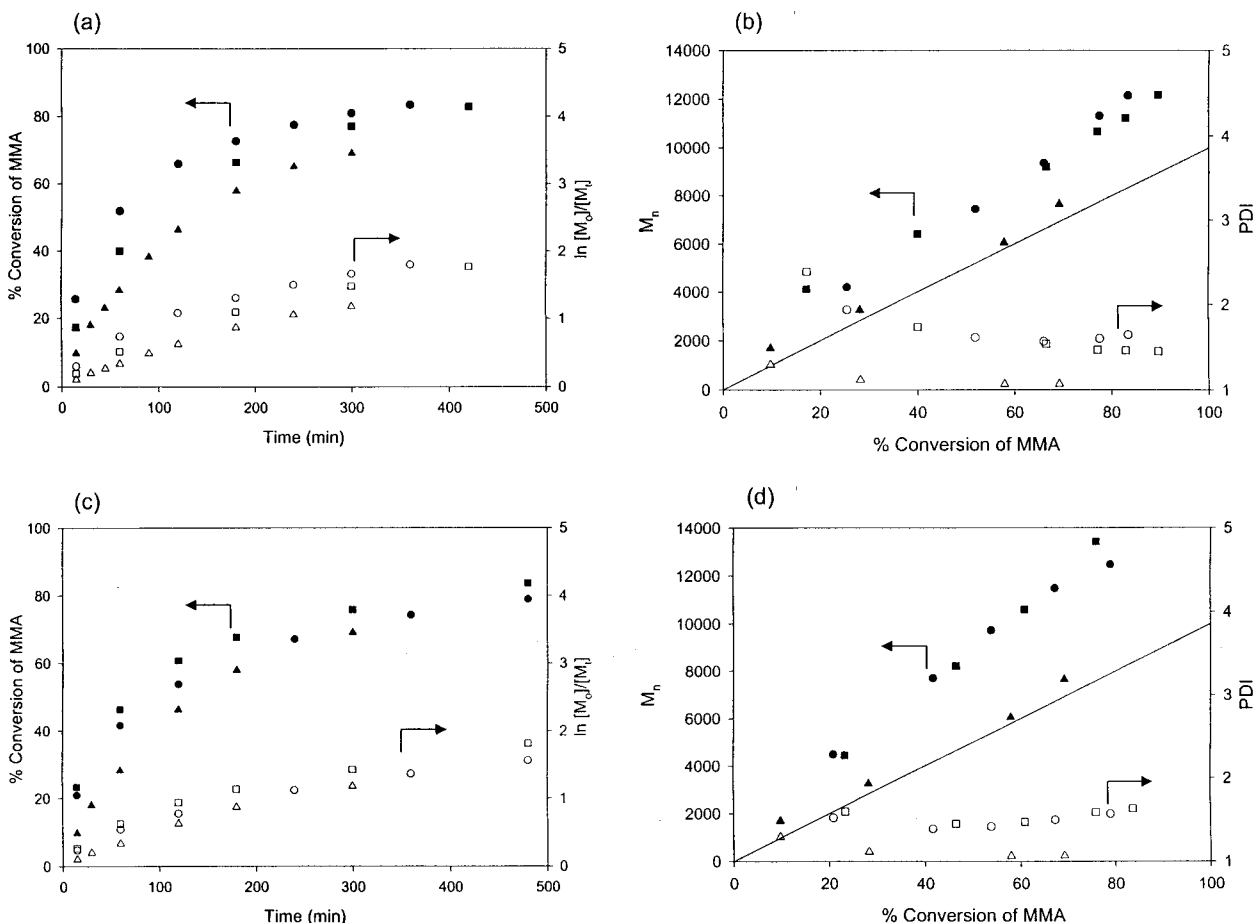


Figure 4. Time evolution of (a,c) the conversion and (b,d) the evolution of M_n and PDI with the monomer conversion for heterogeneous polymerizations with (a,b) (■,□) Cab-O-Sil-CuBr/PMI-M1 and (●,○) Cab-O-Sil-CuBr/PMI-M2 and (c,d) (■,□) Cab-O-Sil-CuBr/PMI-M3 and (●,○) Cab-O-Sil-CuBr/PMI-M4 catalysts and for homogeneous polymerizations with (a-d) (▲,△) the CuBr/PPMI catalyst. The theoretical M_n values are presented by the diagonal line. See the Experimental section for the polymerization conditions.

showed stark differences depending on the pore size of the support. On the narrow-pore, 48-Å SBA15, extremely poor polymerization control was observed, with highly nonlinear kinetics and a very broad PDI of 2.27. In contrast, on more open 100-Å SBA15, M4 yielded a catalyst that produced polymers with moderate control, giving a PDI of 1.6. Potential causes for this difference are discussed later.

