Atom Transfer Radical Polymerization of Methyl Methacrylate in a Novel Ionic Liquid and Recycling of the Catalyst

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ABSTRACT: With 2,2′-bipyridine as the ligand and methyl 2-bromopropionate as the initiator, the copper-mediated atom transfer radical polymerization of methyl methacrylate was first conducted in a novel ionic liquid, N-butyl-N-methyl morpholinium tetrafluoroborate. The polymerization kinetics were confirmed to agree with the features of living/controlled free-radical polymerization. The results showed that the dosage of catalyst for well-controlled polymerization could be reduced obviously in N-butyl-N-methyl morpholinium tetrafluoroborate versus the normal organic solvent. The obtained polymers could be separated easily from the catalyst solution in the ionic liquid. Significantly, the recycled N-butyl-N-methyl morpholinium tetrafluoroborate solution of catalysts had catalytic activity similar to that of the fresh catalyst. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3683–3689, 2008

Key words: atom transfer radical polymerization (ATRP); catalysts; recycling

INTRODUCTION

Recently, atom transfer radical polymerization (ATRP) has emerged as a powerful method for the synthesis of vinyl polymers with controlled molecular weights, narrow polydispersities, and well-defined molecular architectures.[1–4] Much attention has been focused on the kinetics of ATRP, in which a transition-metal complex is used to catalyze the redox process and is responsible for the generation and concentration mediation of the propagating species.[5] However, the reaction generally requires a high concentration of catalyst, which may coprecipitate in the products and thereby contaminate the polymer products. Therefore, how to efficiently and economically reduce/remove the catalyst residue in the products still remains a challenge for ATRP.[6]

Ionic liquids are nonvolatile and nonflammable and are considered to be environmentally friendly alternatives to volatile organic compounds and suitable solvents for green physical and chemical processes, so ionic liquids have received growing attention for various applications such as organic chemical reactions, catalysis, separations, and electrochemistry because of their unique physical and chemical properties. A number of reviews that cover the history, properties, and use of ionic liquids are available.[7–9] Ionic liquids have thus been explored as solvents for biphasic polymerization to facilitate the separation of the catalyst from the products[6,10] because of the good solubility of transition-metal catalysis in an ionic liquid.

The application of ionic liquids as reaction media for ATRP has attracted much attention since Carmichael et al.[11] reported the use of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]) as a solvent for copper-mediated ATRP of methyl methacrylate (MMA). Biedron and Kubisa[12] investigated the ATRP of acrylates in [bmim][PF$_6$] and showed that the substituent of the monomer affected its solubility in the ionic liquid and led to homogeneous or heterogeneous polymerization. Subsequently, they studied the ATRP preparation of block polymers in [bmim][PF$_6$], and the results showed that block copolymers free of homopolymer may be obtained by sequential polymerization with butyl methacrylate as the first monomer and MMA as the second monomer.[13] Sarbu and Matyjaszewski[14] also studied ATRP of MMA and showed that iron-mediated ATRP could be carried out in the absence of added organic ligands in the presence of ionic liquids. However, copper-mediated ATRP of MMA required the presence of an added organic ligand when the ionic liquid had a halide or a carbonate anion, but
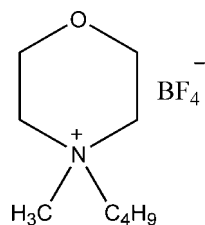
Scheme 1 Structure of [Mor$_{1,4}$][BF$_4$].

not a phosphonate anion. Hongyang and Xinhua[15] studied the reverse ATRP of MMA in an imidazolium ionic liquid. The ionic liquid could be recycled by a simple treatment, and the reverse ATRP with the recycled ionic liquid showed that the obtained polymers were almost the same. Shijie et al.[6] found tethering the catalyst to an ionic-liquid moiety to form an ionic-liquid ATRP catalyst provided an efficient and economical way to remove/reuse the catalyst of ATRP, but the normal organic solvent was also required. Carmichael et al.[11] and Sarbu and Matyjaszewski[14] reported that an ionic-liquid solution of catalysts can be recycled, but a detailed study has not been reported. Although using ionic liquids as solvents in ATRP has been widely studied, there are few detailed reports concerning the recycling of ionic-liquid solutions of catalysts. Moreover, most of the research has focused on imidazolium ionic liquids, which are relatively expensive; here we study a morpholinium ionic liquid.

