Kinetic Study of Atom Transfer Radical Polymerization of Methyl Methacrylate in Ionic Liquids

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ABSTRACT: The kinetics of methyl methacrylate (MMA) homopolymerization performed by atom transfer radical polymerization (ATRP) is investigated in detail using ethyl-2-bromopropionate (EPN-Br) as initiator, CuBr as catalyst, and pentamethyldiethylenetriamine (PMDETA) as ligand in ionic liquids (ILs) and acetonitrile. ILs in this research covered two different substitutional imidazolium cations and anions including halogen and halogen-free ones. The typical cations include 1-butyl-3-methylimidazolium, 1-ethyl-3-methylimidazolium and the typical anions include bromide, tetrafluoroborate. The effects of solvents, temperature, and reaction ingredients ratios on the polymerization kinetics are all investigated in this article and the apparent energy of activation (ΔE_a^{app}) calculated for the ATRP of MMA in 1-butyl-3-methylimidazolium tetrafluoroborate is 6.95 KJ/mol. The number-average molecular weights (M_n) increase linearly with conversion but are much higher than the theoretical values. It is probably due to the low concentration of deactivator at the early stage of polymerization and the lower bond energy of C-Br in PMMA-Br than that in EPN-Br. Moreover, the catalyst is easily separated from the polymer and the regenerated catalyst is reused for more than three times. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 244–252, 2008

Key words: atom transfer radical polymerization; methyl methacrylate; ionic liquid; kinetics

INTRODUCTION

Atom transfer radical polymerization (ATRP), pioneered by Wang and Matyjaszewski[1] and Sawamoto and coworkers,[2] 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. Several postpolymerization purification methods, including passing the polymer catalyst mixture solutions through columns of silica gel or alumina, catalyst extraction using catalyst-soluble solvents,[7] catalyst immobilization on solid supports, such as silica gel particles or polystyrene beads,[8,9] and catalyst adsorption using ion-exchange resins,[10] have been developed for the removal of catalysts from polymers prepared by ATRP on lab scales. 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.[11] Therefore, how to efficiently and economically remove/reduce the catalyst residue concentration in the polymer products still remains a challenge for ATRP. Ionic liquids (ILs), which are typically comprised of an organic cation and weakly coordinating anions, are expected to make this problem relatively easy to solve. They have many fascinating properties such as nonvolatility,[12] polarity, high thermal stability, possibility of recycling,[13] and specific solvent properties that dissolve several organic, inorganic, and metalo-organic compounds.[14] Thus ATRP using ILs as media has been explored to facilitate the separation of the catalyst from the products. Carmichael et al.[15] first took advantages of the IL 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) as ATRP media. The rate of reaction was increased, the polymers obtained had narrow polydispersities, and were easily separated from the catalyst. Sarbu and Matyjaszewski[16] studied the ATRP of methyl methacrylate (MMA) in the

organic solvents together with ILs containing different counterions and using ferrous salts as catalyst. Organic ligand was needless for the iron-catalyst but it was not the case for copper-catalyst except in ILs with a phosphonate anion. In addition, the catalyst was successfully regenerated after the removal of the polymer and unreacted monomer. Biedroń and Kubisa[17] had reported the influence of substituents (methyl, butyl, hexyl, and dodecyl) on the ATRP of acrylates in [bmim]PF$_6$ with CuBr/pentamethyldiethylenetriamine (PMDETA) as a catalyst. However, the ILs used in the ATRP of MMA for most researches reported previously are based on PF$_6^-$ anion which is a relatively expensive counterion and the researches on ATRP using ILs as solvent were mainly concerned the exploitation of new polymerization systems; little attention had been given to kinetics.

With this article, we illustrate the kinetics of ATRP of MMA initiated by ethyl-2-bromopropionate (EPN-Br)/CuBr/PMDETA in acetonitrile and ILs such as 1-butyl-3-methylimidazolium bromide ([bmim]Br), 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim]BF$_4$), and 1-butyl-3-methyl-imidazolium tetrafluoroborate ([bmim]BF$_4$) in detail.

EXPERIMENTAL

Materials

CuBr (98%), purchased from Acros Organics (Geel, Belgium), was purified by washing with glacial acetic acid, ethanol, and diethyl ether successively.[18] EPN-Br and PMDETA were purchased from Aldrich and distilled prior to use. MMA (CP, 99%) was purchased from Acros Organics and distilled to remove inhibitors under reduced pressure. ILs used in the experiments were synthesized in our laboratory and purified according to the procedure described in the literature[19] from 1-methylimidazole, bromobutane, bromoethane, NaBF$_4$, ethyl acetate, and acetone (all from Acros Organics and used as supplied). Methanol, toluene, and tetrahydrofuran (AR, >99.5%) were used without further purification.

Synthesis of 1-butyl-3-methylimidazolium bromide

Sixty-four milliliters (65.6 g, 0.8 mol) of 1-methylimidazole and 88 mL (109.6 g, 0.8 mol) of bromobutane were added to a round-bottomed flask equipped with a condenser. The reaction mixture was heated at 70°C ± 0.1°C for 72 h, while stirring vigorously under a blanket of nitrogen. After reaction, the resulting white solid was washed three times with 30 mL ethyl acetate, and the traces of solvent were removed under vacuum. About 143.5 g (82%) of 1-butyl-3-methylimidazolium bromide was obtained.

Synthesis of 1-ethyl-3-methylimidazolium bromide

About 128.4 g (84%) of 1-ethyl-3-methylimidazolium bromide was synthesized in a manner similar to the synthesis of 1-butyl-3-methylimidazolium bromide from 1-methylimidazole and 1-bromoethane.