A slightly different trend was observed for catalysts supported on the nonporous Cab-O-Sil silica. For this support, all the synthetic methods performed similarly, with the catalyst made via M1 appearing to give slightly more control over the polymerization. It is noteworthy that catalysts prepared with M1 and M2 were ineffective

at controlling the polymerization on SBA15 supports but were reasonably effective at promoting controlled polymerizations on Cab-O-Sil. For both of these methods, the metallations were performed after the ligand immobilization; thus, if there were any bare, unfunctionalized silanols on the silica surface, some of the CuBr could be adsorbed to these PMI-free sites on the silica surface. In a control experiment, CuBr that adsorbed onto silica showed no activity toward the polymerization of MMA. If this adsorption occurred on bare silica, not all the Cu sites would be active for controlling ATRP, and there would be an imbalance in the metal-to-initiator ratio; not all the initiators could be activated at the same time. This could lead to uncontrolled polymerization

and broad molecular weight distributions, as observed in catalysts prepared by M1 and M2 on SBA15. Fourier transform/Raman (FT-Raman) spectra indicate that there likely exists some uncoordinated PMI ligand on the surface in SBA15 catalysts prepared by M1 and M2, and this supports the aforementioned hypothesis.²⁰

In contrast, as mentioned previously, the M1- and M2-derived Cab-O-Sil catalysts give good control over the polymerization. This may be due to a lower percentage of unligated copper species on these materials. The support surface area for Cab-O-Sil is approximately two or three times less than that of the SBA15 supports. Because the ligand loadings were comparable for all the catalysts synthesized (~ 1.0 mmol of PMI/g of catalysts), the available surface area for CuBr to adsorb on the bare silica surface was substantially less than that for Cab-O-Sil. CuBr may have coordinated with the immobilized ligand to a greater extent on the functionalized Cab-O-Sil supports than on the SBA15 supports. The higher ligand density on Cab-O-Sil (2.60 PMI ligands/nm²)²⁰ should improve the coordination in general and make bicoordination more likely than when these methods are used on SBA15 (1.20 and 1.15 PMI ligands/nm² for 48 and 100 Å, respectively²⁰). Thus, with Cab-O-Sil supports with a dense loading of ligands, there may be a greater propensity to form PMI-ligated species, leading to effective catalysts.

As noted before, all the heterogeneous polymerizations behaved kinetically similarly to several previously reported immobilized copper ATRP systems,^{3,13,15,16} with the best control reported here akin to moderate levels of control achievable with other copper complex/support combinations. There was initially a period of uncontrolled polymerization that occurred before the equilibrium between Cu(I) and Cu(II) was established. According to Figure 2(b,d), the observed molecular weights were several times higher than the predicted molecular weights initially for catalysts immobilized on SBA15(48). The same observation can be made for M1, M2, and M3 catalysts immobilized on SBA15(100) [Fig. 3(b,d)]. These observations may be attributable to inefficient initiation. Only the SBA15(100)-M4 and Cab-O-Sil catalysts gave reasonably controlled polymerizations.

Haddleton et al.⁸ and Brittain and coworkers^{10,11} immobilized their PMI ligands via a method most akin to M1. A stepwise procedure was used to graft the PMI ligand onto the various

supports (as in M1 here), but the metallation of the solids was not analogous to this study. Although the catalysts prepared here were recovered and purified after metallation, in the previous studies, the metallation was carried out *in situ* in the presence of the monomer and initiator. Despite this difference, there does not seem to be a significant effect on the polymerization performance between the two different metallation and polymerization procedures, as the Cab-O-Sil-CuBr/PMI-M1 catalyst reported here performs similarly to immobilized PMI (M1) ligand on nonporous silica and crosslinked polystyrene resin supports.⁸ However, there does seem to be a difference in the polymerization behavior when we compare the support's structure and properties. Haddleton et al.⁸ and Brittain and coworkers^{10,11} investigated PMI ligands supported on organic polymers that were more solvent-swallowable and solvent-compatible at reaction temperatures than silica. The compatibility of the support with the solvent appears to have a positive impact on the control of the polymerization. Haddleton et al. obtained a molecular weight distribution of 1.56 for polystyrene-PMI-M1, and Brittain and coworkers obtained 1.45 for polyethylene-PMI-M1 and 1.29 for JandaJel-PMI-M1-supported systems. As mentioned previously, it was postulated that better control was exhibited when JandaJel was used as a support because it had a more flexible crosslinker than the polystyrene resin.¹¹ The increased swellability of these supports and the lack of adsorption sites for ligand precursors (Si-OH groups) overcome the inherent limitations of the ligand immobilization method (M1) that are apparent on the porous silica supports described here. The importance of catalyst accessibility is discussed further later.