In this study, heterogeneous ATRP of MMA was first carried out in a novel ionic liquid, N-butyl-N-methyl morpholinium tetrafluoroborate ([Mor$_{1,4}$][BF$_4$]; Scheme 1), and the polymerization was confirmed to agree with the features of ATRP. The obtained poly(methyl methacrylate) (PMMA) with a well-defined molecular weight and narrow polydispersity could act as a macroinitiator and undergo chain extension and block polymerization with t-butyl methacrylate (t-BMA). After polymerization, the ionic liquids that dissolved the catalysts settled on the bottom of the reactor and could be easily separated from the polymer solution when degassed toluene was introduced. Significantly, the recycled ionic-liquid solution of the catalysts had catalytic activity and good control similar to those of the fresh catalyst.

EXPERIMENTAL

Materials

MMA (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) and t-BMA (Tokyo Kasei Kogyo Co., Ltd.) were purified by distillation in vacuo. CuBr (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) was purified according to the literature.[16] Methyl 2-bromoproprate (MBP) (Tokyo, Japan)

was purchased from Wuhan Shengshi Chemical Co. (Wuhan, China) and distilled before use (143–145°C). All other reagents were used as received.

The synthesis procedure for the ionic liquid followed the previous work.[17,18] The ionic liquid was heated, evacuated, cooled, and flushed with highly pure nitrogen before being used.

Polymerization of MMA in [Mor$_{1,4}$][BF$_4$]

In a typical experiment, CuBr and 2,2′-bipyridine (bpy) were introduced into a reaction flask, and the flask was evacuated and backfilled with highly pure N$_2$ three times. Then, the ionic liquid was added to the flask immediately, and three cycles of evacuating and backfilling with nitrogen were conducted. Finally, MMA and an internal standard (toluene) flushed with highly pure nitrogen for 1 h were injected into the flask, the mixture was frozen in an ice–salt bath, and three cycles of evacuating and backfilling with nitrogen were performed to remove residual oxygen from the system. The flask was placed in a water bath and stirred at the designated temperature for 1 h, and then the initiator methyl 2-bromopropionate was introduced from a syringe that was purged with nitrogen before being used. Samples of the polymerization mixture were withdrawn at desired time intervals if necessary. The resultant polymers were recovered by precipitation in methanol or extraction with toluene. The ionic liquid could be recovered easily by extraction with methanol and passage through the Al$_2$O$_3$ (basic) column.

Chain extension

Chain extension was conducted as reported.[12] To a polymerization tube, 0.0611 g (6.86 × 10^{-3} mmol) of the PMMA macroinitiator, 0.29 g (2.9 mmol) of MMA, 0.016 g (0.11 mmol) of CuBr, 0.061 g (0.39 mmol) of bpy, and 0.928 g of chlorobenzene were added. After three freeze–pump–thaw cycles, the tube was sealed in vacuo and placed in an oil bath at 95°C for 8 h. The reaction mixture was diluted with 10 mL of tetrahydrofuran and added dropwise to 200 mL of methanol. After filtration, washing with methanol, and drying in vacuo, the chain-extended PMMA was obtained.

Block copolymerization

The block copolymerization was carried out with a method similar to that used in chain extension. The reaction conditions were as follows: macroinitiator PMMA, 0.06 g (6.74 × 10^{-3} mmol); CuBr, 0.016 g (0.11 mmol); bpy, 0.061 g (0.39 mmol); chlorobenzene as a solvent, 0.916 g; and block monomer t-BMA, 0.30 g (2.9 mmol).

