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Reverse atom transfer radical polymerization of methyl methacrylate in imidazolium ionic liquids

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Abstract

Reverse atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) employing 2,2-azobisisobutyronitrile (AIBN)/$CuCl_2$/bipyridine(bipy) as the initiating system was approached at 80 °C in two ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4mim][BF_4]) and 1-dodecyl-3-methylimidazolium tetrafluoroborate ([C_{12}mim][BF_4]), respectively. The polymerization in [C_{12}mim][BF_4] proceeded in a well-controlled manner as evidenced by kinetic studies, end group analysis, chain extension, and block copolymerization results, but not in [C_4mim][BF_4] presumably due to poor solubility of PMMA in it. The kinetic study of reverse ATRP of MMA in recycled [C_{12}mim][BF_4] suggested that this ionic liquid could be re-used as reaction solvent after simple purification, without affecting the living nature of polymerization.

Keywords: Reverse ATRP; Methyl methacrylate; Imidazolium ionic liquids

1. Introduction

The advent of 'living' free radical polymerization has provided powerful tools to synthesize polymers with predictable molecular weight, narrow polydispersity and well-defined molecular architecture [1–6]. Among various available 'living' free radical polymerization techniques, atom transfer radical polymerization (ATRP) and reverse atom transfer radical polymerization (rATRP) are the most extensively studied systems [2,3,7–20]. In both cases, a transition metal complex is used to catalyze the redox process, which is responsible for the generation and concentration mediation of the propagating species. Thus, the quantity and solubility of catalyst added in reaction media are crucial to promote the radical polymerization in a well-controlled manner. In addition, removal of catalyst from the resultant polymer to avoid contamination is unavoidable.

Room temperature ionic liquids (RTILs), which are molten organic salts at or near room temperature, have led to an increased interest in chemical research as well industry areas. RTILs have been used as environmental benign solvents for a number of organic reactions and polymerizations as they are nonvolatile, nonflammable, recyclable, and have good solubility to many organic and inorganic compounds [21,22]. Haddleton et al. [23] first reported ATRP of MMA in 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]), a frequently used room temperature ionic liquid. It was found that the reaction rate was higher and the required polymerization temperature was lower in [C_4mim][PF_6] than those in bulk or other organic solvents. In addition, the copper (II) contamination of resultant MMA was reduced due to the good solubility of catalyst in the ionic liquid. Sarbu and Matyjaszewski [24] studied the effect of counterions of ionic liquids on ATRP of MMA. They found iron catalyzed ATRP could be accomplished without using organic ligands in the presence of ionic liquids they employed. However, the organic ligand was needed for copper catalyzed ATRP of MMA in ionic liquids with a halide or a carbonate anion. They also found that the ionic liquids containing catalysts were easily separated from the resultant polymer and un-reacted monomer, and could be re-used without affecting 'living'

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nature of the subsequent ATRP of MMA in it. Other interesting results in this area have been achieved by Kubisa [25,26], Xi [27], Mays [28], and their coworkers.

Recently, we carried out a reverse ATRP of MMA in $[C_4mim][PF_6]$ [29]. The initiating system 2,2-azobisisobutyronitrile (AIBN)/$CuCl_2$/bipyridine(bipy), which had been reported not being able to promote a well-defined process of MMA in bulk [3], was found to effectively mediate the radical polymerization of MMA in a controlled manner in this kind of solvent. The obtained PMMA with well-defined molecular weight and narrow polydispersity could act as macroinitiator to undergo chain extension or copolymerization with styrene. Due to good solubility of transition metal salts in $[C_4mim][PF_6]$, much less amount of catalyst was required to gain control of polymerization. 1,3-Disubstituted imidazolium tetrafluoroborates are commonly used as ionic liquids. Compared with other imidazolium ionic liquids containing PF_6^- anion, they have higher solvating power for transition metal salts [30]. In the present work, we reported the reverse ATRP of MMA induced by AIBN/$CuCl_2$/bipyridine in both 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim][BF_4]$) and 1-dodecyl-3-methylimidazolium tetrafluoroborate ($[C_{12}mim][BF_4]$). The recycling of $[C_{12}mim][BF_4]$ was also attempted.

