Ionic Liquid Catalyst for Biphasic Atom Transfer Radical Polymerization of Methyl Methacrylate

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ABSTRACT: Ionic liquids have recently been used as solvents for biphasic atom transfer radical polymerization (ATRP) to facilitate the separation of the products from the catalysts. Here we report an ionic liquid catalyst for biphasic ATRP of MMA to greatly reduce the amount of ionic liquid needed and to reuse the catalyst: CuBr/*N*,*N*,*N″*,*N″*-tetraethyldiethylenetriamine (TEDETA) anchored on an imidazolium-based ionic liquid (BITT) formed an ionic liquid catalyst insoluble in the mixture of MMA and toluene but could be easily dispersed in the reaction media. With the catalysis of CuBr/TEDETA-BITT, the polymerization of MMA at 60 °C was well-controlled, producing polymers with high initiator efficiency and low polydispersity (∼1.2−1.4). Once the stirring was stopped, the catalyst easily settled on the bottom of the reactor as a thin liquid layer, and thus the catalyst was easily isolated from the polymer solution. After regeneration, the recycled catalysts catalyzed the second run polymerization with similar or even higher activity and improved control. The residual catalyst concentrations in the polymers were in the range 50−100 ppm. The addition of a small amount of silica gel to the polymer solution could further reduce the residual catalyst concentration.

Introduction

Atom transfer radical polymerization (ATRP) is a very versatile process utilizing transition-metal complexes as catalysts to mediate a controlled/living radical polymerization for a wide range of monomers. It is also a robust tool for the preparation of well-defined functional polymers and polymers with various preselectable architectures.[1−6] However, the reaction generally requires a high concentration of homogeneous catalyst. These catalysts coprecipitate in the products and thereby contaminate the polymer products. Therefore, how to efficiently and economically remove/reduce the catalyst residue concentration in the polymer products still remains a challenge for ATRP.[7]

Postpolymerization purification methods are used on lab scales for the removal of catalysts from polymers prepared by ATRP,[7] such as passing the polymer−catalyst mixture solutions through columns of silica gel or alumina, catalyst extraction using catalyst-soluble solvents,[8] and catalyst adsorption using ion-exchange resins.[9] These techniques have drawbacks including high cost, loss of polymer, scale-up difficulty, and difficulties in separating the catalyst from functional polymers that interact with the copper complexes.[7]

Catalyst immobilization on solid supports, such as silica gel particles or polystyrene beads, and JandaJel resins has been explored for catalyst removal and reuse in ATRP. It has advantages of easy separation of the catalysts from their products and the possibility to reuse the catalysts for cost-saving.[10−14] The control level of the polymerization by these covalently solid-supported systems, however, is generally lower than that by unsupported catalysts, which was caused by limited diffusion of the catalysts in solution and thus slowed deactivation of the growing radicals.[7,15] More importantly, catalyst immobilization on solid sacrifices the versatility of ATRP in the synthesis of polymer architectures.[7] The addition of soluble deactivators or free soluble ligand to the solid-supported catalysts (soluble/insoluble hybrid catalysts),[15−17] using soluble supports[18] or using “catalyst sponge”[19,20] that releases free catalysts into solution for homogeneous catalysis could significantly improve the control level of the polymerization.

Biphasic polymerization, in which the catalyst preferentially dissolves in one phase while the product is in the other, has the advantage of direct catalyst/product separation and is widely used in industry.[7] Fluorous solvents were first explored for the biphasic ATRP of MMA.[21] Recently, ionic liquids, the “green” solvents, have been explored as the polymerization solvents[22] due to their nonvolatility, chemical and thermal stability, and nonflammability.[23] Ionic liquids were thus explored as the solvents for biphasic ATRP to facilitate the separation of the catalyst from the products. Haddleton et al.[24] studied ATRP of MMA in ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]-[PF_6]) and found that CuBr/*N*-propyl-2-pyridylmethanimine catalyst was very soluble in [bmim][PF_6], but [bmim][PF_6] was immiscible with organic solvents such as toluene. After the polymerization was complete, the formed polymer dissolved in toluene, and most of the catalyst was in the ionic liquid phase. Therefore, the polymers could be easily separated from the catalyst. Matyjaszewski et al.[25] found that when $FeBr_2$ or $FeCl_2$ was used to mediate ATRP in the presence of ionic liquids, no ligand was needed, but copper-mediated ATRP of MMA required the presence of organic ligands when the ionic liquid had a halide or a carbonate anion.

The biphasic ATRP using ionic liquids indeed facilitates the catalyst separation but requires using a large quantity of expensive ionic liquids. Thus, we proposed an ionic liquid catalyst for ATRP (Scheme 1): The catalyst itself is an ionic liquid and thus can be dispersed in organic solvents to catalyze biphasic ATRP, but after the polymerization the catalyst settles on the bottom of the reactor to form a thin liquid layer for separation and recycling. This approach can avoid