TABLE I
Polymerization of MMA in an Ionic Liquid (1 : 1 w/w) with Methyl 2-Bromopropionate as the Initiator and CuBr/bpy as the Catalyst

Sample	[M]/[I]/[CuBr]/[bpy]	Temperature	Conversion	M_n GPC	M_n Calcd	M_w/M_n	Time (min)	Efficiency
1	100 : 2 : 0.1 : 0.2	50°C	35.9	27700	1962	1.25	240	0.0708
2	100 : 2 : 0.3 : 0.6	60°C	47.5	35040	2542	1.21	160	0.0725
3	100 : 2 : 0.3 : 0.6	80°C	86.8	29860	4507	1.41	360	0.1594
4	100 : 2 : 0.3 : 0.6	80°C	80.7	28200	4202	1.10	300	0.1490

Polymerization in a recycled catalyst solution in [Mor$_{1,4}$][BF$_4$]

In the recycling experiment, at the end of the polymerization, 10 mL of toluene flushed with nitrogen before use was added, and the upper layer, containing a toluene solution of the polymer, was isolated from the lower ionic-liquid layer with a syringe. Extraction was conducted three times as before, and then the ionic liquid containing catalyst was dried at 70°C *in vacuo*. When fresh MMA and methyl 2-bromopropionate were introduced into the ionic liquid containing catalyst (a complex of CuBr and bpy), the polymerization could be carried out again.

Characterization

^{1}H-NMR spectra were recorded on a Varian Mercury VX-300 MHz instrument (Varian, USA) with CDCl$_3$ (or D$_2$O for the ionic liquid) as a lock solvent and trimethylsilane (TMS) as a standard for chemical shifts. Conversion measurements were made on a Thermo Finnigan gas (Thermoelectron Corporation, Massachusetts, USA) chromatograph/mass spectrometer equipped with a fused silica capillary column (DB-5, 30 m × 0.25 mm × 0.25 μm) threaded into the ion source region of a Trace DSQ mass spectrometer (Thermoelectron Corporation, Massachusetts, USA) (with toluene as an internal standard). Molecular weights and molecular weight distributions were measured on a gel permeation chromatography (GPC) system consisting of a Waters 515 pump (Waters Corporation, Milford, USA) and Wyatt Technology Optilab DSP and DAWN EOS. The columns consisted of an MZ gel SDplus linear 5-μm column and 500-Å column.

RESULTS AND DISCUSSION

Heterogeneous ATRP of MMA in [Mor$_{1,4}$][BF$_4$]

The solubility of MMA and the initiator in [Mor$_{1,4}$][BF$_4$] was determined by gas chromatography/mass spectrometry, and the solubility of the catalyst in [Mor$_{1,4}$][BF$_4$] was determined by ultraviolet–visible as reported.[13] The solubility of MMA in

[Mor$_{1,4}$][BF$_4$] was about 21–25% at the reaction temperature, and the partition of the initiator in the two phases was equal to MMA. The ultraviolet–visible results showed that more than 99.9% of the catalyst was present in the ionic-liquid phase.

ATRP of MMA in [Mor1,4][BF$_4$] was carried out at the designated temperature with MBP/CuBr/bpy as the initiating and catalyzing system. MMA and MBP were partially soluble in the ionic liquid, whereas the catalyst (the complex of CuBr and bpy) was absolutely soluble in the ionic liquid. This led to phase separation of MMA from the ionic liquid containing 21–25% MMA monomer. The results of the heterogeneous ATRP of MMA are shown in Table I. All experiments were conducted until the reaction mixtures were semisolid and could not be stirred fluently. In the polymerization of MMA conducted under the typical conditions (CuBr/bpy as the catalytic system), nearly a 90% yield was obtained at 80°C in 6 h (sample 3 in Table I).

The GPC curves of the final products often showed a small peak following the main peaks (Fig. 1) when the polymers were only extracted with toluene and dried *in vacuo*. However, the small tails disappeared when the polymers were precipitated with methanol. This difference showed that precipitation with metha-
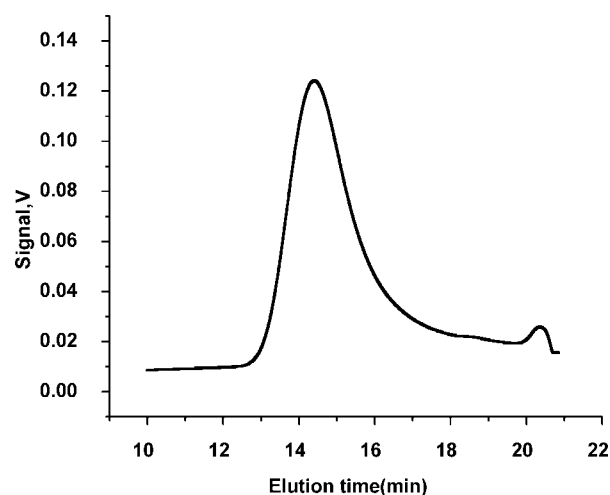