Effect of the Silica Support Structure

Of the three silica supports evaluated, Cab-O-Sil EH5 was by far the most effective. This material is a commercially available fumed silica with a very small primary particle size, which makes it moderately miscible in hot toluene. Furthermore, it has no measurable porosity, and this means that all of its surface area is external. In contrast, SBA15 is a mesoporous silica material with straight mesopores in a hexagonal array. Although the mesopores are connected by small micropores,²⁶ these micropores can be considered unimportant for the diffusion of relatively large species such as polymer chains. Hence, in these

polymerizations, each pore in SBA15 is essentially an isolated reaction environment with only a single entrance point and exit point at each end. These very different porosities of the supports can be expected to play a role in the effectiveness of the polymerizations. Indeed, porosity does play a key role because the accessibility of the catalyst complex can be limited by the size of the pore and growing polymer.

Transport limitations within porous solid catalysts when small-molecule reactions are being promoted are usually thought to reduce reaction rates and lead to slower overall kinetics. For ATRP, internal transport limitations can have a number of potential effects. The fact that Cab-O-Sil-supported catalysts give the best control over the polymerization, regardless of the synthetic method (M1–M4), points to the paramount importance of access of the growing polymer chain to the metal complexes. In this case, when there is no porosity and the catalyst particle size allows partial miscibility in the reaction media, the growing polymer chains can access the CuBr_2 complexes relatively easily and return to their dormant state. The ease of this deactivation process is critical for a controlled polymerization. When considering the porous SBA15 catalysts, we observe that the polymerizations are generally less controlled, with the restricted mobility of the growing chains within the pores affecting the polymerization process. In addition, the presence of porosity directly affects the rates of polymerization. The average initial rates for each support were 0.53, 0.88, and $1.74 \text{ mol L}^{-1} \text{ h}^{-1}$ for SBA15(48), SBA15(100), and Cab-O-Sil, respectively. The initial rate of polymerization with the homogeneous CuBr/PPMI complex was $0.78 \text{ mol L}^{-1} \text{ h}^{-1}$. The conversion after 1 h increased as follows: SBA15(48) < SBA15(100) < Cab-O-Sil. Interestingly, the support that gave the slowest rate resulted in the worst control over the polymerization. This is the opposite of the trend that might be expected with homogeneous catalysts. For homogeneous systems, the greater the equilibrium is shifted toward the deactivated complex, the slower the propagation rate is and the better the expected degree of control is in the process. The combination of slow polymerization rates and concomitant poor control in SBA15(48)-supported materials may be attributed to inefficient deactivation caused by the narrow, noninterconnected pores, which create isolated reaction environments. Increasing the pore size with SBA15(100) increases the overall rate and results

in slightly better control of the polymerization. These observations are consistent with the entrapment of some growing polymer chains within the mesopores of the support. When the nonporous Cab-O-Sil support is used, the overall polymerization rate is higher than in the homogeneous system but the polymerization is less controlled than in the solid-free system. This is consistent with inefficient deactivation causing both increased reaction rates and increased polydispersity among the polymer chains.

As noted previously, the catalyst SBA15(48)– $\text{CuBr}/\text{PMI-M4}$ displayed unique behavior in the polymerization of MMA. Although FT-Raman spectra indicated that nearly all the PMI ligands were coordinated to copper and elemental analysis data implied copper loadings comparable to those of other catalysts, this catalyst was observed to give the poorest control over the polymerization. In addition, the catalyst prepared with M3 on the same support gave relatively good control over the polymerization, as did catalysts derived from M3 and M4 over SBA15(100).

These observations might be rationalized if we consider the sizes of the pores with respect to the biscoordinated CuBr/PMI complex. In M4, a preformed, biscoordinated complex is added to the support material. If the immobilizable PMI ligand is fully extended, the ligand extends roughly 12 Å from the silica surface. With a 48-Å pore diameter, it is easy to visualize how one or more biscoordinated CuBr/PMI complexes could effectively block all access to the channels, preventing access to any complexes that are immobilized inside the pores. This could lead to the inefficient transport of species from inside the pores to the bulk solution and ineffective initiation and utilization of the sites within the mesopores. In contrast, with M3 for catalyst immobilization, a preformed complex is not used, and a substantially higher concentration of smaller, monocoordinated PMI ligands is expected to occur on the surface. This could lead to less pore blockage and could facilitate transport between the pore space and the bulk solution, producing a more effective catalyst. In addition, on a support with 100-Å pores, pore blockage is expected to be less problematic, and so catalysts prepared via M3 and M4 are expected to have similar internal transport rates. Indeed, these catalysts behave similarly.