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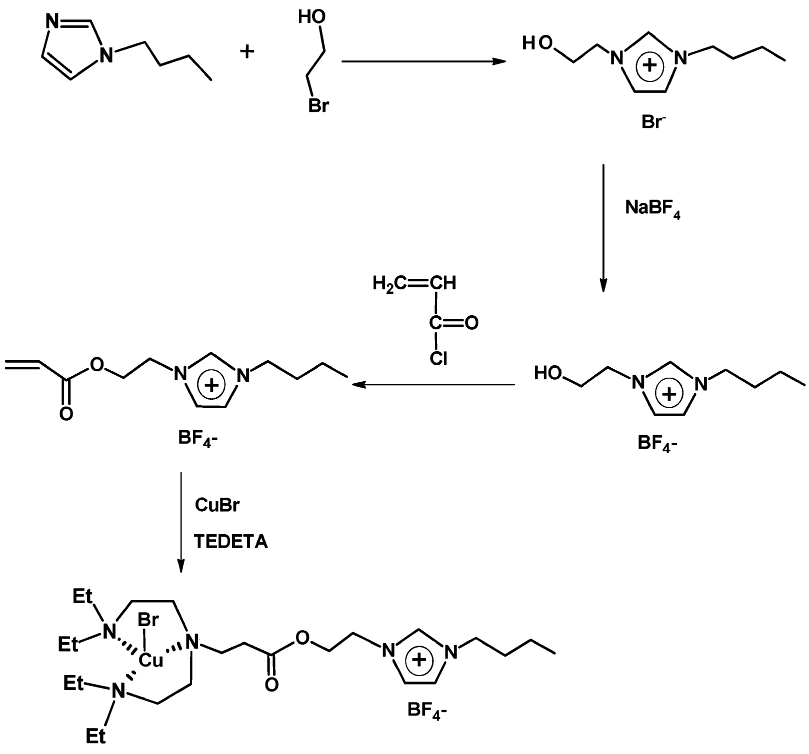
Scheme 1. Synthesis of Ionic Liquid Catalyst CuBr/1-[2-({3-[Bis(2-*N*,*N*-diethylaminoethyl)amino]propanoyl}oxy)ethyl]-3-butylimidazolium Tetrafluoroborate (CuBr/TEDETA-BITT)



using a large quantity of ionic liquids with the possibility of reusing the catalyst.

In this paper, we report the biphasic polymerization of MMA catalyzed by an ionic liquid catalyst (Scheme 1). The used ionic liquid was only 5 wt % of the organic solvent. The polymerization by the ionic liquid catalyst was well-controlled, producing polymers with controlled molecular weights and low polydispersity. After the polymerization, the ionic liquid catalyst settled on the bottom of the reactor and could be easily separated from the polymer solution. Significantly, the recycled catalysts regenerated with copper metal had even higher catalytic activity and better control than that of fresh catalyst.

Experimental Section

Chemicals. 1-Butylimidazole (Aldrich, 98%), 2-bromoethanol (Aldrich, 95%), acryloyl chloride (Lancaster, 96%), acetonitrile (EMD, 99.99+%), methyl α-bromophenylacetate (Aldrich, 97%, MBP), sodium tetrafluoroborate (Aldrich, 98%, NaBF$_4$), *N*,*N*,*N*″,*N*″-tetraethyldiethylenetriamine (Aldrich, tech. 90%, TEDETA), *N*,*N*, *N*′,*N*″,*N*″-pentamethyldiethylenetriamine (Aldrich, 99%, PMDETA), nitric acid (EM, A.C.S.), phenyl ether (Aldrich), 1,4-dioxane (Aldrich, 99+%), and silica gel (Mallinckrodt, 453.6 Gm) were used directly without further purification. Toluene (Baker) and methyl methacrylate (Aldrich, 99%, MMA) were distilled before use. Copper(I) bromide (Aldrich, 98%) was stirred with glacial acetic acid, filtered, washed with ethanol, and dried.[26]

Synthesis of Ligand 1-[2-({3-[Bis(2-*N*,*N*-diethylaminoethyl)amino]propanoyl}oxy)-ethyl]-3-butyl-imidazolium Tetrafluoroborate (TEDETA-BITT) (Scheme 1). The TEDETA ligand was anchored onto an imidazolium-based ionic liquid moiety via two-step reactions: the synthesis of 1-(2-acryloyloxyethyl)-3-butylimidazolium tetrafluoroborate using a modified procedure reported in the literature[27−29] and its Michael reaction with TEDETA.

A mixture of 1-butylimidazole (9.50 g, 0.076 mol) and 2-bromoethanol (9.56 g, 0.076 mol) was stirred at 75 °C for 20 h. The resulting product, 1-(2-hydroxyethyl)-3-butylimidazolium bromide (19.1 g, 0.076 mol), was dissolved in 100 mL of dry acetonitrile and stirred with NaBF$_4$ (9.0 g, 0.082 mol) under N$_2$ atmosphere at room temperature. After the mixture was stirred for 48 h, the sodium bromide precipitate was removed by filtration and the filtrate was concentrated. The concentrated filtrate was diluted with methylene chloride (200 mL) and filtered through a column of silica gel. Removal of the solvent yielded 15.0 g (76.6% yield) of ionic liquid 1-(2-hydroxyethyl)-3-butylimidazolium tetrafluoroborate. ^{1}H NMR (d_6-DMSO, 400 MHz) δ (ppm): 9.15 (s, 1H, NC*H*N), 7.78 (d, 2H, NC*H*C*H*N), 5.17 (t, 1H, O*H*), 4.20 (m, 4H, NCH_2), 3.74 (t, 2H, HOCH_2), 1.78 (m, 2H, NCH$_2$CH_2), 1.27 (m, 2H, CH_2CH$_3$), 0.91 (t, 3H, CH_3).

A solution of acryloyl chloride (8.02 g, 0.087 mol) in 10 mL of dry methylene chloride was added dropwise to a vigorously stirred solution of 1-(2-hydroxyethyl)-3-butylimidazolium tetrafluoroborate (15.0 g, 0.059 mol) in dry methylene chloride (100 mL) over 20 min at room temperature. The reaction mixture was refluxed at 40 °C for 48 h, and the HCl byproduct formed during the reaction was distilled out. After the solvent was removed via vacuum, the crude product was washed with ether (3 × 50 mL), producing 14.5 g (79.8% yield) of 1-(2-acryloyloxyethyl)-3-butylimidazolium tetrafluoroborate. ^{1}H NMR (d_6-DMSO, 400 MHz) δ (ppm): 9.23 (s, 1H, NC*H*N), 7.80 (d, 2H, NC*H*C*H*N), 6.33 (d, 1H, CH_2═), 6.14 (q, 1H, ═C*H*), 5.98 (d, 1H, CH_2═), 4.47 (m, 4H, NCH_2), 4.17 (t, 2H, OCH_2CH$_2$N), 1.74 (m, 2H, NCH$_2$CH_2), 1.21 (m, 2H, CH_2CH$_3$), 0.88 (t, 3H, CH_3).