Figure 1 GPC of PMMA polymerized in [Mor$_{1,4}$][BF$_4$]. The polymerization conditions are described in Table I (sample 4).
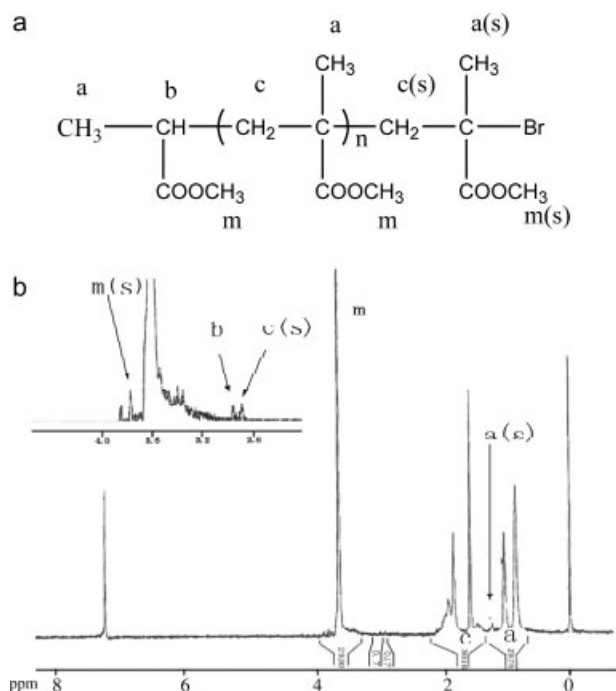
Figure 2 ^{1}H-NMR spectrum of PMMA polymerized in [Mor$_{1,4}$][BF$_4$] at 80°C (M_n = 8900, M_w/M_n = 1.20; in CDCl$_3$ at 300 MHz).

nol may cause the loss of some small-molecule PMMA that possibly had no time for propagation at the high viscosity.

Figure 2 shows the 300-MHz ^{1}H-NMR spectrum of a well-defined PMMA. It is quite consistent with the chemical structure of PMMA. The signals at 0.82–1.25, 1.40–2.06, and 3.40–3.84 ppm were attributed to the protons of the methyl groups (peak a), methylene groups (peak c), and methoxy groups (peak m), respectively.[16] In addition, the absorptions at 3.65 [peak m (s)], 2.88 [peak c (s)],[19] and 1.25 ppm [peak a (s)] proved the presence of the end group, —CH$_2$CBr(CH$_3$)(COOCH$_3$).

In the polymerization of MMA with [Mor1,4][BF$_4$] as the solvent at different temperatures, linear plots of ln([M]$_0$/[M]$_t$) versus time t were obtained, and they showed that the polymerization kinetics were first-order in the monomer and that the number of propagating species remained constant during the polymerization processes (see Fig. 3). There was a little jumping for the polymerization at 80°C, indicating some radical termination in the first stage, whereas there was no obvious jumping for the polymerization at 50 and 60°C. The slope of ln([M]$_0$/[M]) versus time showed that the polymerization rate was low and the conversions at the same time were low at the low temperature (Fig. 3). This may be due to several reasons. First, with the temperature elevated, the catalysis equilibrium shifted to the right, and this led the propagating radical concentration to increase and the propagating rate to also increase
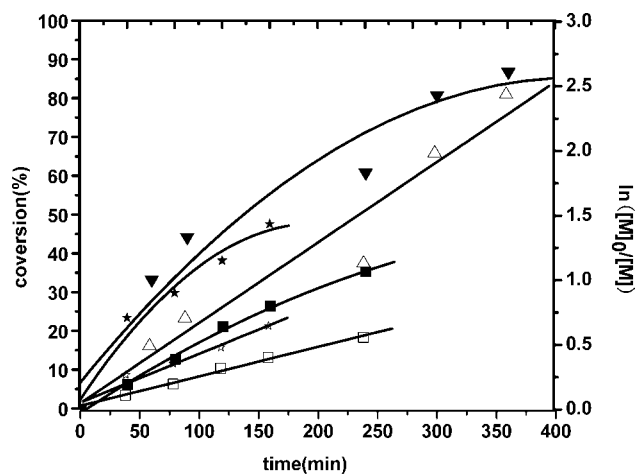