Synthesis of 1-butyl-3-methylimidazolium tetrafluoroborate

About 109.5 g (0.5 mol) of 1-butyl-3-methylimidazolium bromide and 55.0 g (0.5 mol) of NaBF$_4$ were reacted in a mixture of 100 mL acetone at 30°C ± 0.1°C for 2 days. The resulted [bmim][BF$_4$]-sodium bromide-acetone mixture was filtered to remove sodium bromide and the filtrate was taken in a round-bottomed flask to be roto-evaporated at 75°C ± 0.1°C under a vacuum in order to remove any residual acetone. About 85.8 g (76%) of 1-butyl-3-methylimidazolium tetrafluoroborate was obtained.

Synthesis of 1-ethyl-3-methylimidazolium tetrafluoroborate

About 72.2 g (73%) 1-ethyl-3-methylimidazolium tetrafluoroborate was synthesized in a manner similar to the synthesis of 1-butyl-3-methylimidazolium bromide from 1-butyl-3-methylimidazolium bromide and NaBF$_4$.

Polymerization

In a typical experiment, CuBr (0.22 g, 1.5 mmol), PMDETA (0.47 mL, 3 mmol), and MMA (16.05 mL, 0.15 mol) were dissolved in 40.12 g [bmim]BF$_4$. The formed solution was added into five reaction tubes at equimolar amount and bubbled with nitrogen for 5 min. The tubes were tightly sealed with rubber septums and then immersed in an oil bath preset at 80°C for 20 min. Subsequently, 0.04 mL (0.3 mmol) initiator (EPN-Br) was introduced into every tube from a degassed 100-μL syringe. At different time intervals, tubes were withdrawn from oil bath and about 10 mL THF was added to dissolve the reaction mixture and the above layer was precipitated into 150 mL of a 50% aqueous methanol solution. The polymer was finally dried under vacuum at 60°C to constant weight.

In another experiment, the bottom layer containing the IL solution of the transition metal had been retained in the tube from an earlier run. It was washed twice with 3 mL toluene. Then excessive copper metal beads (1 g), PMDETA [19.4% (mol) of the originally charged ligand] and ILs (2 mL) were added and stirred with the retained IL solution at 40°C for 12 h. Having been eliminated the residual copper metal beads, the resulted ILs-Cu(I)/PMDETA

mixture was transferred into a degassed, tightly sealed tube. Then degassed MMA and initiator were added and the polymerization was performed with the procedures same as the first polymerization run.

Measurements

The conversion was determined by gravimetry. The molecular weight and its distribution were determined by a Waters 150C gel permeation chromatography (GPC) in THF at 40°C and flow rate of 1 mL/min. Column calibrations were performed with poly(MMA) standards. The content of Cu(I) was determined by PE 800 atom absorption spectrophotometer ($Cu^{2+} = 0.5$ μg/mL as standard).

RESULTS AND DISCUSSION

Kinetic character of ATRP of MMA and the effect of ILs on the polymerization

ATRP is one of the controlled/"living" radical polymerizations. According to the polymerization mechanism of ATRP, the rate equation was defined as follows [eq. (1)]:[4]

$$R_p = -d[M]/dt = k_p[M\cdot][M] \tag{1}$$

Through integral, it can be written as [eq. (2)]

$$\ln([M]_0/[M]) = k_p[M\cdot]t \tag{2}$$

where $[M]_0$ and $[M]$ are the monomer concentration at initial time and time t, respectively; $[M\cdot]$ is the concentration of radicals; k_p is the specific rate constants for the propagation.

However, in an ideal polymerization process of ATRP, where no chain termination exists or few bimolecular termination and chain transfer reaction occur which can be neglected, the concentration of active centers holds constantly throughout the reaction. So the logarithmic conversion data plotted against time $(\ln([M]_0/[M])$ versus time) should display a first order kinetics with respect to monomer with the slope defined as the apparent propagation rate constant $k_p^{app} = k_p[M\cdot]$, and the molecular weights with low polydispersities (PDI < 1.5) should also increase linearly with the conversion.

Figure 1 shows the linear semilogarithmic plots of ln ($[M]_0/[M]$) versus time for the ATRP of MMA in ILs ([bmim]Br, [emim]BF$_4$, [bmim]BF$_4$) and acetonitrile. The apparent propagation rate constant (k_p^{app}) were 10.4×10^{-5} s^{-1} for [bmim]BF$_4$, 9.1×10^{-5} s^{-1} for [emim]BF$_4$, 7.2×10^{-5} s^{-1} for [bmim]Br, and 3.0×10^{-5} s^{-1} for acetonitrile. The effect of solvents on the apparent propagation rate constant shows that the rate in ILs is higher than that in acetonitrile. It has been found b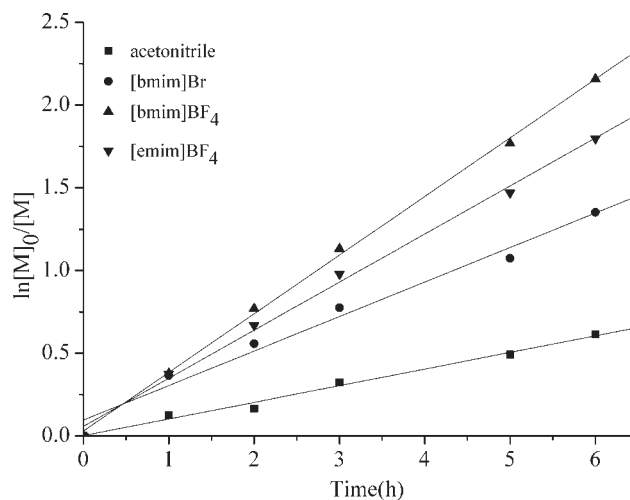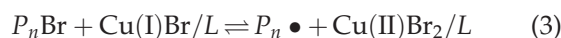y Harrison et al.[20] that the rate constant of MMA propagation (k_p) increases considerably when polymerization is carried out in IL. This may be related to increasing polarity of medium that favors transition state involving charge transfer and/or to complex formation between IL and either monomer or radical. Although according to the authors of the cited paper[20] none of the explanations are entirely satisfactory, the increase of the k_p is an experimentally observed fact. Biedroń and Kubisa[21] and Carmichael et al.[15] reported a similar result and they also consider that either instantaneous concentration of radicals or the propagation rate constant is higher than in organic media. As concerned the three ILs, k_p^{app} of [bmim]BF$_4$ is higher than that of [emim]BF$_4$ which is also higher than that of [bmim]Br. This appears to be due simply to the viscosity of the reaction medium. The rate of termination decreases as the viscosity of the reaction medium increases and thus the concentration of radical is higher. The differences of the viscosity of the three ILs are discussed in detail in the next paragraph.