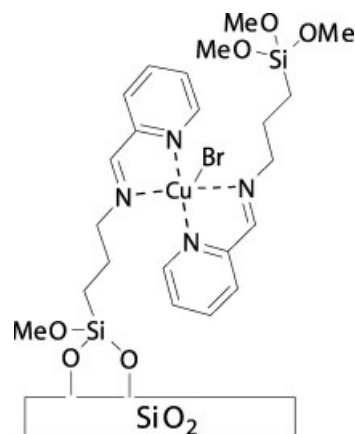
The results in part 1 of this work indicate that relatively well-defined copper complexes akin to those used in homogeneous experiments are most likely to occur when specific immobilization meth-

ods are used. In particular, it was determined that the metallation efficiency was $M4 > M2 \geq M3 > M1$. Here we observe that the various synthetic protocols had the largest impact when mesoporous silica supports were used, with the ability of each catalyst to mediate a controlled polymerization roughly following the aforementioned trend. In all cases on SBA15 supports, polymerizations were only moderately controlled at best. In contrast, on nonporous semisoluble supports, the synthetic method was found to have little impact on performance, and all catalysts gave a moderate degree of control over the polymerization. These results imply that complex accessibility and support–solvent compatibility are paramount, and the exact structure of the copper sites (monocoordinated, biscoordinated, etc.) is of substantially less importance on supported catalysts. These observations agree with results of other investigations that show that soluble or flexible supports and long support–surface linkages lead to systems with better control.^{11,14,16,17}

Catalyst Leaching

All the catalysts exhibited a loss of copper during the polymerization. The polymerization solutions were a light yellowish color after the reaction was complete. The color could be a result of a free ligand or complex because [3-(trimethoxysilanyl)propyl]-2-pyridylmethanimine (PMITMS) and PPMI ligands in toluene produce a yellow solution. The copper-coordinated ligand is reddish brown for Cu(I) and dark green for Cu(II). This observation suggests the yellow color was mainly due to free PMITMS ligand. There were possibly some free ligands or complex physisorbed to the silica surface despite the use of the dichloromethane wash, which was shown to remove a large fraction of the adsorbed species, as Zhu and coworkers^{12,13,18} showed that nitrogen-containing ATRP ligand/CuBr complexes adsorb strongly to silica. This free ligand could effectively stabilize homogeneous species, removing copper from surface sites. There could also be coordinated PMITMS ligand not covalently immobilized to the surface, as shown in Scheme 2. A further possible cause of leaching could be structural rearrangements of the surface copper species during the reaction, with the structural changes required upon copper oxidation leading to the creation of unstable species that led to leaching.

Elemental analyses on the recovered polymers for ppm levels of copper were performed, and the



Scheme 2

results are summarized in Table 1. The theoretical residual copper content (R_{Cu}) was calculated under the assumption all the immobilized copper leached into the polymerization solution (the monomer conversion and mass of the initiator were accounted for in the calculation). If a 100% conversion of the monomer was achieved and all the copper remained in the polymer, R_{Cu} would be 6173 ppm. The maximum copper concentration increases when the degree of polymerization is lower. In all the polymerizations performed, copper leached into the polymerization solution, but the level was no higher than 317 ppm or no more than 0.0317% (w/w) Cu in the polymer. The percentage leached shows that in most cases the percentage of leached copper was less than 1% of the theoretical R_{Cu} value, but in some cases it was 2% or higher. Catalysts immobilized by M4 (pre-assembled complexes) consistently leached less copper than the other methods. The amount of leaching that is observed is similar to that of other systems reported in the literature (not all the publications quantify leaching). Hognifort and Brittain¹¹ reported that 5–7% of the original copper used in the ATRP reaction remained in the unpurified polymer in their supported CuBr/PMI systems. Zhu and coworkers^{14,15,17} reported no more than 33.4 ppm residual copper in the polymers and no more than a 2–3% loss of the initial catalysts used when grafted CuBr/tetraethyldiethylenetriamine systems were used. Matyjaszewski and coworkers^{4,5} reported no more than 107 ppm residual copper in the polymers with mixed soluble/heterogeneous systems based on CuBr/bipyridine (bpy). In our work with immobilized CuBr/bpy complexes, the bpy ligand appeared to