Figure 3 Polymerization of MMA mediated by CuBr/bpy in [Mor$_{1,4}$][BF$_4$] at different temperatures: (□,■) sample 1, (☆,★) sample 2, and (△,▼) sample 3. The polymerization conditions are described in Table I.

(646 L mol^{-1} s^{-1} for 50°C, 831 L mol^{-1} s^{-1} for 60°C, and 1312 L mol^{-1} s^{-1} for 80°C).[20] The propagating radicals could be calculated to be 4.87 × 10^{-8} mol/L for 50°C, 7.54 × 10^{-8} for 60°C, and 6.59 × 10^{-8} for 80°C. This result shows that the stable radical concentration of the polymerization mixture at 80°C was not the highest, and this may have been led by radical termination. Second, monomer diffusion was slow because of the relatively high viscosity of the ionic liquid, and the initiating process was also slow at the low temperature.

The number-average molecular weight (M_n) of the obtained PMMA increased linearly with an increase in the conversion (see Fig. 4), and the molecular weight distribution of the polymers remained nar-
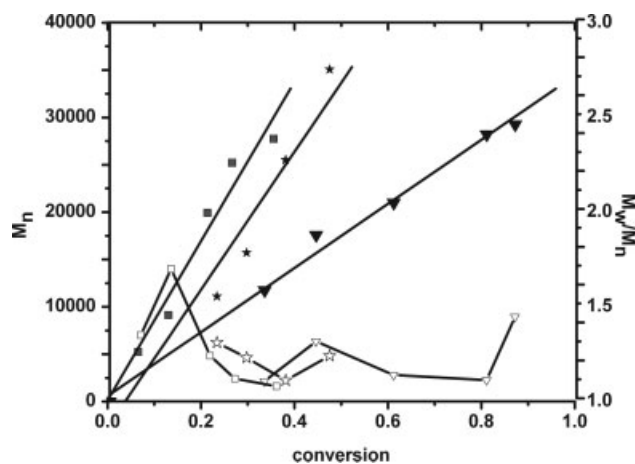

Figure 4 Molecular weight and polydispersity of PMMA as a function of conversion in MMA polymerization mediated by CuBr/bpy in [Mor$_{1,4}$][BF$_4$] at different temperatures: (□,■) sample 1, (☆,★) sample 2, and (△,▼) sample 3. The polymerization conditions are described in Table I.

TABLE II
Results of ATRP of MMA in a Recovered Ionic Liquid Containing Catalyst

| Reused time | Yield (%) | M_n ($\times 10^{-4}$) | | M_w/M_n | Efficiency |
		GPC	Calcd		
1	95.2	1.54	0.4927	1.63	0.3199
2	96.2	1.12	0.4977	1.28	0.4443
3	>90.0	1.15	~ 0.4667	1.36	0.4058
4	94.6	1.61	0.4897	1.23	0.3041

[MMA]/[MBP]/[CuBr]/[bpy] = 100 : 2 : 1 : 3 mol/mol; [MMA]/[ionic liquid] = 1 : 1; temperature = (1–3) 80 or (4) 70°C; time = 2 h.