The evolution of number-average molecular weight M_n and polydispersity (M_w/M_n) with respect to monomer conversion for these systems are shown in Figures 2 and 3, respectively. M_n had increased linearly with monomer conversion but the values seemed much higher than theoretical ones [$M_{n,th} = ([MMA]_0/[EPN-Br]_0) \times 100 \times$ Conversion $+ M_n$ (EPN-Br)]. There may be two reasons for this phenomenon. The main one is coupling termination reaction of radicals. Because an ATRP process works on the basis of equilibrium of radical and dormant chain species [eq. (3)],

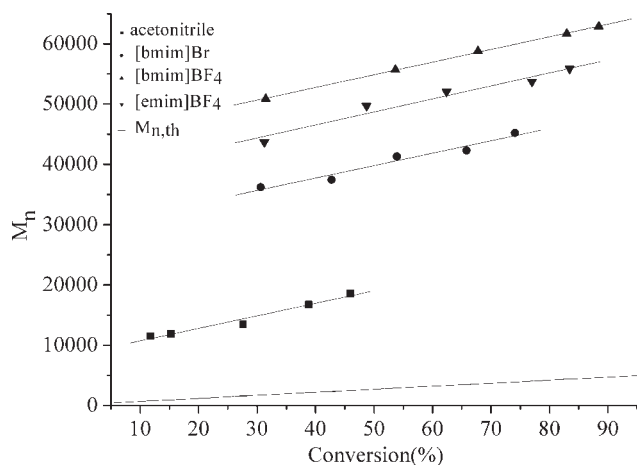$$P_nBr + Cu(I)Br/L \rightleftharpoons P_n \bullet + Cu(II)Br_2/L \tag{3}$$

Figure 1 Kinetic plots for the ATRP of MMA in different solvents at 50°C, $[MMA]_0 : [EPN-Br]_0 : [CuBr]_0 : [PMDETA]_0 = 50 : 1 : 1 : 1$, $V_{solvent} : V_{MMA} = 5 : 3$.

Figure 2 Dependences of M_n on conversion for the ATRP of MMA in different solvents at 50°C, $[MMA]_0 : [EPN\text{-}Br]_0 : [CuBr]_0 : [PMDETA]_0 = 50 : 1 : 1 : 1$, $V_{solvent} : V_{MMA} = 5 : 3$.

But at the beginning of the polymerization, the concentration of Cu(II) is much lower than the Cu(I) concentration and there is no equilibrium of radical and dormant chain species. The amount of Cu(II) halide is not sufficient to deactivate all radicals generated in the initiation process. Therefore, during the initial stage of polymerization, the concentration of the radicals is large enough that the rate of deactivation ($= K_{deact} \times [Cu(II)Br][R\cdot]$) is much slower than the rate of termination ($= K_t \times [R\cdot]^2$). So radical coupling is an important termination process at the early stage of polymerization which consumes the initiators and causes the low initiation efficiency. The polymers obtained are of higher molecular weights than theoretical values. But as Cu(I) reacts with the initiator, the concentration of Cu(II) is higher, more and more radicals are deactivated, and the equilibrium of radical and dormant chain species is established, which results in the low concentration of free radicals and reduction of the termination. Thus, the M_n values increased linearly with the conversion at the relative high conversion with the slope closed to the theoretical one (Fig. 2). So the addition of Cu(II) to the system may be effective for the control of the molecular weights which is certainly an important part of our further studies. The other one is relatively lower bond energy of C-Br in PMMA-Br than that in EPN-Br,[22] and so, in some degree, the monomer is initiated by the polymer produced but not by EPN-Br. Thus the initiation efficiency is low because of the result of incomplete initiation of EPN-Br.

Therefore, both initial radical coupling and incomplete initiation of EPN-Br can decrease the propagation chains and produce the polymers with high molecular weights and low polydispersities.