TEDETA (1.25 g, 5.42 mmol) and 1-(2-acryloyloxyethyl)-3-butylimidazolium tetrafluoroborate (1.60 g, 5.16 mmol) were dissolved in 10 mL of dry acetonitrile and stirred at room temperature for 48 h. The volatile was then removed, and the product was dissolved in methylene chloride. The TEDETA ligand anchored on the ionic liquid moiety, 1-[2-({3-[bis(2-*N*,*N*-diethylaminoethyl)amino]propanoyl}oxy)ethyl]-3-butylimidazolium tetrafluoroborate (TEDETA-BITT), was precipitated in ether and purified by reprecipitation. The resulted product was 2.0 g (80.0% yield). ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 9.53 (s, 1H, NC*H*N), 7.69 (s, 1H, NC*H*CHN), 7.34 (s, 1H, NCHC*H*N), 4.63 (t, 2H, NCH_2), 4.50 (t, 2H, NCH_2), 4.28 (t, 2H, OCH_2), 2.79 (m, 18H, NCH_2), 2.60 (t, 2H, $C(O)CH_2$), 1.90 (m, 2H, NCH_2CH_2), 1.40 (m, 2H $NCH_2CH_2CH_2$), 1.16 (m, 12H, NCH_2CH_3), 0.98 (t, 3H, $CH_2CH_2CH_3$).

Polymerization. A typical polymerization procedure is as follows: Cu^IBr (0.0270 g, 0.188 mmol), the ionic liquid ligand TEDETA-BITT (0.0989 g, 0.188 mmol), and a stirring bar were put into a reaction tube. The tube was tightly sealed with a rubber septum. The degassed solvent (toluene, 2.0 mL) was added via a degassed syringe. The mixture was stirred and bubbled with nitrogen for 5 min. The degassed monomer (MMA, 1.89 g, 18.8 mmol) was added, and then the mixture was degassed again for 2 min. The tube was immersed in an oil bath preset at the polymerization temperature. Finally, the initiator (MBP, 30.0 μL, 0.191 mmol) was added to the mixture with stirring. At different time intervals, samples (0.050 mL) were withdrawn from the tube with nitrogen-purged syringes and dissolved in $CDCl_3$. The conversion was monitored by ^1H NMR spectroscopy by the ratio of the OCH_3 signal intensity in polymer (3.60 ppm) and monomer (3.75 ppm).[12] The molecular weight and polydispersity of the polymer were measured by GPC. The results are shown in Figures 1 and 2.

Catalyst Regeneration and Reuse. After the completion of the polymerization, the tube was removed from the oil bath. The reaction mixture was diluted with toluene (3 mL) and centrifuged, and the upper layer solution was withdrawn carefully by a degassed syringe. The remaining catalyst in the tube was washed twice with a total of 6 mL of toluene. About 1 g of copper metal beads (~1 mm diameter), 23.3 mg of TEDETA-BITT (19.3 mol % of the originally used ligand), and 2.0 mL of toluene were added and stirred at 40 °C overnight. The catalyst was separated from the copper beads and transferred into a degassed, tightly sealed tube. Then degassed MMA (1.89 g, 18.8 mmol), toluene (2.0 mL), and MBP (30.0 μL, 0.191 mmol) were added, and the polymerization was performed following the same procedure as the first polymerization run. The results are shown in Figures 5 and 6.

Polymerization in the Presence of Silica Gel. CuBr (27.0 mg, 0.188 mmol), silica gel (54.0 mg), and TEDETA-BITT (0.0989 g, 0.188 mmol) were added to a reaction tube. The tube was sealed tightly and degassed by 10 vacuum−nitrogen cycles. Degassed toluene (2.0 mL) was added to the tube, and the mixture was bubbled with nitrogen for 5 min with stirring. Then MMA (1.89 g, 18.8 mmol) was added by a degassed syringe, and the mixture was bubbled for another 2 min. Upon stirring, the silica particles became light green and floated in the solution. The reaction tube was then put into an oil bath with preset temperature. MBP (30.0 μL, 0.191 mmol) was introduced dropwise to the tube, and the polymerization began. The light green particles immediately became blue. The polymerization was then performed following the same procedure as described above. The results are shown in Figures 9 and 10.

Characterization. Gel permeation chromatography (GPC) was used to determine polymer molecular weights and molecular weight distributions (PDI) using polystyrene standards (Polysciences Corp.) to generate a universal calibration curve. The measurements were operated on a Waters SEC equipped with a Waters 2414 refractive index detector and two 300 mm Solvent-Saving GPC columns (molecular weight ranges: $1 \times 10^2 - 5 \times 10^3$, $5 \times 10^3 - 5 \times 10^5$) at a flow rate of 0.30 mL/min using THF as solvent at 30 °C. Data were recorded and processed using the Waters software package. ^1H NMR spectra were recorded on a Bruker Avance DRX-400 spectrometer using $CDCl_3$ as solvent. Chemical shifts were reported downfield from 0.00 ppm using tetramethylsilane (TMS) as internal reference.

The residue copper concentration in polymer products was measured by inductively coupled plasma mass spectrometry (ICP-MS) at the Department of Geology of the University of Wyoming. The polymer solution was dried under vacuum, and then the polymer powder (50.0 mg) was dissolved in nitric acid with heating and was then diluted to 25.0 mL for ICP-MS analysis.