row [weight-average molecular weight/number-average molecular weight (M_w/M_n) ≈ 1.2], but the experimental molecular weights were much higher than the calculated value for living/controlled polymerization (see Table II). This can be related to the low initiating efficiency due to the slow initiating process and low solubility of the initiator in [Mor1,4][BF$_4$]. The initiating efficiency increased with the temperature but was still low even at 80°C. This different initiating efficiency led to the different molecular weights for the same conversion at different temperatures. The reason is that using MBP as the initiator for the polymerization of MMA often caused a low initiating efficiency because the C—Br bond of the propagating radical was more labile than the C—Br bond of the initiator. The molecular weight distributions were a little wider (1.1–1.5) than those of the polymers obtained by normal ATRP (<1.2). This could probably be attributed to the fact that the relatively high viscosity slowed the rates of both reactions of the catalyst equilibrium, and the duration of every living radical (R·) was increased, so the simultaneous propagation of the dormant species (R—X) was delayed; this led to the relatively broad molecular weight distribution. However, this phenomenon could be overcome by vigorous stirring or the addition of some polar solvent that could be dissolved in the ionic liquid (e.g., acetonitrile and dimethylformamide). Moreover, the good solubility of the catalyst in the ionic liquid also led to a higher radical concentration, which meant that the radical termination could not be neglected, and the molecular weight distribution was broad. Generally, in the normal solvent, the molecular weight distributions decreased with the conversion, whereas the conversions were not very high, and the chain termination could be neglected.[1] However, the molecular weight distribution became broad when the conversion was high (often >80%), and chain termination obviously existed. This was also detected for the ATRP of MMA in [Mor1,4][BF$_4$] (Fig. 4). However, the conversion over 80% was inflected for the high temperature (80°C), whereas it was no more than 50% for the low

temperature (50 or 60°C). This was different from the normal organic solvent in which the inflection was higher for the low temperature.

Chain extension

The chain extension was carried out in chlorobenzene with bromine-atom-ended PMMA as the macroinitiator, CuBr as the catalyst, and bpy as the ligand. The polymerization temperature was kept at 95°C. Figure 5 shows the GPC curves of PMMA before and after chain extension. The increase in the molecular weight was evidenced by the obvious shift of the GPC trace of chain-extended PMMA toward the left, although there was a small trace following the main peak. The small trace was probably PMMA without a bromo end, which may have been led by the labile C—Br bond[21] and the relatively long reaction time and strong polarity of the ionic liquid.[1]

Block polymerization of PMMA with t-BMA

Block copolymerization was also used to prove the living characteristics of the polymerization. Bromine-atom-ended PMMA, obtained through ATRP, was used to initiate conventional ATRP of t-BMA. The polymerization was carried out with a method similar to the aforementioned chain-extension experiment, except that t-BMA was used instead of MMA and the reaction temperature was raised to 110°C. Figure 6 shows the GPC curve of the polymers. The obvious shift of the GPC curve indicates the successful
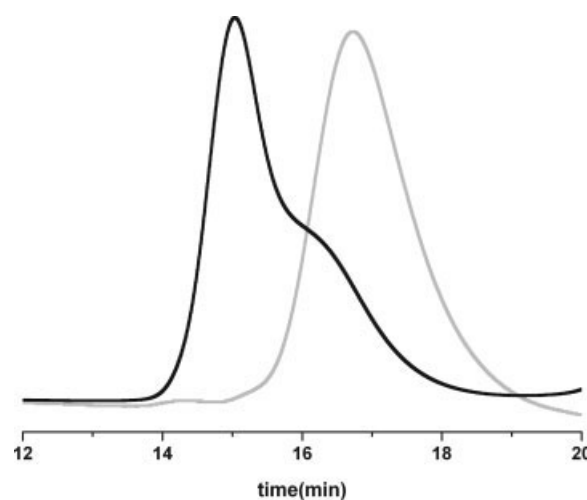