GPC analysis shows considerable differences in molecular weight and polydispersities for PMMA synthesized in different solvents at the same conversion (shown in Figs. 2 and 3). The molecular weights of PMMA obtained in ILs were much higher than that in acetonitrile. However, the polydispersities of PMMA in ILs were lower than those in acetonitrile. The results were accordant with Strehmel et al. report.[22] The higher viscosity of ILs when compared with acetonitrile presumably is regarded as one reason for this phenomenon ([bmim]Br is in solid state and [bmim]BF$_4$ viscosity is 233 cP at 30°C, the viscosities of [emim]BF$_4$ and acetonitrile are 203 cP[23] and 0.35 cP[24] at 20°C, respectively). Because of the high viscosity polymerization medium, both chain terminations and/or chain transfers were diminished in viscous system. In the case of ILs having the same cation ([bmim]BF$_4$, [emim]BF$_4$), the viscosity of ILs increases with the chain length of the alkyl group substituted at the nitrogen atom of the imidazolium ring. Meanwhile, the longer chain of the substituted alkyl group increases the solubility of PMMA in ILs, which makes the viscosity of the polymerization system grow much higher. Although the mechanism of the polymerization in ILs was not completely understood at the present time, according to the "diffusion-controlled termination" mechanism proposed by Zhang et al.,[25] both of these effects could contribute to the observed relative increase in molecular weight. However, in the case of the ILs having the same cation ([bmim]BF$_4$, [bmim]Br), the molecular weight of PMMA produced in [bmim]Br is lower although the viscosity of [bmim]Br is much higher than that of [bmim]BF$_4$. The reason may be that the viscosity of [bmim]Br is
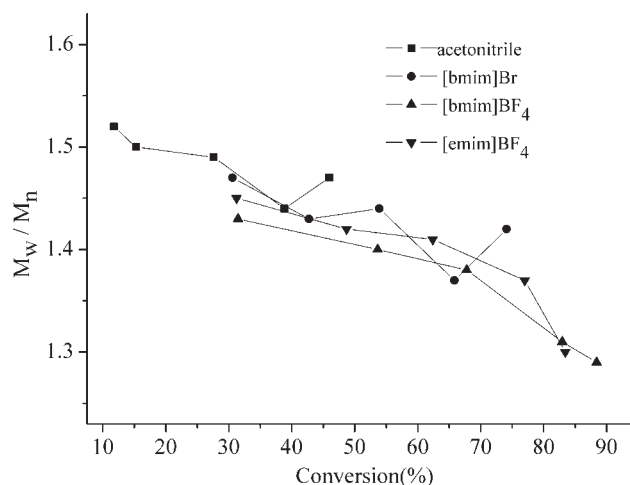

Figure 3 Dependences of M_w/M_n on conversion for the ATRP of MMA in different solvents at 50°C, $[MMA]_0 : [EPN\text{-}Br]_0 : [CuBr]_0 : [PMDETA]_0 = 50 : 1 : 1 : 1$, $V_{solvent} : V_{MMA} = 5 : 3$.

TABLE I
ATRP of MMA in [bmim]BF$_4$ at Different Temperatures

Reaction[a]	Temperature (°C)	Time (h)	Conversion (%)	$M_{n,\text{GPC}}$ ($\times 10^{-4}$)	$M_{n,\text{th}}$[b] ($\times 10^{-3}$)	PDI
1	50	1	31.48	5.09	1.76	1.43
2	50	2	53.65	5.57	2.87	1.40
3	50	3	67.76	5.88	3.57	1.38
4	50	5	82.95	6.17	4.33	1.31
5	50	6	88.43	6.29	4.61	1.29
6	60	1	38.79	4.77	2.12	1.37
7	60	2	58.15	4.92	3.09	1.35
8	60	3	72.38	5.23	3.80	1.30
9	60	5	86.68	5.50	4.52	1.10
10	60	6	89.38	5.64	4.65	1.05
11	70	1	45.52	3.45	2.46	1.47
12	70	2	64.63	3.83	3.42	1.31
13	70	3	74.60	4.33	3.92	1.18
14	70	5	88.88	4.58	4.63	1.16
15	70	6	91.54	4.78	4.76	1.13
16	80	1	52.80	2.76	2.82	1.45
17	80	2	68.81	3.08	3.62	1.38
18	80	3	80.09	3.45	4.19	1.31
19	80	5	91.36	3.57	4.75	1.19
20	80	6	93.10	3.71	4.84	1.14
21	90	1	67.46	1.01	3.56	1.68
22	90	2	76.84	2.00	4.03	1.59
23	90	3	85.00	2.14	4.44	1.50
24	90	5	90.86	2.93	4.73	1.45
25	90	6	92.47	3.09	4.81	1.43

[a] $[\text{MMA}]_0/[\text{EPN-Br}]_0/[\text{CuBr}]_0/[\text{PMDETA}]_0 = 50:1:1:1$, $V_{[\text{bmim}]\text{BF4}} : V_{\text{MMA}} = 5:3$.
[b] $M_{n,\text{th}} = ([\text{MMA}]_0/[\text{EPN-Br}]_0) \times M_n (\text{MMA}) \times \text{Conversion} + M_n (\text{EPN-Br})$.

so high that the radicals are wrapped and cage reaction exists. Thus the reaction rate and the molecular weights decrease while polydispersities increase.

These results confirmed that the ILs especially [bmim]BF$_4$ are indeed excellent solvents for ATRP of MMA which can increase dramatically the rate of polymerization and molecular weights of PMMA while the polydispersities are even lower.

Polymerization kinetics of ATRP of MMA performed in [bmim]BF$_4$

Effect of temperature on the polymerization kinetics

The polymerization of MMA in [bmim]BF$_4$ was performed at different temperatures. The obtained kinetic data were summarized in Table I. Figure 4 shows the kinetic plots of $\ln([M]_0/[M])$ versus time. The apparent propagation rate constants (k_p^{app}) for all the reaction at below 80°C are 9.7×10^{-5} s^{-1} for 50°C, 10.6×10^{-5} s^{-1} for 60°C, 11.4×10^{-5} s^{-1} for 70°C and 12.9×10^{-5} s^{-1} for 80°C. It confirms that the higher the reaction temperature is, the quicker is the reaction. From the Arrhenius plot (Fig. 5), apparent energy of activation (ΔE_a^{app}) for this system is calculated to be 6.95 KJ/mol which is much lower than ATRP of MMA in diphenyl ether

(62.7 KJ/mol[26]) and indicates that ATRP of MMA in ILs is much easier.