2. Experimental

2.1. Materials

1-Methylimidazole (99%, Acros), 1-bromododecane (99%, Beijing Chemical Co.), tetrafluoroboric acid (40 wt% solution in water, Beijing Chemical Co.) and 2,2′-bipyridine (bipy, Beijing Chemical Co., AR) were used as purchased. Methyl methacrylate (Beijing Chemical Co., AR) was purified first by silica column to remove inhibitor, followed by vacuum distillation from CaH_2. 2,2′-Azobisisobutyronitrile (AIBN, Wuhan Chemical Co., AR) was recrystallized from ethanol and dried under vacuum. Tetrahydrofuran (THF) and chlorobenzene (all from Beijing Chemical Co., AR) were distilled over CaH_2. CuCl (Beijing Chemical Co., AR) was purified according to a literature method [14]. $CuCl_2$ (99%, Beijing Chemical Co.) was dried in oven at 80 °C for 24 h before use. 1-Butyl-3-methylimidazolium ($[C_4mim][BF_4]$) and 1-dodecyl-3-methylimidazolium tetrafluoroborates ($[C_{12}mim][BF_4]$) were prepared following the literature method [31]. Other solvents and reagents were used without further purification except as noted.

2.2. Polymerization

To a dry glass tube, 0.014 g (0.1 mmol) of $CuCl_2$, 0.500 g (5.0 mmol) of MMA, 0.031 g (0.2 mmol) of bipyridine, 0.008 g (5×10^{-2} mmol) of AIBN and 1.500 g of ionic liquid were added. The mixture was degassed by three freeze-pump-thaw cycles and sealed under vacuum. The tube was placed in a water bath at 80 °C maintained by a thermostat. After a required time, the tube was placed into an ice bath to stop the reaction. The reaction mixture was diluted with 10 ml of THF and added dropwise into 200 mL of methanol. After filtration and washing with 3×50 mL of methanol, PMMA was obtained. The polymer was dried under infrared light for 24 h and the monomer conversion was determined gravimetrically.

2.3. Chain extension

Chain extension was performed employing conventional ATRP technique. To a polymerization tube, 0.033 g (6.23×10^{-3} mmol) of PMMA macroinitiator, 0.303 g (3.03 mmol) of MMA, 0.011 g (0.11 mmol) of CuCl, 0.082 g (0.53 mmol) of bipyridine, and 0.916 g of chlorobenzene were added. After three freeze-pump-thaw cycles, the tube was sealed under vacuum and placed into a water bath at 95 °C for 8 h. The reaction mixture was diluted with 10 ml of THF and added dropwise into 200 mL of methanol. After filtration, washing with 3×50 mL of methanol, drying under infrared light, the chain-extended PMMA was obtained.

2.4. Block copolymerization

The block copolymerization was carried out using a similar method as in chain extension except styrene was used in place of MMA. In addition, the reaction temperature, 120 °C, was higher than that in above chain extension-reaction.

2.5. Polymerization in recovered ionic liquid

To a dry glass tube, predetermined quantities of $CuCl_2$, MMA, bipyridine, AIBN and recovered ionic liquid were added. The mixture was degassed by three freeze-pump-thaw cycles and sealed under vacuum. The tube was placed in a water bath at 80 °C maintained by a thermostat. After 3.7 h, the tube was placed into an ice bath to stop the reaction. After filtration and washing with 3×50 mL of methanol, PMMA was obtained. The polymer was dried under infrared light for 24 h.

2.6. Measurements

The number-averaged molecular weights (M_n) and molecular weight distributions (PDI) of PMMA samples were measured at 35 °C on a Waters 2410 GPC instrument with a set of HT2 + HT3 + HT4 μ-Styragel columns (Waters, pose size: 10^2, 10^3 and 10^4 Å) calibrated with a series of standard polystyrenes. THF was used as eluent (1.0 mL/min). ^1H NMR spectrum was taken at 25 °C on a Bruker ARX400 NMR spectrometer using chloroform-*d* as solvent and tetramethylsilane (TMS) as an internal reference.