Figure 5 GPC curves of PMMA before and after chain extension (reaction conditions: MMA = 0.287 g, PMMA macroinitiator = 0.061 g, CuBr = 0.016 g, bpy = 0.056 g, chlorobenzene = 0.928 g, time = 8 h, and temperature = 95°C). The gray line indicates the macroinitiator with M_n = 8.9 × 10^3 and PDI = 1.20. The black line indicates PMMA after chain extension with M_n = 2.74 × 10^4, PDI = 1.28, and a 44.23% yield.
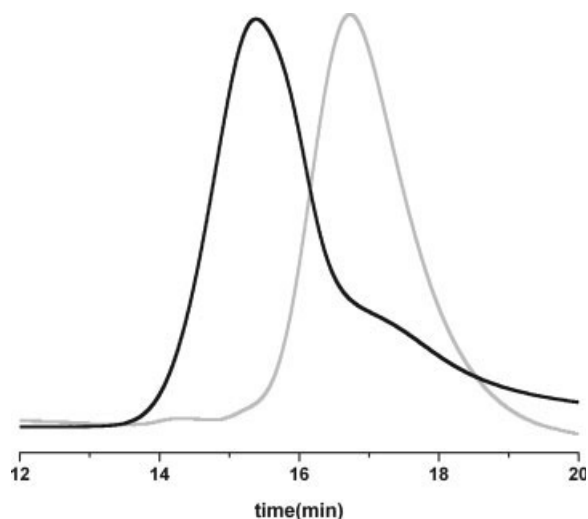
Figure 6 GPC curves of the PMMA macroinitiator and the resulting block copolymer PMMA-*b*-Pt-BMA (reaction conditions: *t*-BMA = 0.300 g, PMMA macroinitiator = 0.060 g, CuBr = 0.016 g, bpy = 0.061 g, chlorobenzene = 0.916 g, time = 8 h, and temperature = 110°C). The gray line indicates the macroinitiator with $M_n = 8.9 \times 10^3$ and PDI = 1.20. The black line indicates PMMA-*b*-Pt-BMA with $M_n = 3.34 \times 10^4$, PDI = 1.48, and a 55.06% yield.

block polymerization. Figure 7 shows the ^{1}H-NMR spectrum of the block copolymer. The signal at 1.413 (peak c), attributed to the protons of *t*-butyl groups, conformed to the GPC results. The small trace in the GPC curve occurred for the same reason as that in the chain extension.

Polymerization of MMA in the recycled ionic liquid containing catalyst

The recycling and reuse of catalysts for ATRP are important because the dosage of catalysts for ATRP is relatively high and the transition metal is expensive.
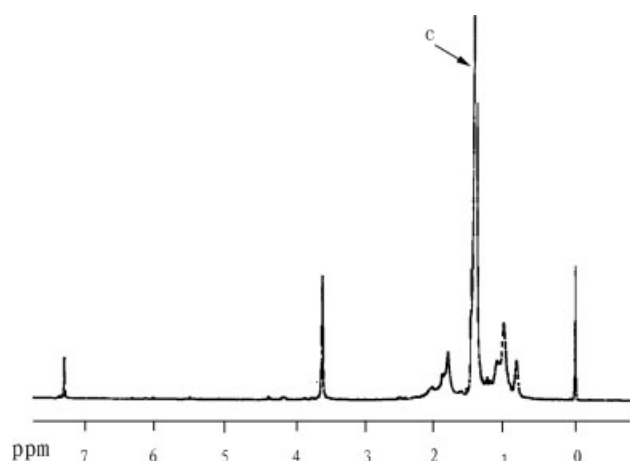

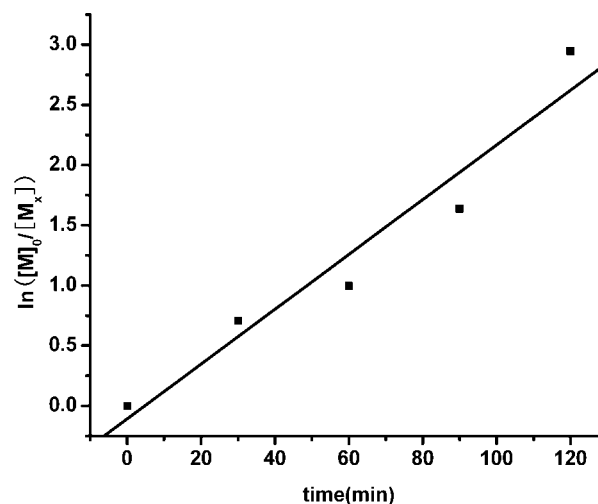**Figure 7** ^{1}H-NMR spectrum of PMMA-*b*-Pt-BMA (in CDCl$_3$ at 300 MHz).