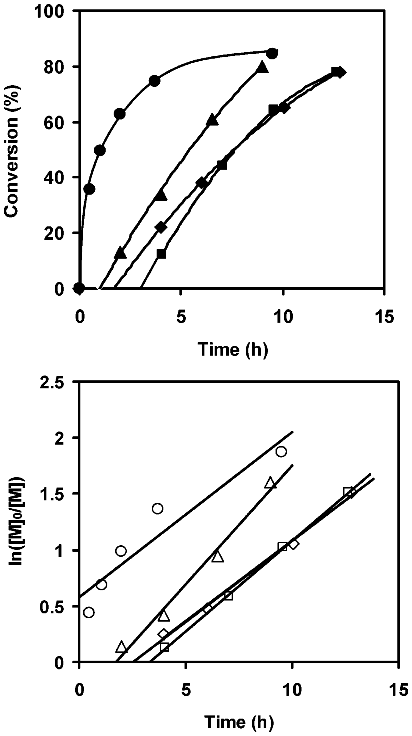


Figure 1. Methyl methacrylate (MMA) polymerization with ionic liquid catalyst CuBr/1-[2-({3-[bis(2-*N*,*N*-diethylaminoethyl)-amino]propanoyl}oxy)ethyl]-3-butylimidazolium tetrafluoroborate (CuBr/TEDETA-BITT) in different solvents and the polymerization catalyzed by unmodified catalyst CuBr/*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) in toluene. Experimental conditions: 60 °C, [MMA] = 4.71 mol/L, [CuBr] = [ligand] = [methyl α-bromophenylacetate (MBP)] = 0.0471 mol/L. CuBr/TEDETA-BITT in phenyl ether (▲, △), toluene (◆, ◇), and 1,4-dioxane (■, □); CuBr/PMDETA catalyst in toluene (●, ○).

Results and Discussion

The synthesis of the ionic liquid catalyst is shown in Scheme 1. The ionic liquid 1-(2-acryloyloxyethyl)-3-butylimidazolium tetrafluoroborate was first synthesized via a modified procedure.[27−29] The Michael reaction of the acryloyloxy group with TEDETA anchored the ligand onto the ionic liquid moiety (TEDETA-BITT). The complex of the TEDETA moiety with copper halide tethered the catalyst onto the ionic liquid moiety, forming the ionic liquid ATRP catalyst. The CuBr/TEDETA-BITT complex was a light green liquid insoluble in toluene, phenyl ether, and 1,4-dioxane or their mixture with MMA at room temperature.

Upon stirring, the catalyst suspended in the reaction mixture as tiny droplets but easily settled on the bottom of the reactor as a thin liquid layer. After the addition of the initiator MBP, the color of the droplets immediately changed from light green to blue. Figure 1 shows the polymerization of MMA in toluene, phenyl ether, and 1,4-dioxane. The polymerization catalyzed by CuBr complexed with *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) or *N*,*N*,*N*,*N*″-tetraethyldiethylenetriamine (TEDETA) was also conducted under identical conditions for comparison.

All of the polymerizations catalyzed by CuBr/TEDETA-BITT had induction periods about 1.5 h for the polymerization in phenyl ether and 2−3 h for those in toluene and dioxane. After the induction periods, the polymerizations proceeded smoothly in first order with respect to the monomer concentration. The polymeri-

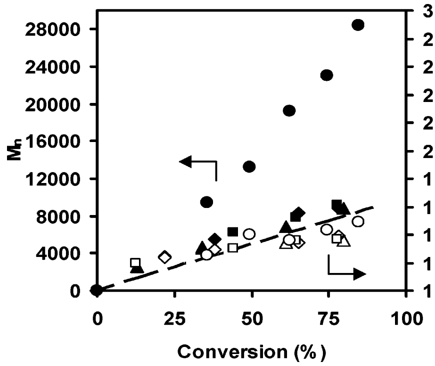


Figure 2. Poly(methyl methacrylate) molecular weights and molecular weight distribution as a function of conversion in the polymerization of methyl methacrylate (MMA) in different solvents catalyzed by CuBr/1-[2-({3-[bis(2-*N*,*N*-diethylaminoethyl)amino]propanoyl}oxy)ethyl]-3-butylimidazolium tetrafluoroborate (CuBr/TEDETA-BITT and the polymerization catalyzed by unmodified catalyst CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) in toluene. See Figure 1 for experimental conditions. CuBr/TEDETA-BITT) in phenyl ether (▲, △), toluene (◆, ◇), and 1,4-dioxane (■, □); CuBr/PMDETA in toluene (●, ○); theoretical molecular weight M_n (- - -).

zation in phenyl ether was the fastest, whereas the polymerizations in toluene and 1,4-dioxane were almost the same. In contrast, the MMA polymerization catalyzed by CuBr ligated with TEDETA or PMDETA had no induction period and a fast initial polymerization rate (only CuBr/PMDETA shown in Figure 1). The polymerization slowed down afterward. Except for the initial period, its ln([M]$_0$/[M]) vs time plot was parallel to that of the polymerization by CuBr/TEDETA-BITT in toluene, indicative of that CuBr/TEDETA-BITT had a very similar activity to the CuBr/PMDETA.

Figure 2 shows the molecular weights and molecular weights distribution as a function of conversion in the polymerization of MMA catalyzed by CuBr/TEDETA-BITT. The molecular weights of PMMA produced in these three solvents were all very close to the theoretical values. In contrast, the molecular weights of PMMA produced by CuBr/PMDETA were much higher than the theoretical values with even broader distribution, indicating the low initiator efficiency due to the consumption of the initiators by radical terminations, as indicated by the precipitation of Cu(II) complex.

The polydispersity of the polymers produced from the ionic liquid catalyst was in the range 1.2−1.4, slightly broader than that of polymers prepared by most homogeneous catalysts. This is caused by the restricted access of growing radicals in the organic phase to the catalyst in the ionic liquid phase because the ionic liquid is immiscible with the toluene−MMA phase and only dispersed in the organic phase as fine droplets. Thus, the growing radicals could not be deactivated as fast as those in the homogeneous systems, causing less controlled chain growth.[7] This polydispersity, however, is lower than that of polymers prepared by most solid-supported catalysts.[7] This is probably due to that the ionic liquid catalyst can be dispersed into very small droplets, which experience less diffusion limitation.