3. Results and discussion

3.1. Reverse ATRP of MMA

Reverse ATRP of MMA was carried out at 80 °C in [C_4mim][BF_4] and [C_{12}mim][BF_4], respectively, with AIBN/$CuCl_2$/bipy as an initiating system. All reagents including initiator, transition metal salts, organic ligand and monomer were soluble in both ionic liquids. But PMMA with high molecular weight was not readily soluble in [C_4mim][BF_4]. The reaction mixture in [C_4mim][BF_4] kept homogeneous until the monomer conversion was less than 9.8% and M_n was less than 4.68×10^3. While the polymerization proceeded further, PMMA precipitated and led to an ill-controlled radical reaction as seen in Fig. 1. The solubility of PMMA in [C_{12}mim][BF_4], which had a long dodecyl group in molecule, was much higher than that in [C_4mim][BF_4], indicating a strong dependence of solvating power of ionic liquids on the length of the substituted groups of the cations. The reaction mixture remained homogeneous in [C_{12}mim][BF_4] at 80 °C until the monomer conversion reached 80%. Although the polymer precipitated when the monomer conversion exceeded 80%, the polymerization still proceeded in a well-controlled manner until the 92% of monomer was reacted. However, when the monomer conversion was above 92%, the polymerization became ill-controlled as shown in Fig. 2.

In order to prove the living nature of reverse ATRP of MMA in [C_{12}mim][BF_4], kinetic studies were performed. Fig. 3 showed the plot of ln([M]$_0$/[M]) versus reaction time. The linear first order kinetic plot indicated that the radical concentration was constant throughout the polymerization.

The relationship between the number-averaged molecular weights (M_n) and monomer conversion was shown in Fig. 4. While the molecular weight was increased linearly with an increase in monomer conversion, the polydispersity of PMMA obtained decreased at first and then kept almost unchanged. Fig. 5 showed the GPC curves of the obtained polymers. All were narrow and symmetrical.

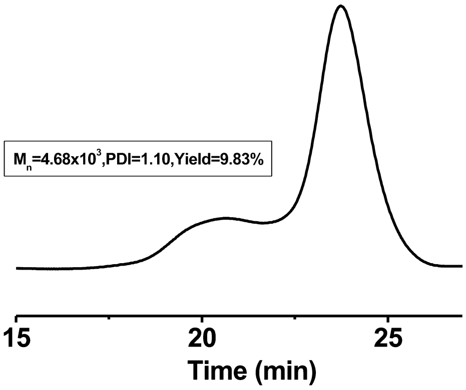

Fig. 1. GPC curve of PMMA polymerized in [C_4mim][BF_4].

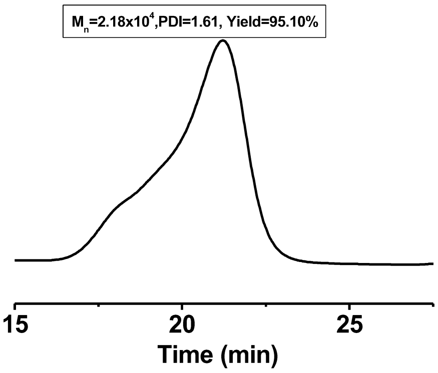

Fig. 2. GPC curve of PMMA polymerized in [C_{12}mim][BF_4].

It had been reported that the AIBN/$CuCl_2$/bipy initiating system, was not able to promote the living radical polymerization of MMA in bulk because of the poor solubility of the catalyst [3]. It was known that imidazolium ionic liquids containing BF_4^- anion were good solvents for inorganic salts [30]. Therefore, the 'living' characteristics of reverse ATRP of MMA might be attributed to good solubility of $CuCl_2$ in [C_{12}mim][BF_4].

It should be noted that the initiating efficiency based on $f = M_{n,th}/M_{n,GPC}$ ($M_{n,th} = 100 \times (\Delta[MMA]/2[AIBN]_0) \times$ conv.) was lower in [C_{12}mim][BF_4] than that in conventional organic solvent. There might be two reasons for this phenomena. One was the cage effect of high viscous ionic liquid which led to more coupling reaction of primary radicals. The other one was relatively lower solubility of PMMA in [C_{12}mim][BF_4] than that in conventional organic solvents like anisole and chlorobenzene, which was reflected by the fact that PMMA precipitated at later stage of polymerization. The high molecular weight of PMMA was reasonably attributed to prolonged life of the propagation radicals.

3.2. End group analysis of obtained PMMA

Fig. 6 showed the 400 MHz ^{1}H NMR spectrum of a

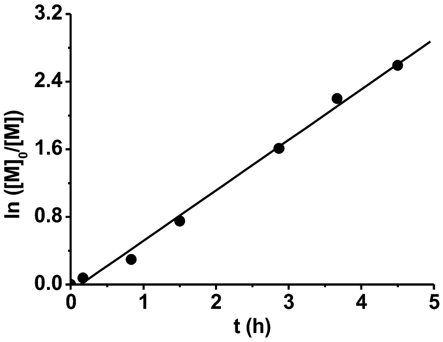

Fig. 3. The relationship between ln([M]$_0$/[M]) and reaction time. The polymerization conditions: [MMA]/[AIBN]/[$CuCl_2$]/[bipy] = 100:1:2:6 (molar ratio), [MMA]/[ionic liquid] = 1:3 (w/w), T = 80 °C.