Figure 8 Polymerization of MMA mediated by CuBr/bpy in recovered [Mor1,4][BF$_4$] (polymerization conditions: [MMA]/[MBP]/[CuBr]/[bpy] = 100:2:1:3 mol/mol, [MMA]/[ionic liquid] = 1 : 1 w/w, and temperature = 70°C).

Moreover, the recycling of an ionic liquid as a reaction solvent also benefits the environment. Therefore, a recycling study of a catalyst solution in an ionic liquid was conducted as previously mentioned.

The ATRP of MMA was performed again in recovered [Mor$_{1,4}$][BF$_4$] containing catalyst. Figures 8 and 9 show ln([M]$_0$/[M]) versus time and M_n and polydispersity values versus conversion for the fourth reuse times of the catalyst, respectively (see Table II). The results show that ln([M]$_0$/[M]) increased linearly with time and that M_n increased linearly with the conversion, whereas the polydispersities remained relatively narrow. This indicated that the polymerization in the recycled ionic liquid containing catalyst agreed with the features of ATRP. The study
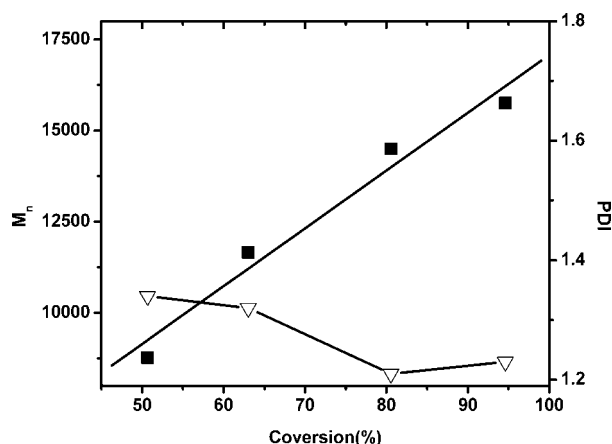

Figure 9 Molecular weight and polydispersity index (PDI) of PMMA as a function of conversion in MMA polymerization mediated by CuBr/bpy in [Mor$_{1,4}$][BF$_4$] in the recovered Mor$_{1,4}$ BF$_4$ containing catalyst at 70°C.

also showed that increasing the dosage of the catalyst could obviously increase the polymerization rate, and the initiating efficiency significantly increased from about 15 to 30–45% in comparison with sample 3 (Table I) in the recycling experiment (first, second, and third reuse times in Table II).

The effect of recycling times on the polymerization was also investigated in this work. As shown in Table II, the [Mor1,4][BF$_4$] solution of the catalyst was able to be recovered and reused. M_w/M_n of the first polymerization for the recycled experiment at 80°C was higher for ATRP. This may be attributed to the fast polymerization rate and relatively high catalyst concentration, which led to obvious radical termination. However, M_w/M_n was relatively acceptable. M_w/M_n decreased in the second and third recycled experiments, and this may be attributed to the small amount of Cu(II) complex produced by the termination of the first recycled experiment. When the reaction temperature was kept at 80°C, the reaction rate was fast, and the conversion reached 90% at 2 h, so the sample could not be withdrawn with a syringe. Therefore, the reaction temperature was reduced to facilitate the sample withdrawal. As reported,[1] good control at a low temperature was also confirmed by M_w/M_n in Table II. However, when other conditions were kept identical (the first, second, and third reuse times in Table II), the molecular weights, polydispersities, and yields of the polymers were almost the same.

CONCLUSIONS

A novel ionic liquid ([Mor1,4][BF$_4$]) was synthesized, and heterogeneous ATRP of MMA was carried out in this ionic liquid with methyl 2-bromopropionate as the initiator and CuBr/bpy as the catalyst. The kinetic study confirmed the living feature of the poly-merization. The bromine-atom-ended PMMA was able to act as a macroinitiator to induce copolymerization with *t*-BMA by conventional ATRP. The resultant polymers were easily isolated, and the ionic liquid containing catalyst could be recovered and reused with a simple treatment.

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