The cause of the induction periods is the slow dispersion of the ionic liquid catalyst. At the beginning of the polymerization, the formed ionic liquid catalyst droplets were large but gradually became very tiny after stirring for a while. Large droplets of the catalyst had limited contact with the organic phase and thus could not effectively catalyze the polymerization.To eliminate the induction period caused by slow dispersion, the ionic liquid catalyst was first stirred in the toluene/MMA reaction solution at 60 °C for 3−5 h. The initiator was then added to the mixture to start the polymerization. Figure 3 shows that by premixing of the ionic liquid catalyst with the organic phase the induction period indeed disappeared, and the polymerization rate increased. This experiment also confirms that the induction period of the polymerization catalyzed by ionic liquid catalyst was indeed caused by the slow dispersion. Figure 4 shows that the premixing did not cause any change in the control of polymerization.

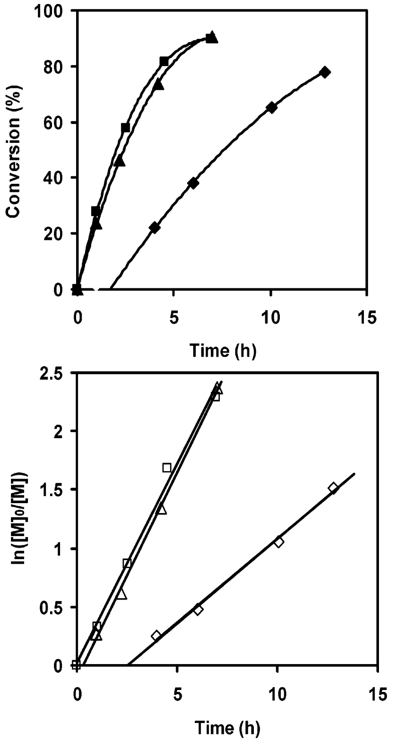


Figure 3. Methyl methacrylate (MMA) polymerization in toluene catalyzed by CuBr/1-[2-({3-[bis(2-*N*,*N*-diethylaminoethyl)amino]propanoyl}oxy)ethyl]-3-butylimidazolium tetrafluoroborate (CuBr/TEDETA-BITT) with or without premixing of the ionic liquid catalyst. 60 °C, [MMA] = 4.71 mol/L, [CuBr] = [TEDETA-BITT] = [methyl α-bromophenylacetate (MBP)] = 0.0471 mol/L. The initiator was added after the CuBr/TEDETA-BITT was stirred in toluene/MMA mixture at 60 °C for 0 h (◆, ◇), 3 h (■, □), and 5 h (▲, △).

Once the stirring was stopped, the catalyst settled on the bottom as a thin liquid layer and could be easily separated from the polymer solution. Although the polymerization in phenyl ether was faster and the polymerization was slightly better controlled, the color of resulting polymer product was greenish, indicating a high residual copper concentration, whereas the polymer produced in toluene was colorless. ICP-MS measurement showed that the copper concentration in the polymer was 117 ppm (Table 1). Therefore, toluene is a preferable solvent in terms of the control of the polymerization and the low residual catalyst concentration.

The green liquid catalyst settled on the bottom of the reactor could be easily isolated. This recycled catalyst had a low catalytic activity probably due to the presence of Cu(II) produced by the persistent radical effect,[4] which can be found in other supported catalyst systems.[7] Thus, the catalyst was regenerated by the

Table 1. Copper Residue Concentration in Polymers Produced under Different Conditions[a]

expt	polymers obtained from	copper concn (ppm)
1	fresh catalyst	117
2	regenerated catalyst with 19.3 mol % extra TEDETA-BITT	46
3	addition of 2.0 times silica gel (relative to the weight of originally used CuBr) to the polymer solution of 1	23
4	fresh catalyst with addition of 0.41 times silica gel (relative to the weight of CuBr)	67
5	fresh catalyst with addition of 0.74 times silica gel (relative to the weight of CuBr)	75
6	fresh catalyst with addition of 2.0 times silica gel (relative to the weight of CuBr)	58

[a] 60 °C, in toluene, [methyl methacrylate (MMA)] = 4.71 mol/L, [CuBr] = [1-[2-({3-[bis(2-*N*,*N*-diethylaminoethyl)amino]propanoyl}oxy)ethyl]-3-butylimidazolium tetrafluoroborate (TEDETA-BITT)] = [methyl α-bromophenylacetate (MBP)] = 0.0471 mol/L.

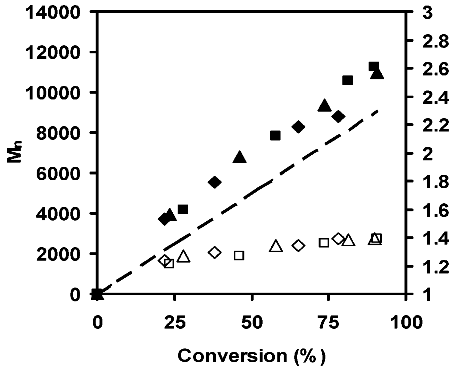


Figure 4. Poly(methyl methacrylate) molecular weight and polydispersity as a function of conversion in the polymerization of methyl methacrylate in toluene catalyzed by CuBr/1-[2-({3-[bis(2-*N*,*N*-diethylaminoethyl)amino]propanoyl}oxy)ethyl]-3-butylimidazolium tetrafluoroborate (CuBr/TEDETA-BITT) with or without premixing of the ionic liquid catalyst. See Figure 3 for experimental conditions. The initiator was added after the CuBr/TEDETA-BITT was stirred in toluene/MMA mixture at 60 °C for 0 h (◆, ◇), 3 h (■, □), and 5 h (▲, △).