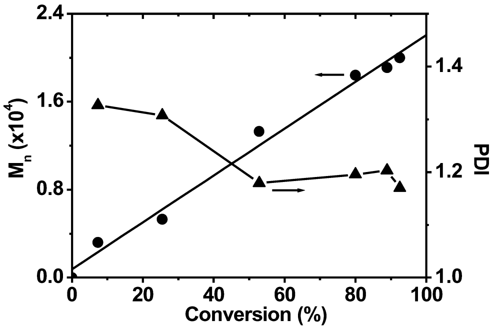

Fig. 4. Plots of the number-averaged molecular weight (M_n) and polydispersity versus conversion. Polymerization conditions as in Fig. 3.

well-defined PMMA. It was well consistent with the chemical structure of PMMA [32]. The signals at 0.82–1.25, 1.40–2.06 and 3.40–3.84 ppm were attributed to the protons of α-methyl groups (peak *a*), methylene groups (peak *b*) and methoxy groups (peak *c*), respectively. In addition, the absorptions at 3.65 ppm (peak *c*(*ω*)), 2.49 ppm (peak *b*(*ω*)) and 1.25 ppm (peak *a*(*ω*)) proved the presence of the end group, $-CH_2CCl(CH_3)(COOCH_3)$.

From ^1H NMR spectrum, the number average molecular weight ($M_{n,NMR}$) of PMMA was estimated from the ratio of the methylene protons b and the terminal one, *b*(*ω*). The $M_{n,NMR}$ value of 2.49×10^4 was close to that from GPC (2.00×10^4), another evidence of well-defined PMMA with chlorine terminal substituent.

3.3. Chain extension with MMA

With conventional ATRP technique, the chain extension was carried out in chlorobenzene. The chlorine atom ended PMMA was employed as a macroinitiator, CuCl as a catalyst and 2,2′-bipyridine as a ligand. The polymerization temperature was kept at 95 °C. Fig. 7 showed the GPC curves of PMMA before and after chain extension. The increase in molecular weight was evidenced by the obvious shift of the GPC trace of chain-extension-PMMA toward left.

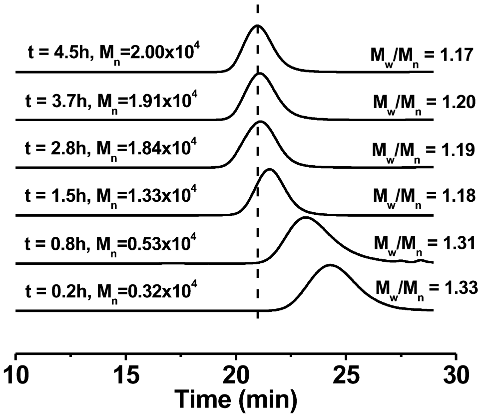

Fig. 5. GPC traces of PMMA obtained. Polymerization conditions as seen in Fig. 3.