Table 2. Catalyst Recycling Results for CuBr/PMI-Immobilized Catalysts^a

Entry	Materials	Time (h)	Conversion (%)	M_n^{Theor}	M_n^{Exp}	PDI	R_{Cu}^b
1	SBA(100)-CuBr/PMI-M4-1	5	82	8,200	15,800	1.73	70
2	SBA(100)-CuBr/PMI-M4-2	7	75	7,500	12,600	1.52	32
3	SBA(100)-CuBr/PMI-M4-3	9	69	6,900	12,100	1.53	64
4	SBA(100)-CuBr/PMI-M4-4	12	28	2,800	9,900	1.59	104
5	Cab-O-Sil-CuBr/PMI-M4-1	7	83	8,300	17,000	1.57	49
6	Cab-O-Sil-CuBr/PMI-M4-2	7	70	7,000	10,800	1.24	10
7	Cab-O-Sil-CuBr/PMI-M4-3	12	84	8,400	12,100	1.24	99
8	Cab-O-Sil-CuBr/PMI-M4-4	12	76	7,600	10,900	1.21	187
9	Cab-O-Sil-CuBr/PMI-M4-5	19	70	7,000	9,800	1.24	85
10	Cab-O-Sil-CuBr/PMI-M4-6	48	83	8,300	11,800	1.35	151
11	Cab-O-Sil-CuBr/PMI-M3-1	17	89	8,900	17,300	1.74	94
12	Cab-O-Sil-CuBr/PMI-M3-2	14	85	8,500	12,100	1.28	134

^a Polymerization conditions: 100/1/1 [MMA]/[Cu]/[BPN] in 25% (v/v) MMA in toluene at 90°C.

^b Determined by elemental analyses (detection limit = 10 ppm).

coordinate more strongly to Cu than to PMI, and observed Cu leaching was lower.²⁷

Catalyst Recycling

Several of the catalysts were tested for recyclability, and the results are summarized in Table 2. Whereas Hong and Matyjaszewski⁵ and Zhu et al.¹⁵ sometimes regenerated the catalyst by reducing the majority of the Cu(II) back to the Cu(I) state, in this work, the catalysts were recycled without any regeneration.^{12-14,16,17} The first use of each catalyst behaved similarly to the results described previously. Interestingly, the second use resulted in polymers with narrower molecular weight distributions, but the observed polymerization rates were lower. After the fourth reuse of SBA15(100) catalysts, the activity was greatly reduced (28% conversion in 12 h). This could be due to catalyst structural changes or to a buildup of polymer that could not be washed away, remaining entangled in the pores and blocking accessible immobilized CuBr/PMI complexes. As for the recycling of the Cab-O-Sil-supported catalysts, the polymerization rates were not significantly reduced until after the fourth reuse. In addition, the polymerizations were still well controlled after the sixth catalyst reuse (high conversion and relatively low PDI). With the procedure described here, these catalysts can be recycled without catalyst regeneration. Potential reasons that catalyst reuse results in improved control are discussed later.

The residual copper content in the polymer was determined by elemental analysis. According to

Table 2, no more than 187 ppm copper was in the final polymer. After each subsequent reuse of the catalysts, more copper leached into solution, and this loss of copper may have affected the control of the polymerization. Several control experiments were performed to shed some light on the observations from catalyst reuse. The various experiments and results are described and summarized in Table 3. There are two key attributes that the used catalysts have that the fresh catalysts do not: (1) Cu(II) and (2) leached copper species. One potential reason that lower PDIs and better control are observed after the first use is that the catalyst complex leaches off the support and cannot be washed away during centrifugation. After the catalyst was recovered from the first polymerization, the recovered polymerization solution was notably a light yellowish color, and this was attributed to the leached ligand and/or complex, as noted previously. To test whether the leached ligand and complex could effectively control the polymerization, we undertook an experiment with the addition of 5 mol % of a soluble CuBr/PPMI catalyst to a polymerization reaction with fresh immobilized CuBr (Cab-O-Sil-CuBr/PMI-M4; Table 3, entry 3). The polymer that was produced had a slightly broader molecular weight distribution, but the experimental number-average molecular weight (M_n^{Exp}) was closer to the theoretical number-average molecular weight (M_n^{Theor}). This experiment shows that the addition of a small amount of a soluble CuBr catalyst cannot produce polymers with good control and low PDI. In contrast, the addition of the same amount of a soluble CuBr₂/PPMI complex results