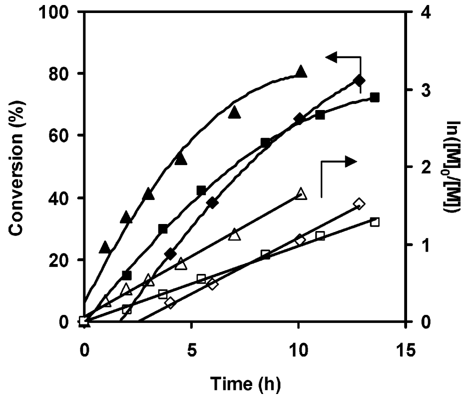


Figure 5. Methyl methacrylate (MMA) polymerization in toluene with fresh and regenerated CuBr/1-[2-({3-[bis(2-*N*,*N*-diethylaminoethyl)amino]propanoyl}oxy)ethyl]-3-butylimidazolium tetrafluoroborate (CuBr/TEDETA-BITT). 60 °C, [MMA] = 4.71 mol/L, [CuBr] = [TEDETA-BITT] = [methyl α-bromophenylacetate (MBP)] = 0.0471 mol/L. Fresh catalyst (◆, ◇), catalyst regenerated with 38.4 mol % extra ligand (relative to the first charge; same in the following) (▲, △), catalyst regenerated with 19.3 mol % extra ligand (■, □).

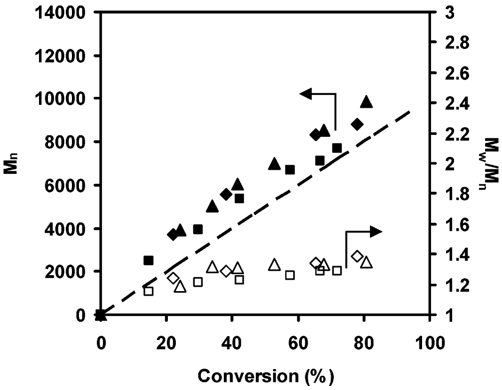


Figure 6. Poly(methyl methacylate) molecular weight and polydispersity as a function of conversion in the polymerization of methyl methacrylate catalyzed by fresh and regenerated CuBr/1-[2-({3-[bis(2-*N*,*N*-diethylaminoethyl)amino]propanoyl}-oxy)ethyl]-3-butylimidazolium tetrafluoroborate (CuBr/TEDETA-BITT). See Figure 5 for experiment conditions. Fresh catalyst (◆, ◇), catalyst regenerated with 38.4 mol % extra ligand (relative to the first charged amount of ligand) (▲, △), catalyst regenerated with 19.3 mol % extra ligand (■, □); theoretical molecular weight M_n (- - -).

reaction with Cu(0) metal. Additional TEDETA-BITT ligand was added during the regeneration. Figure 5 shows the polymerizations catalyzed by the regenerated catalysts. The regenerated catalysts had the same activity as the fresh catalyst but did not have any induction periods. This is because the recycled ionic liquid catalyst dissolved a small amount of toluene (though not miscible) and thus could be easily dispersed in the reaction media. The catalyst regenerated in the presence of excess free TEDETA-BITT ligand (38.4 or 19.3 mol % relative to original charged TEDETA-BITT) had a higher catalyst activity. The polymerization by the recycled catalysts also had good control over the polymerization similar to that by the fresh catalyst. Actually, the control of polymerization by the catalyst regenerated in the presence of 19.3 mol % TEDETA-BITT was even better than that by the fresh catalyst (Figure 6). The copper residue concentration in the polymer produced by this catalyst was even lower, only around 50 ppm determined by ICP-MS (Table 1).

The polymerization of MMA by the ionic liquid catalyst at different temperatures was also investigated. Figure 7 shows that with the increase of temperature the polymerization rate increased. The induction period also disappeared at 70 and 90 °C. This might be due to the fact that ionic liquid catalyst CuBr/TEDETA-BITT was easier to be dispersed into fine droplets at elevated temperatures. However, the molecular weights of PMMA produced at 90 °C were much higher than theoretical values with broader molecular weight distribution, around 1.4−1.5 at high conversions (Figure 8). This is due to the fact that some catalysts lost their activity at high temperature, and thus radical termination occurred. We found that the color of polymerization solution at 90 °C quickly changed from blue to light green and then to yellowish brown at higher conversion. We heated TEDETA-BITT/toluene solution at 90 °C for 4 h and then analyzed both the toluene layer and ionic liquid layer by NMR spectroscopy. ^{1}H NMR spectra (400 MHz, $CDCl_3$) showed that besides the signals of TEDETA-BITT there were new signals at 6.45 ppm (d, 1H, C*H*$_2$=), 6.14 ppm (q, 1H, =C*H*), 5.98 ppm (d, 1H, C*H*$_2$=) corresponding to CH_2=CH− structure, and 9.57 ppm (s, 1H, NC*H*N) and 7.18 ppm (d, 2H, NC*H*C*H*N) signals