The molecular weights of PMMA produced at all temperatures below 80°C display linear dependences on conversion (Fig. 6) and the polydispersities are low (1.05–1.47) (Table I). Although all the molecular
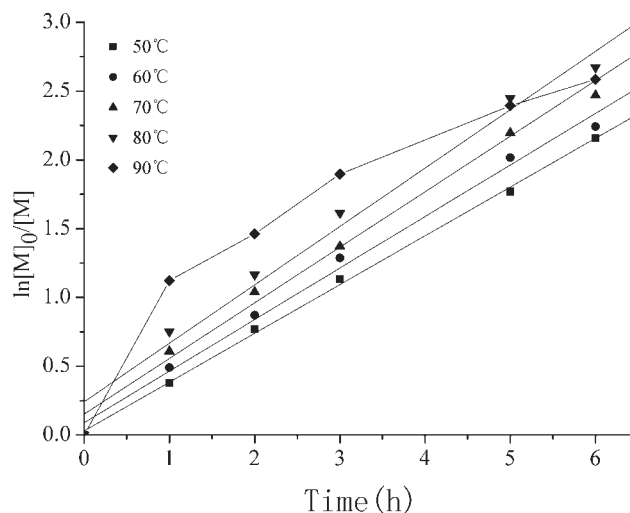
Figure 4 Kinetic plots for the ATRP of MMA at different temperatures in [bmim]BF$_4$, $[\text{MMA}]_0 : [\text{EPN-Br}]_0 : [\text{CuBr}]_0 : [\text{PMDETA}]_0 = 50:1:1:1$, $V_{[\text{bmim}]\text{BF4}} : V_{\text{MMA}} = 5:3$.
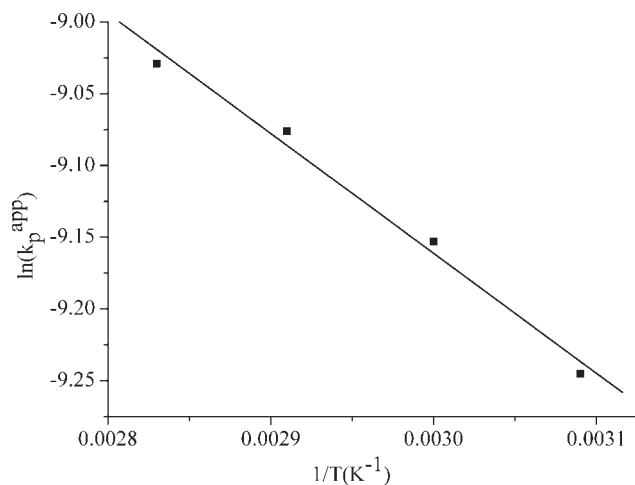
Figure 5 Effect of polymerization temperatures on k_p^{app} for ATRP of MMA, $[MMA]_0 : [EPN\text{-}Br]_0 : [CuBr]_0 : [PMDETA]_0 = 50 : 1 : 1 : 1$, $V_{[bmim]BF4} : V_{MMA} = 5 : 3$.

Figure 6 Dependence of M_n on conversion for the ATRP of MMA in [bmim]BF$_4$ at different temperatures, $[MMA]_0 : [EPN\text{-}Br]_0 : [CuBr]_0 : [PMDETA]_0 = 50 : 1 : 1 : 1$, $V_{[bmim]BF4} : V_{MMA} = 5 : 3$.

weighs are much higher than the theoretical ones, they decline with the elevation of temperature. The higher the temperature is, the quicker the reaction of EPN-Br and CuBr/PMDETA is, and more radicals are produced. Thus the initiating efficiency enhances.

However, when the temperature was up to 90°C, the first-order kinetic plots of polymerization shows significant curvature and the molecular weights, with broader molecular weight distributions (1.43 $< M_w/M_n <$ 1.68) (Table I), increase unlinearly with monomer conversion (Fig. 5). It indicates a progressive decrease of the concentration of active species since the initial phases of polymerization. This is due to the fact that radicals' termination process is fast and cannot be neglected at high temperature.

So the temperature is found to strongly affect the polymerization. For this system, when the tempera-
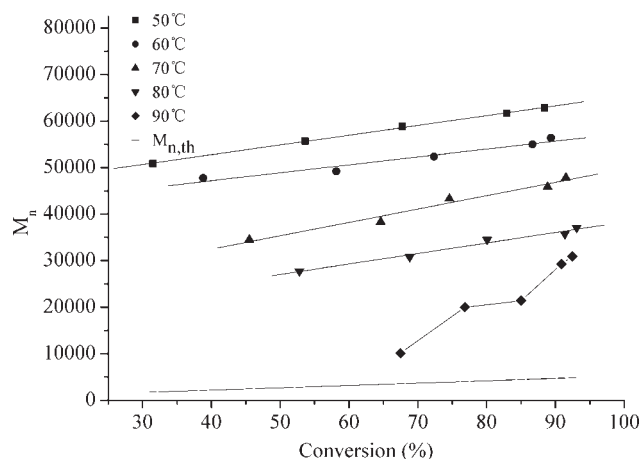
ture is controlled to be at 80°C, a fast and well-controlled polymerization is obtained.