Table 3. Control Experiments^a

Entry	Experiment	Time (h)	Conversion (%)	M_n^{Theor}	M_n^{Exp}	PDI
1	Cab-O-Sil-CuBr/PMI-1	7	83	8,300	17,000	1.57
2	Cab-O-Sil-CuBr/PMI-2	7	70	7,000	10,800	1.24
3	Control 2: 5 mol % CuBr/PPMI ^b	24	83	8,300	13,900	1.71
4	Control 3: 5 mol% CuBr ₂ /PPMI ^c	24	21	2,100	3,800	1.25
5	Control 4: 0.3 mol % CuBr ₂ /Me ₆ TREN ^d	24	89	8,900	16,000	1.77
6	Control 5: Sequence ^e	24	91	9,100	20,700	1.62
7	Control 6: Initiator pretreatment ^f	24	92	9,200	11,800	1.38
8	Control 7: Hot toluene wash ^g	24	93	9,300	14,300	1.85
9	Control 8: Cab-O-Sil-CuBr/CuBr ₂ /PMI-M4 50/50 ^h	24	93	9,300	18,500	1.63

^a Polymerization conditions: 100/1/1 [MMA]/[Cu]/[BPN] in 25% (v/v) MMA in toluene at 90°C.

^b 5 mol % CuBr/PPMI added to immobilized CuBr for polymerization with Cab-O-Sil-CuBr/PMI-M4.

^c 5 mol % CuBr₂/PPMI added to immobilized CuBr for polymerization with Cab-O-Sil-CuBr/PMI-M4.

^d 0.3 mol % CuBr₂/Me₆TREN added to immobilized CuBr for polymerization with Cab-O-Sil-CuBr/PMI-M4.

^e MMA added after Cab-O-Sil-CuBr/PMI/initiator/toluene had been brought to the temperature (2 h).

^f Cab-O-Sil-CuBr/PMI-M4 pretreated with the initiator at 90°C for 2 h and recovered, and catalysts washed with toluene.

^g Cab-O-Sil-CuBr/PMI-M4 stirred in toluene at 90°C for 2 h and recovered, and catalysts washed with toluene.

^h 50/50 Cu(I)/Cu(II) metal ratio incorporated into the synthesis of the Cab-O-Sil-CuBr/CuBr₂/PMI-M4 catalyst.

in a well-controlled polymerization (Table 3, entry 4). This observation is consistent with previous studies of homogeneous ATRP systems in which the addition of a CuBr₂ complex at the beginning of the polymerization helps to control the polymerization initially.^{24,25,28} A CuBr₂ complex reduces the rate of polymerization, reduces the amount of uncontrolled propagation, and, therefore, yields a narrower PDI.

Matyjaszewski and coworkers^{4,5} used this approach to produce a mixed soluble/heterogeneous catalyst system that exhibited good polymerization control. A soluble deactivator complex, CuBr₂/Me₆TREN, was used in tandem with polymer-immobilized CuBr/dMBpy complexes to control the polymerization, that particular homogeneous complex being chosen because of its strong reducing power and preference for the Cu(II) state. When the deactivator is in the Cu(I) state, it readily reduces the immobilized CuBr₂/ligand complex and is itself oxidized into Cu(II). It has been shown that a soluble complex with a stronger reducing power than the tethered complex is desirable in a mixed soluble/heterogeneous catalyst system.⁵ A soluble CuBr₂/dMBpy deactivator complex cannot control polymerizations like CuBr₂/Me₆TREN when it is used with its immobilized CuBr/dMBpy counterpart. Therefore, a free CuBr₂/PMITMS complex should be a poor reducing complex because it would be similar electronically to the immobilized catalyst. Interestingly, we observed that the addition of 5 mol % of a homogeneous analogue with a structure sim-

ilar to that of the tethered species (CuBr₂/PPMI) appeared to control the polymerization well, although the conversions were lower.

The preferred deactivator complex developed by Matyjaszewski was evaluated with our catalyst system.^{4,5} The experiment was carried out under conditions similar to those that yielded the best published results (0.3 mol % CuBr₂/Me₆TREN with respect to immobilized CuBr/dMBpy), except that the immobilized catalyst was Cab-O-Sil-CuBr/PMI-M4. The results indicate that this amount of added deactivator cannot control the polymerization with the CuBr/PMI/SiO₂ system. Although the soluble deactivator effectively functions with Matyjaszewski's polymer-supported CuBr/dMBpy systems, the deactivator fails to polymerize controllably with these silica-immobilized catalysts of ours. It is possible that this small amount of the deactivator complex is strongly adsorbed to the silica surface, and this potentially prevents the complex from freely moving in solution and deactivating the growing polymer chain. Zhu and coworkers^{12,13,18} showed that the aliphatic amine complex, CuBr/hexamethyltriethylenetetramine (HMTETA), strongly adsorbed to silica, and we verified this with CuBr₂/Me₆TREN in our laboratories.²⁷ Experiments with a larger amount of CuBr₂/Me₆TREN (5 mol %) resulted in less than satisfactory results (conversion = 94%, M_n^{Exp} = 14,800, and PDI = 1.81) as well. In contrast, the addition of the soluble CuBr₂/PPMI complex (entry 4) performed quite

well. This may be due to weaker adsorption on bare silica for this bulkier complex.