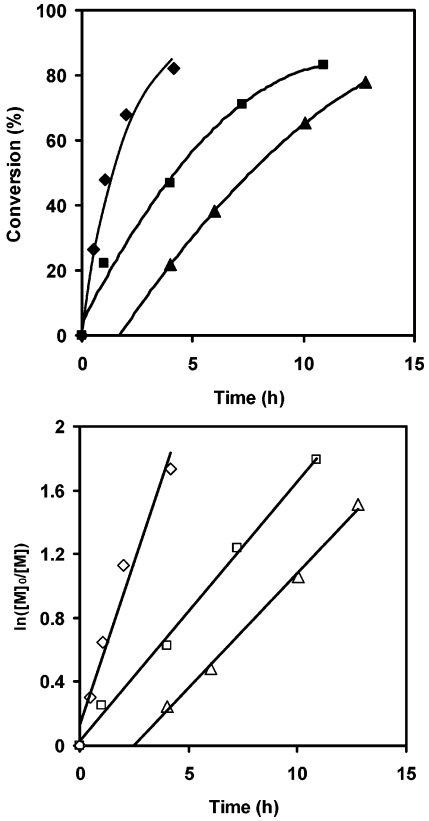


Figure 7. Polymerization of methyl methacrylate (MMA) in toluene mediated by CuBr/1-[2-({3-[bis(2-*N*,*N*-diethylaminoethyl)amino]propanoyl}oxy)ethyl]-3-butylimidazolium tetrafluoroborate (CuBr/TEDETA-BITT) at different temperatures. Experiment conditions: 90 °C (◆, ◇), 70 °C (■, □), [MMA] = 3.14 mol/L, [CuBr] = [TEDETA-BITT] = [methyl α-bromophenylacetate (MBP)] = 0.0314 mol/L; 60 °C (▲, △) [MMA] = 4.71 mol/L, [CuBr] = [TEDETA-BITT] = [MBP] = 0.0471 mol/L.

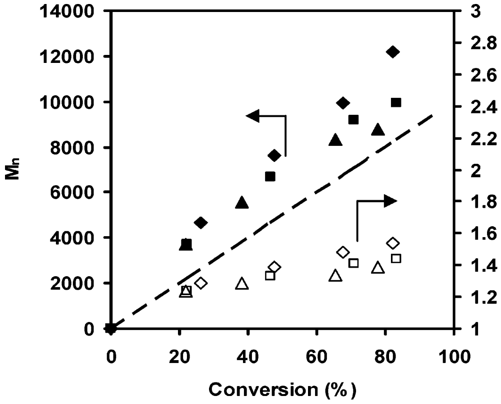


Figure 8. Dependence of poly(methyl methacrylate) molecular weight and polydispersity on conversion in the polymerization of methyl methacrylate (MMA) catalyzed by CuBr/1-[2-({3-[bis(2-*N*,*N*-diethylaminoethyl)amino]propanoyl}oxy)ethyl]-3-butylimidazolium tetrafluoroborate (CuBr/TEDETA-BITT) in toluene at different temperatures. See Figure 7 for experiment conditions. 90 °C (◆, ◇), 70 °C (■, □), 60 °C (▲, △); theoretical molecular weight M_n (- - -).

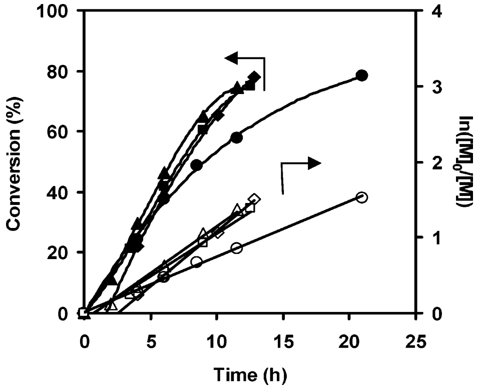


Figure 9. Polymerization of methyl methacrylate (MMA) in toluene catalyzed by CuBr/1-[2-({3-[bis(2-*N*,*N*-diethylaminoethyl)amino]propanoyl}oxy)ethyl]-3-butylimidazolium tetrafluoroborate (CuBr/TEDETA-BITT) in the presence of silica gel. 60 °C, [MMA] = 4.71 mol/L, [CuBr] = [TEDETA-BITT] = [methyl α-bromophenylacetate (MBP)] = 0.0471 mol/L. The ratio of silica gel to CuBr (w/w) = 0 (◆, ◇), 0.41 (▲, △), 0.74 (■, □), 2.0 (●, ○).

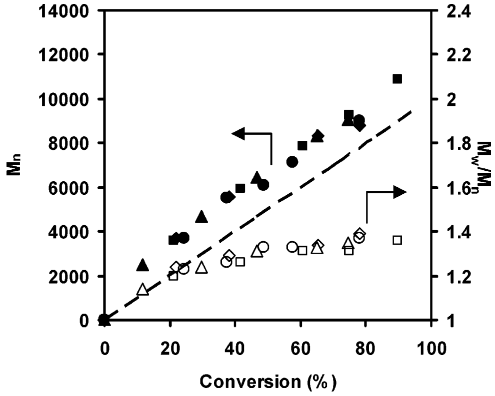


Figure 10. Dependence of poly(methyl methacrylate) molecular weight and polydispersity on conversion in the polymerization of methyl methacrylate (MMA) in toluene catalyzed by CuBr/1-[2-({3-[bis(2-*N*,*N*-diethylaminoethyl)amino]propanoyl}oxy)ethyl]-3-butylimidazolium tetrafluoroborate (CuBr/TEDETA-BITT) in the presence of silica gel. See Figure 9 for experiment conditions. The ratio of silica gel to CuBr (w/w) = 0 (◆, ◇), 0.41 (▲, △), 0.74 (■, □), 2.0 (●, ○); theoretical molecular weight M_n (- - -).

corresponding to the imidazolium structure of 1-(2-acryloyloxyethyl)-3-butylimidazolium tetrafluoroborate. This indicates that some (about 30−40% by NMR) of TEDETA/BITT decomposed at 90 °C caused by reverse Michael addition.[30] Therefore, high temperature caused the decomposition of the catalyst. In contrast, at 60 and 70 °C, the polymerization solution remained green throughout the polymerization, and no decomposition was found. The molecular weights of PMMA produced at both temperatures were very close to the theoretical ones, and the polydispersity was low (1.2−1.4) (Figure 8).