Effect of reaction ingredients ratios on the polymerization kinetics

The effect of various ingredients ratios on the polymerization was also researched. The obtained kinetic data is summarized in Table II. As shown in Figures 7–12, for this system, when the ratios of $[MMA]_0/[EPN\text{-}Br]_0$, $[PMDETA]_0/[CuBr]_0$ and $[CuBr]_0/[EPN\text{-}Br]_0$ are set at ranges of 50 : 1 to 100 : 1, 1 : 1 to 3 : 1 and 1 : 1 to 1.5 : 1, respectively, reactions display linear dependences of $\ln([M]_0/[M])$ on time and molecular weights on conversion. The polydispersities are low (1.14 $< M_w/M_n <$1.43) as expect for living polymerization. But again the initiation efficiency is

TABLE II
The Kinetic Data for PMMA Synthesized in [bmim]BF$_4$ at Different Ratios

Ratios ($[M]_0 : [I]_0 : [C]_0 : [L]_0$)[a]	Conversion (%)	$M_{n,GPC}$ ($\times 10^{-4}$)	$M_{n,th}$[b] ($\times 10^{-3}$)	PDI	k_p^{app} ($\times 10^{-4}$ s^{-1})
50 : 1 : 1 : 1	80.09	3.45	4.19	1.31	1.29
75 : 1 : 1 : 1	58.49	3.86	4.57	1.29	1.17
100 : 1 : 1 : 1	69.13	4.45	7.10	1.25	0.98
125 : 1 : 1 : 1	62.80	6.00	8.04	1.19	0.77
150 : 1 : 1 : 1	38.73	6.79	6.00	1.14	0.45
100 : 1 : 1 : 1.5	84.84	3.73	8.67	1.18	1.40
100 : 1 : 1 : 2	79.57	2.93	8.15	1.35	1.39
100 : 1 : 1 : 2.5	75.37	2.57	7.73	1.35	1.33
100 : 1 : 1 : 3	72.87	2.00	7.48	1.34	1.15
100 : 1 : 1 : 1.6	85.01	3.07	8.70	1.19	1.43
100 : 1 : 1.5 : 2.4	85.11	3.48	8.70	1.20	1.45
100 : 1 : 2 : 3.2	87.83	2.18	8.97	1.43	–
100 : 1 : 2.5 : 4	88.24	2.13	9.01	1.37	–

Reaction time: 3 h; $V_{[bmim]BF4} : V_{MMA} = 5 : 3$; reaction temperature: 80°C.
[a] $[M]_0$, $[I]_0$, $[C]_0$, and $[L]_0$ are the initial concentration of MMA, EPN-Br, CuBr, and PMDETA, respectively.
[b] $M_{n,th} = ([MMA]_0/[EPN\text{-}Br]_0) \times M_n$ (MMA) $\times$ Conversion $+ M_n$ (EPN-Br).
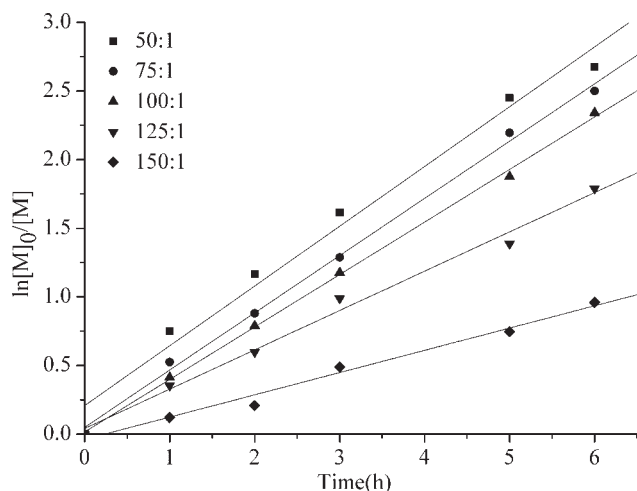
Figure 7 Kinetic plots for the ATRP of MMA in [bmim]BF_4 at different $[MMA]_0/[EPN-Br]_0$ ratios, [EPN-Br]$_0$: [CuBr]$_0$: [PMDETA]$_0$ = 1 : 1 : 1, reaction temperature: 80°C.

Figure 9 Kinetic plots for the ATRP of MMA in [bmim]BF_4 at different $[PMDETA]_0/[CuBr]_0$ ratios, $[MMA]_0$: [EPN-Br]$_0$: [CuBr]$_0$ = 100 : 1 : 1, reaction temperature: 80°C.

low, resulting in polymers that showed higher molecular weights than theoretical values. As concerned different $[MMA]_0/[EPN-Br]_0$ ratios, k_p^{app} decreases from 1.29×10^{-4} (s^{-1}) to 0.45×10^{-4} (s^{-1}) as the ratios increase from 50 : 1 to 150 : 1 (Table II) but the molecular weights increase although they are not proportional to the monomer/initiator ratio which presumably due to some side reactions (Fig. 8). The polydispersities are also lower for the higher $[MMA]_0/[EPN-Br]_0$ ratios (Table II). So we conclude that using ratio of monomer to initiator of 100, polymer with high molecular weight and low polydispersity is obtained. As $[MMA]_0/[EPN-Br]_0$ ratio is set at 100 : 1, k_p^{app} increases significantly when $[PMDETA]_0/[CuBr]_0$ ratios increase from 1 : 1 to 1.5 : 1 and when the $[PMDETA]_0/[CuBr]_0$ reached to 1.6 (2.4 : 1.5), it increased to the maximum (Table II).
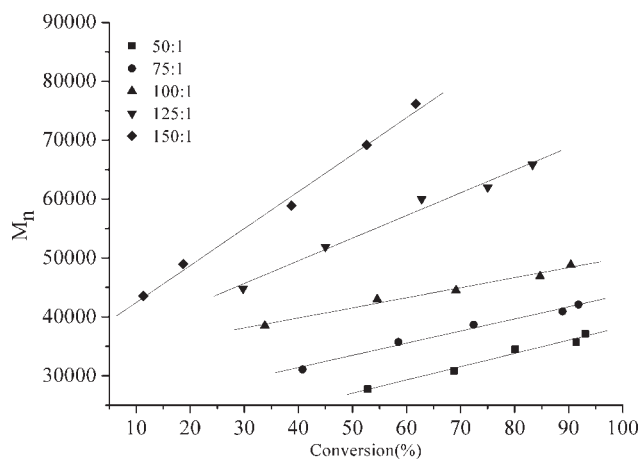
This is due to the limited coordinate sphere of active Cu(I) center. For an ligand/Cu(I) ratio of 1, there is insufficient ligands for Cu(I) to coordinate, the solution may take long time to become homogenous while Cu(I) halide dissolves much faster when an excess amount of ligand is used. So by increasing the $[PMDETA]_0/[CuBr]_0$ ratio, the polymerization rate elevated dramatically. But when the $[PMDETA]_0/[CuBr]_0$ reached to 1.6, the coordinate sphere was saturated, higher concentration of PMDETA would block the transfer of halogen atom and thus slow the polymerization rate. Figure 10 shows that the disparity between $M_{n(GPC)}$ and $M_{n(theory)}$ declines for the higher $[PMDETA]_0/[CuBr]_0$ ratios. The reason presumably is that higher $[PMDETA]_0/[CuBr]_0$ ratios would lead to the formation of more active catalyst center, thus resulting in