After the first use of the catalysts, an established concentration of CuBr_2 exists as a result of bimolecular terminations in the first polymerization. Upon catalyst reuse, this Cu(II) is believed to contribute to the improved control in comparison with the first use of the catalyst. This Cu(II) would efficiently deactivate the polymer chains at early stages of the polymerization, allowing for increased control of the reaction process. This would be analogous to previous homogeneous studies in which a percentage of Cu(II) was added to the polymerization so that the need for self regulation and radical termination processes became unimportant.²⁸ To develop a system that exhibited controlled polymerization, we undertook several additional experiments. In control 5, we attempted to generate CuBr_2 *in situ* by adding the monomer after the Cab-O-Sil-CuBr/PMI-M4, initiator, and toluene mixture were heated for 2 h at 90 °C. The premise of this experiment was that the initiator could function with the immobilized complex to pre-establish a finite Cu(II) concentration before the polymerization began. The experiment proved to be unsuccessful because an improved PDI was not achieved and M_n^{Exp} was considerably higher than the values of previous experiments ($M_n^{\text{Exp}} = 20,700$; Table 3, entry 6). The high molecular weight may be attributed to bimolecular coupling of the initiator radicals, which effectively terminated two radicals before the monomer was added. To circumvent this problem, we undertook another experiment (Table 3, entry 7), in which the Cab-O-Sil-CuBr/PMI-M4 catalyst was pretreated with 1 equiv of the initiator CuBr in toluene at 90 °C for 2 h in a pressure tube reactor. Afterward, the mixture was returned to the glove box, in which the catalyst was recovered and washed with copious amounts of fresh toluene; this removed any initiator or initiator-derived organic species. The recovered catalyst was returned to the pressure tube reactor, and appropriate amounts of fresh MMA, toluene, and an additional 1 equiv of the initiator were added. This time the polymerization proceeded at a level of control closer to the second reuse of the Cab-O-Sil-CuBr/PMI-M4 catalyst (Table 3, entries 2 and 7). To eliminate the unlikely possibility that the increased control was due to the additional washing of the free ligand with hot toluene, we performed control 7 similarly to control 6, except without the initiator pretreatment. The catalyst was stirred in toluene at 90

°C for 2 h, recovered, and washed with copious amounts of fresh toluene. The polymerization with this recovered catalyst was ineffective in comparison with the previous control experiment (Table 3, entry 8). This was strong evidence that the low PDI for control 6 was directly caused by the pretreatment with the initiator and not by the additional solvent wash. Surprisingly, upon the immobilization of a 50/50 mixture of Cu(I) and Cu(II) , improved control over the polymerization was not observed (Table 3, entry 9; $M_n^{\text{Exp}} = 18,500$ and PDI = 1.63). This result implies that the presence of Cu(II) in solution may be what causes good polymerization control and that Cu(II) on the solid support at the outset of the polymerization is not in itself enough to give good control. Furthermore, it indicates that substantial leaching may primarily occur after exposure to the initiator, possibly because of a structural change that occurs after the complex is oxidized into the Cu(II) state.^{29,30} These results are consistent with studies on a related bpy system in our laboratory. For silica-immobilized bpy complexes, little or no leaching is observed, and the catalyst cannot be effectively recycled²⁷ in the absence of added homogeneous species. This result is also consistent with the good behavior of Matyjaszewski's combination polymer-immobilized CuBr/dM with soluble $\text{Me}_6\text{TREN/CuBr}_2$ polymerization system, which is made effective by the addition of small amounts of Cu(II) . Interestingly, there are no reports in the open literature of supported ATRP catalysts that give good control over the polymerization yet have been conclusively shown to result in no leaching of copper species. A small amount of leaching may be a prerequisite for achieving good control.