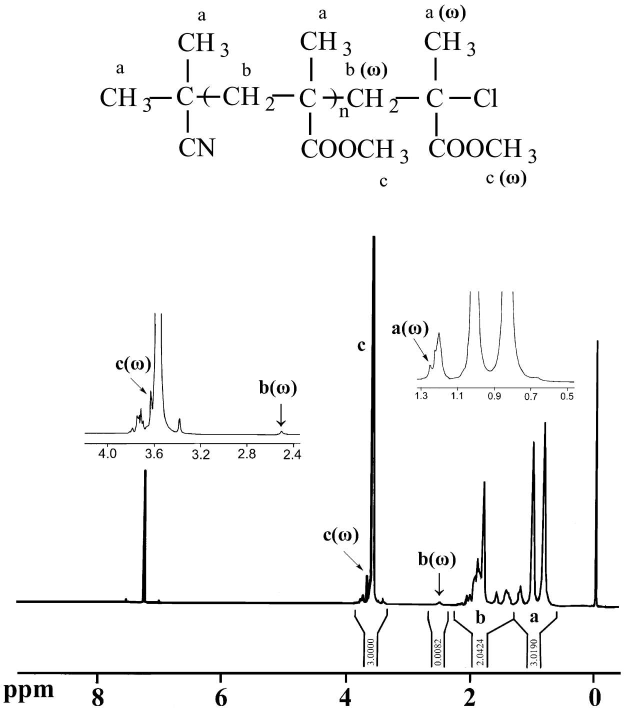

Fig. 6. ^1H NMR spectrum of the PMMA polymerized in [C_{12}mim][BF_4] at 80 °C. $M_n = 2.00 \times 10^4$ g/mol, $M_w/M_n = 1.17$ (in $CDCl_3$, 400 MHz).

3.4. Block copolymerization with styrene

Block copolymerization is another commonly used method to prove the living characteristics of a polymerization [13,14]. We employed two chlorine atom ended PMMA molecules obtained through rATRP to initiate conventional ATRP of styrene. The polymerization was carried out with a similar method to the above chain extension experiment except that styrene was used instead of MMA and the reaction temperature was raised to 120 °C.

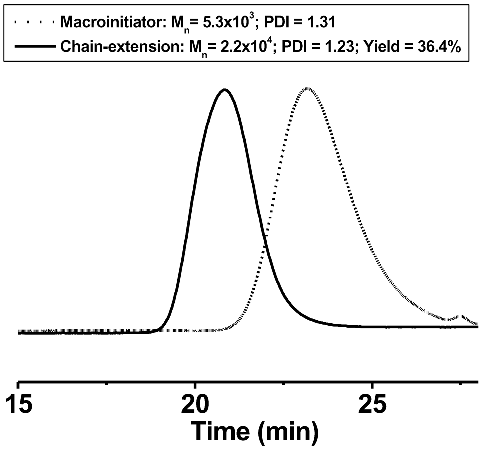

Fig. 7. GPC curves of PMMA before and after chain extension via ATRP at 95 °C. Reaction conditions: MMA = 0.303 g, PMMA macroinitiator = 0.033 g, CuCl = 0.011 g, bipy = 0.082 g, chlorobenzene = 0.916 g, *t* = 8 h.

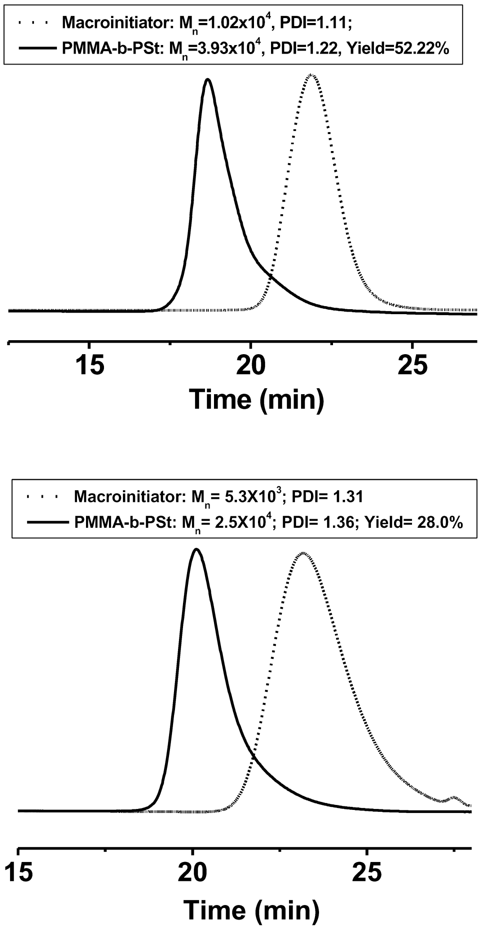

Fig. 8. GPC curves of PMMA macroinitiator and resulting PMMA-*b*-PSt via ATRP at 120 °C. Reaction conditions: St = 0.515 g, PMMA macroinitiator = 0.050 g, CuCl = 0.011 g, bipy = 0.076 g, chlorobenzene = 1.520 g, *t* = 48 h.

Two block copolymers PMMA-*b*-PSt with different molecular weights were prepared. Fig. 8 showed the GPC curves of the two polymers.