Figure 8 Dependence of M_n on conversion for the ATRP of MMA in [bmim]BF_4 at different $[MMA]_0/[EPN-Br]_0$ ratios, [EPN-Br]$_0$: [CuBr]$_0$: [PMDETA]$_0$ = 1 : 1 : 1, reaction temperature: 80°C.
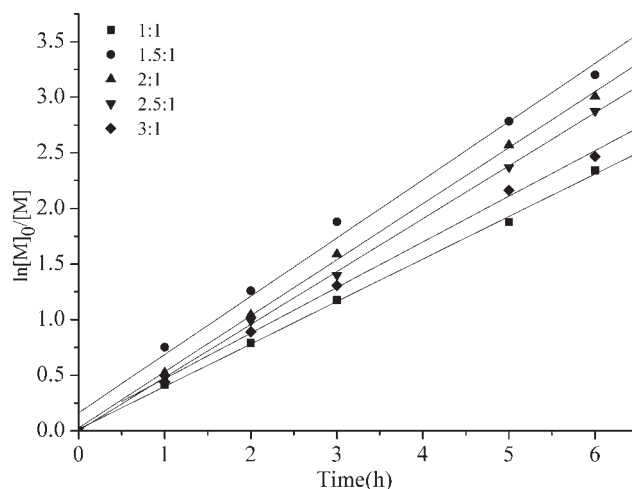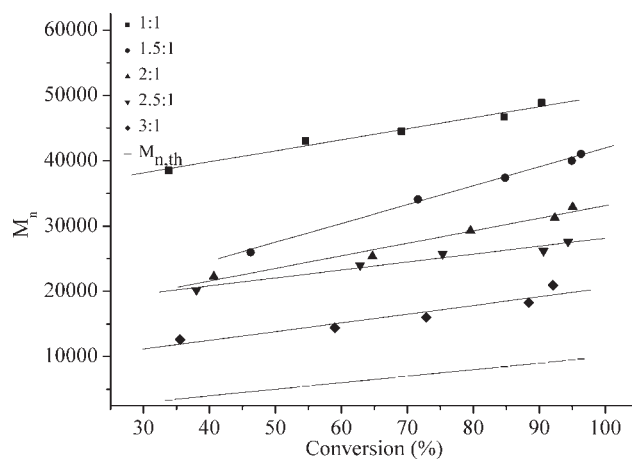

Figure 10 Dependence of M_n on conversion for the ATRP of MMA in [bmim]BF_4 at different $[PMDETA]_0/[CuBr]_0$ ratios, $[MMA]_0$: [EPN-Br]$_0$: [CuBr]$_0$ = 100 : 1 : 1, reaction temperature: 80°C.
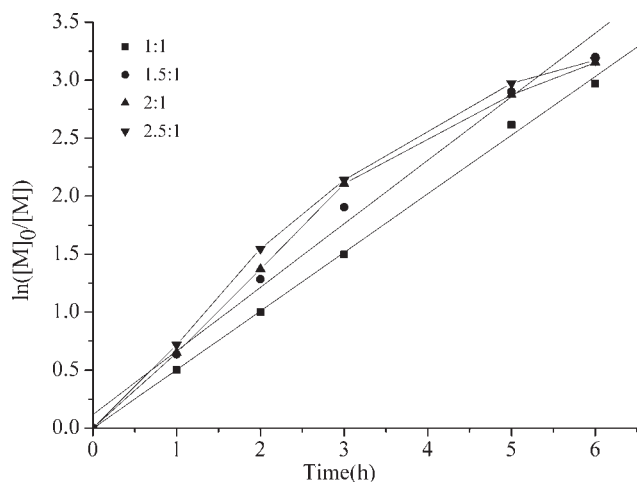
Figure 11 Kinetic plots for the ATRP of MMA in [bmim]BF$_4$ at different [CuBr]$_0$/[EPN-Br]$_0$ ratios, [MMA]$_0$: [EPN-Br]$_0$ = 100 : 1, [CuBr]$_0$: [PMMDETA]$_0$ = 1 : 1.6, reaction temperature: 80°C.