The fine dispersion of the ionic-liquid-modified catalyst and thereby elimination of the induction periods was also achieved by the addition of a small amount of fine silica gel powders. After the catalyst CuBr/TEDETA-BITT formed, 0.41, 0.74, and 2.0 times of silica gel (in weight) relative to the weight of CuBr was added to the reaction media. MMA was then added and polymerized in toluene at 60 °C. Upon stirring, the silica particles became light green and floated in the solution. Figure 9 shows that with the addition of 0.41 and 0.74 times of silica gel, the polymerization rates were unchanged compared to the one without the silica gel, whereas with 2.0 times of silica gel, the polymerization was slightly slower. The induction periods of the polymerization, however, disappeared with the addition of silica gel. This suggests that the silica gel facilitated the dispersion of catalyst in the solution, and its role is different from that of silica gel in the silica gel-supported

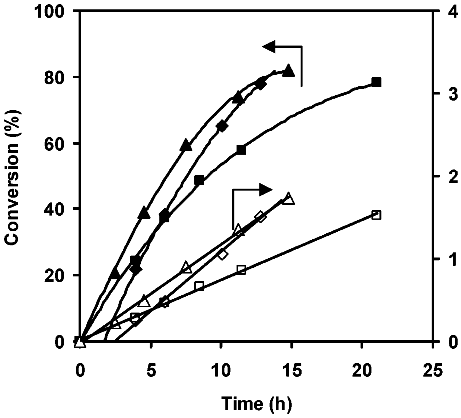


Figure 11. Polymerization of methyl mathacrylate (MMA) in toluene catalyzed by fresh and regenerated CuBr/1-[2-({3-[bis(2-*N*,*N*-diethylaminoethyl)amino]propanoyl} oxy)ethyl]-3-butylimidazolium tetrafluoroborate (CuBr/TEDETA-BITT) in the presence of silica gel. 60 °C, [MMA] = 4.71 mol/L, [CuBr] = [TEDETA-BITT] = [methyl α-bromophenylacetate (MBP)] = 0.0471 mol/L. Fresh catalyst without the silica gel (◆, ◇); fresh catalyst with 2.0 times of the silica gel (relative to CuBr (w/w)) (■, □), regenerated catalyst with 2.0 times of the silica gel (relative to CuBr (w/w)) (▲, △).

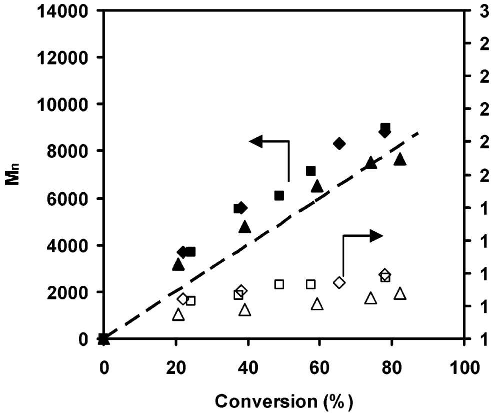


Figure 12. Dependence of poly(methyl methacrylate) molecular weight and polydispersity on conversion in the polymerization of methyl methacrylate (MMA) in toluene catalyzed by fresh and regenerated CuBr/1-[2-({3-[bis(2-*N*,*N*-diethylaminoethyl)amino]propanoyl}oxy)ethyl]-3-butylimidazolium tetrafluoroborate (CuBr/TEDETA-BITT) in the presence of silica gel. See Figure 11 for experimental conditions. Fresh catalyst without the silica gel (◆, ◇); fresh catalyst with 2.0 times of the silica gel (relative to CuBr (w/w) (■, □), regenerated catalyst with 2.0 times of the silica gel (relative to CuBr (w/w) (▲, △); theoretical molecular weight M_n (- - -).

CuBr/1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) system, in which a much more amount of silica gel (minimum silica gel/CuBr (w/w) = 2) was used, and the CuBr/HMTETA was completely adsorbed on the silica gel during the polymerization.[14] In the current system, the ionic liquid catalyst and the small amount of silica gel formed a solid-in-liquid dispersion.

The molecular weights of the resulting polymers were all very close to the theoretical values, and the polydispersity was close to the one without the silica gel (Figure 10). This means the addition of small amount of silica gel did not affect the control of polymerization.

The catalyst adsorbed on silica gel could also be recycled and regenerated. The activity of the regenerated catalyst was also very close to the fresh catalyst (Figure 11), and the polydispersity of the resulting polymers was even lower, around 1.2 (Figure 12). This indicated that the addition of silica gel can improve the control of the polymerization mediated by the recycled/regenerated catalyst.

The catalyst residue concentration was about 100 ppm in the polymers produced by the fresh catalyst (Table 1). The addition of silica gel during the polymerization could reduce the copper residue concentration to 50−70 ppm. Unexpectedly, the catalyst residue concentration was only about ~50 ppm in the polymers produced by the regenerated catalysts.

The copper residue concentration in the polymers could be more effectively reduced by the addition of a small amount of silica gel, which adsorbed the catalyst on its polar surface,[7,14] to the isolated polymer solutions. For example, if we added a small amount of silica gel (2.0 times relative to the weight of originally used CuBr) to the solution taken from the polymerization in toluene at 60 °C catalyzed by CuBr/TEDETA-BITT, the copper residue concentration could be reduced to 20−30 ppm.

Conclusion

We have demonstrated that tethering the catalyst to an ionic liquid moiety to form ionic liquid ATRP catalyst provided an efficient and economical way to remove/reuse the catalyst of ATRP. The needed ionic liquid for the biphasic ATRP was only 5 wt % of the organic solvent. The ionic liquid catalyst CuBr/TEDETA-BITT effectively mediated the ATRP of MMA, producing polymers with well-controlled molecular weights and low polydispersity (~1.2−1.4). With the addition of small amount of silica gel, the copper residue concentration in polymer product could be reduced from 100 ppm to less than 30 ppm. After regeneration, the recycled catalyst could be reused for second run polymerization with similar or even higher catalytic activity and similar or even better control over the polymerization.

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