3.5. Recycling of [C$_{12}$mim][BF$_4$]

As a reaction solvent, it was very important for ionic liquids to be separated from other reagents and products and to be re-used. To prove this, the [C$_{12}$mim][BF$_4$] was recovered after polymerization. When polymerization was stopped, the reaction mixture was diluted with THF and added slowly into large amount methanol. The pure PMMA was obtained after filtration and washing with methanol. The filtrate was allowed to pass through a neutral aluminum oxide column to remove copper complex, and to evaporate in reduced pressure to remove methanol, THF and unreacted monomer. The recovered [C$_{12}$mim][BF$_4$] was dried at 70 °C in vacuum.

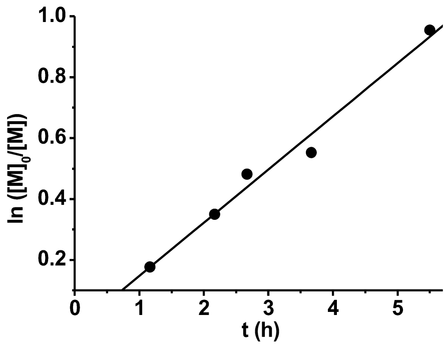

Fig. 9. The relationship between ln([M]$_0$/[M]) and polymerization time in recovered [C$_{12}$mim][BF$_4$] at 80 °C. Polymerization conditions as in Fig. 3.

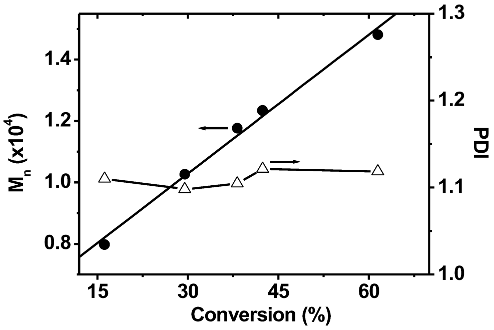

Fig. 10. Plots of the number-averaged molecular weights and molecular distributions of PMMAs polymerized in recovered [C$_{12}$mim][BF$_4$] at 80 °C versus monomer conversion.

The reverse ATRP of MMA was performed again in recovered [C$_{12}$mim][BF$_4$]. Fig. 9 displayed the plot of ln([M]$_0$/[M]) versus time, a linear relationship was observed revealing a living character of the polymerization process.

The plots of the number-averaged molecular weights and the polydispersities versus conversion were shown in Fig. 10. While M_n increased linearly with conversion, polydispersities remained relatively narrow. Fig. 11 depicted the GPC traces of the obtained PMMAs.

The effect of recycling times on polymerization was also investigated in this work. As shown in Table 1, [C$_{12}$mim][BF$_4$] was able to be recovered and re-used. When other conditions were kept identical, the molecular weights, polydispersities, and yields of the polymers

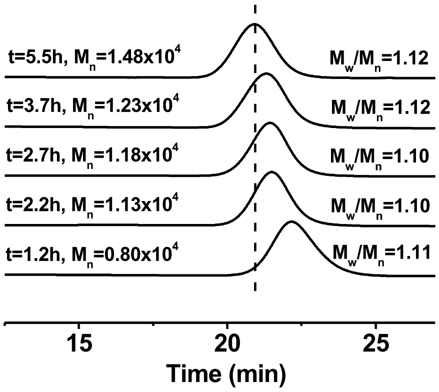

Fig. 11. GPC traces of PMMAs polymerized in the recovered [C$_{12}$mim][BF$_4$] at 80 °C.

Table 1
Results of reverse ATRP of MMA in recovered [C_{12}mim][BF_4]

Re-used times[a]	Yield (%)	M_n ($\times 10^4$)	PDI
1	53.9	1.29	1.14
2	42.5	1.12	1.10
3	42.4	1.23	1.12
4	53.5	1.20	1.15

[a] [MMA]/[AIBN]/[$CuCl_2$]/[bipy] = 100:1:2:6 (molar ratio), [MMA]/[ionic liquid] = 1:3 (w/w), $T = 80$ °C, time = 3.7 h.

obtained in [C_{12}mim][BF_4], which was recycled different times, were almost same.

4. Conclusions

A well-controlled reverse ATRP of MMA was achieved in an imidazolium ionic liquid, [C_{12}mim][BF_4], with AIBN/$CuCl_2$/bipy as the initiating system. The chlorine atom ended PMMA was able to act as macroinitiator to induce copolymerization with styrene by conventional ATRP. The resultant polymers and the catalysts were easily isolated. The ionic liquid could be recovered and reused with simple treatment.

Acknowledgements

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