Chain Extension of the PMMA-Br Macroinitiator

Chain-extension experiments were performed to determine whether the polymerizations proceeded in a pseudoliving manner. In addition, these preliminary experiments could show if the block copolymers could be synthesized. A seed or macroinitiator polymer was synthesized with a pretreated Cab-O-Sil-CuBr/PMI-M4 catalyst to ensure that the polymer's molecular weight distribution was narrow initially. The polymerization conditions were 100/1/1 [MMA]/[Cu]/[BPN] in 25% (v/v) MMA in toluene at 90 °C, and the reaction was stopped after 3 h to reduce the

amount of chain termination that occurred at a higher conversion. The polymerization reached 63% conversion, and the macroinitiator polymer that was recovered had $M_n^{\text{Exp}} = 6800$ and PDI = 1.30; it was designated PMMA-Br. The subsequent polymerization for the chain extension used a higher [monomer]/[initiator] ratio, so that a significant separation should be observed between the macroinitiator polymer and extended polymer in the GPC traces {300/1/1 [monomer]/[Cu]/[PMMA-Br] in 25% (v/v) monomer in toluene for 24 h at 90 °C with fresh pretreated Cab-O-Sil-CuBr/PMI-M4}. The extension of the macroinitiator polymer chain was performed with MMA to create an extended homopolymer because the required polymerization conditions were well established. The polymerization for the PMMA-PMMA homopolymer proceeded to 78% conversion ($M_n^{\text{Theor}} = 30,200$, $M_n^{\text{Exp}} = 26,900$, and PDI = 1.63). M_n^{Exp} was lower than M_n^{Theor} because some dead chains likely existed at the beginning of the polymerization. These dead chains would lower M_n and broaden the molecular weight distribution of the polymer. A clear shift of the GPC traces between the macroinitiator and extended homopolymer was observed. In addition to the synthesis of a chain-extended homopolymer, Sty was also used for the extension of the macroinitiator polymer for the preparation of the block PMMA-*block*-polystyrene copolymer. The polymerization for the block copolymer proceeded to 46% conversion ($M_n^{\text{Theor}} = 21,300$, $M_n^{\text{Exp}} = 28,700$, and PDI = 1.89). Although the molecular weight distribution was broader in this chain-extension case, the incorporation of a polystyrene block was accomplished. An ultraviolet-visible/GPC trace and ^1H NMR confirmed the incorporation of a polystyrene block that was not previously present in the macroinitiator (PMMA-Br). Further experimentation is needed to optimize the copolymer polymerization conditions required to obtain narrower molecular weight distributions. Nevertheless, polymers synthesized with a silica-immobilized CuBr/PMI catalyst could be extended to make homopolymers and block copolymers, and this demonstrates that at least some of the polymer chains have reactive halocarbon end groups.

CONCLUSIONS

Four different synthesis methodologies for the immobilization of CuBr/PMI ATRP complexes on three different silica supports were evaluated in

the polymerization of MMA. CuBr/PMI complexes immobilized on porous SBA15 supports were ineffective catalysts when prepared via M1 and M2. M3 was a relatively effective immobilization method for all supports. M4 was only effective for the larger pore support SBA15(100) and nonporous Cab-O-Sil EH5. Cab-O-Sil EH5 was an effective support for all the immobilization methodologies because of its small particle size, nonporous nature, and relative miscibility in the polymerization solution. Overall, the polymerization results indicated that the fresh silica-supported catalysts described here were less efficient at controlling the polymerization than Haddleton et al's⁸ and Brittain and coworkers'^{10,11} immobilized PMI catalysts, which were immobilized on polymers.

All the catalysts leached ligand and/or complex into the solutions according to the yellowish color of the solutions after the polymerizations and the elemental analysis results. The catalyst particles were effectively recovered by filtration and centrifugation techniques. A trace analysis of copper in the polymer revealed a small amount of copper remaining in the polymer [no more than 0.032% (w/w) Cu in the polymer in all samples tested or no more than 5 mol % Cu leached off the catalyst]. Although the use of a dichloromethane wash during synthesis was able to remove a majority of the physisorbed species, some leachable species clearly remained, or leaching was induced by structural changes in the surface copper species during polymerization.

Several catalysts were tested for recyclability. It was demonstrated that these catalysts could be recycled without regeneration back to the Cu(I) oxidation state. Catalysts immobilized by M4 on SBA15(100) and Cab-O-Sil were used up to four and six times, respectively. The polymerization rate was significantly reduced after each reuse for SBA15(100), possibly because of polymer entanglement in the pores. Polymerizations with Cab-O-Sil immobilized catalysts did not exhibit these features, and the activity did not significantly decrease until the fourth reuse (still with good control up to the sixth reuse). Control experiments showed that the recyclability of the catalysts was most likely due to the presence of small amounts of homogeneous Cu(II) species present in this catalyst system.

Overall, of the four catalyst design methods, M4, the preassembled-complex approach, appears to be the most effective method for immobilizing structurally homogeneous complexes on silica supports that effectively polymerize MMA. How-

ever, CuBr/PMI complexes can be immobilized by other methods and still exhibit good polymerization behavior if a nonporous support with a small particle size such as Cab-O-Sil EH5 is used. It has been shown that the slight leaching that occurs with these catalysts can actually lead to enhanced polymerization behavior and improved control.

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