Figure 12 Dependence of M_n on conversion for the ATRP of MMA in [bmim]BF$_4$ at different [CuBr]$_0$/[EPN-Br]$_0$ ratios, [MMA]$_0$: [EPN-Br]$_0$ = 100 : 1, [CuBr]$_0$: [PMMDETA]$_0$ = 1 : 1.6, reaction temperature: 80°C.

higher initiation efficiency. Fixing the [PMDETA]$_0$/[CuBr]$_0$ ratio to 1.6, the effect of different [CuBr]$_0$/[EPN-Br]$_0$ ratios is also investigated. The data in Table II shows that when [CuBr]$_0$/[EPN-Br]$_0$ ratios increase from 1 : 1 to 1.5 : 1, k_p^{app} increases slightly. But the molecular weight is not controlled well with the slope of the plot of molecular weight versus conversion much higher than the theoretical one when [CuBr]$_0$/[MMA]$_0$ ratio is at 1.5 : 100 (Fig. 12).

However, when the [CuBr]$_0$/[EPN-Br]$_0$ ratio is at 2/1 or 2.5/1, the significant curvature of the first-order kinetic plots of monomer consumption are observed (Fig. 11) and the molecular weights increase unlinearly with conversion (Fig. 12). The polydispersities are even broader (1.37 < M_w/M_n < 1.53) (Table II) and the initiation efficiency is higher. These lead to the conclusion that high catalyst concentration increases the reaction rate but too high a concentration results in the generation of a high concentration of radicals which would lead to termination and thus cause deterioration in the degree of control over the polymerization.

Taking all the effects of ratios on the polymerization into consideration, we have drawn the conclu-
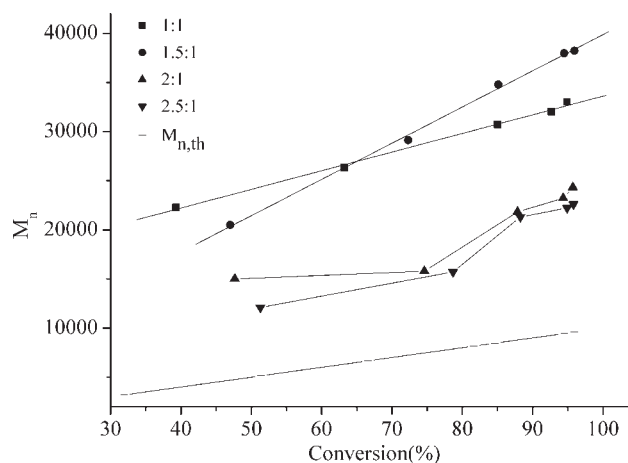
sion that when the ratio of [MMA]$_0$: [EPN-Br]$_0$: [CuBr]$_0$: [PMDETA]$_0$ is set at 100 : 1 : 1 : 1.6, polymerization is under best control for all studied systems.

Catalyst regeneration and reuse

The Cu^I catalyst is very soluble in [bmim][BF$_4$] which in turn is immiscible with organic solvents, such as tetrahydrofuran. This allows the reaction solution to be washed with tetrahydrofuran so as to extract the poly(MMA) (PMMA) product. The catalyst remains in the IL layer allowing isolation of the polymer product while leaving the catalyst solution for potential reuse. Analysis of the PMMA (reaction 1 in Table III) for residual copper by atom absorption spectrophotometer shows a copper content of 2.9 × 10^{-3} % in respect to the mass of PMMA obtained (2% expected if no copper is removed).

Furthermore, the recycled catalysts could still effectively mediate polymerizations in a well-controlled living manner. The conversion remains nearly the same and the polymers produced are of

TABLE III
Molecular Mass and Conversion Data for PMMA Synthesized in Recovered Ionic Liquids

Reaction	Recycle times	Conversion (%)	$M_{n,GPC}$ (×10^{-4})	PDI
1	0	85.01	3.07	1.25
2	1	80.24	2.34	1.23
3	2	82.17	2.53	1.17
4	3	84.21	2.89	1.21
5	4	83.79	2.72	1.27

[bmim]BF$_4$; [MMA]$_0$/[EPN-Br]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 100 : 1 : 1 : 1.6; reaction temperature: 80°C; reaction time: 3 h.

high molecular weights and very low polydispersities as shown in Table III.

CONCLUSIONS

Polymerization of MMA has been conducted successfully by ATRP in the selected three ILs and acetonitrile. The IL [bmim]BF$_4$ has been demonstrated to be a preferable solvent for CuBr/PMDETA-mediated living radical polymerization of MMA. The effects of reaction temperature and reaction ingredients ratios on the kinetics show that polymerization performed in [bmim]BF$_4$ are in better control when the temperature is set at 80°C and the ratio of [MMA]$_0$: [EPN-Br]$_0$: [CuBr]$_0$: [PMDETA]$_0$ is set at 100 : 1 : 1 : 1.6. ATRP of MMA in [bmim]BF$_4$ is much easier than that in diphenyl ether. The polymer is recovered essentially copper free by a simple solvent wash and the IL [bmim]BF$_4$-catalyst mixture is recycled and reused for more than three times successfully. Although a great deviation of the molecular weights for the resulting products from the theoretical values is observed, the procedure proposed in this work still maintains the usual advantages of ATRP leading to good linear dependence of molecular weights on the conversion and low polydispersities. According to our investigation in the evolution of M_n over the full conversion range, we deduce that the partial loss of control is mainly due to the termination of bimolecular coupling caused by the low concentration of Cu(II) at early stage of polymerization which breaks the equilibrium of radical and dormant chain species. However, it is possible that the addition of Cu(II) in the polymerization system will permit better control over the "livingness" of the polymerization. Moreover, the incomplete initiation of EPN-Br as a result of relatively lower bond energy of C-Br in PMMA-Br than that in EPN-Br is presumably to be another reason for the low initiation efficiency. So further studies involving the control of the molecular weights and the synthesis of diblocks are certainly required and now are in progress in our laboratories.

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