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Reverse ATRP of ethyl acrylate with ionic liquids as reaction medium

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ABSTRACT

Novel ionic liquids, [C_{12}mim][BF_4], [C_8mim][BF_4] and [C_4mim][BF_4], were firstly used as the reaction media for reverse atom transfer radical polymerization of ethyl acrylate (EA) initiated by azobisisobutyronitrile (AIBN) with $CuBr_2$ and *N*,*N*,*N*′,*N*″,*N*″-pentamethyl diethylene triamine (PMDETA) as catalyst and ligand. Compared with the polymerization in [C_8mim][BF_4] and [C_4mim][BF_4], the polymerization in [C_{12}mim][BF_4] not only showed better control of molecular weight and narrower molecular weight distribution but also provided more rapid reaction rate with the ratio of [EA]:[AIBN]:[$CuBr_2$]:[PMDETA] at 400:1:3:4. Block copolymer PEA-b-PSt was obtained via a conventional ATRP process in [C_{12}mim][BF_4] by using the resulting PEA as macroinitiator. [C_{12}mim][BF_4] and $CuBr_2$/PMDETA could be easily recycled and reused and had no effect on the living nature of reverse atom transfer radical polymerization of EA.

1. Introduction

Poly(ethyl acrylate) (PEA) is an industrially important polymer because of its low glass transition temperature, durability and the potential use as the soft segment in thermoplastic elastomer and has widespread uses in plastics, fibers, adhesives and surface coatings [1]. PEA is generally prepared via conventional radical polymerization but with unpredictable molecular weight and broad molecular weight distribution [2]. In order to obtain the well-defined PEA, living/controlled free radical polymerization techniques could be employed to prepare polymers with predictable molecular weight, narrow polydispersity and well-defined architecture [3,4]. Atom transfer radical polymerization (ATRP) is the most powerful, versatile, simple and inexpensive method in living/controlled free radical polymerization [5–7]. ATRP of ethyl acrylate (EA) has been studied systemically to obtain PEA with high molecular weight and narrow polydispersity [8–10]. To overcome the oxidation of the catalyst M_n^t/LX in ATRP, the use of conventional radical initiators in the presence of complexes of transition metals in their higher oxidation state has been reported and referred to as reverse ATRP by Matyjaszewski and co-workers [11–13] and the other researchers [14]. However, it is evident from the literature that no work has been reported so far for reverse ATRP of EA.

Both ATRP and reverse ATRP processes involve an equilibrium reversible redox reaction between a transition metal catalyst complex and the initiator, or dormant species forming a radical and the metal halide in a higher oxidation state [15–21]. As a result, a large amount of catalyst and higher solubility of catalyst in reaction media are ordinarily needed to achieve a higher polymerization rate. The removal of catalyst from the resultant polymer to avoid contamination becomes very necessary and important. Novel reaction media is being developed. Ionic liquids are organic salts that are liquid at or near room temperature. They have been considered and used as a new generation of green solvents for a number of polymerizations as they are non-volatile, non-flammable, recyclable, and have good solubility to many organic and inorganic compounds [22–29]. Carmichael et al. [30] first reported the successful use of 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]), a frequently used room temperature ionic liquid, as a solvent for ATRP of methyl methacrylate (MMA). Matyjaszewski and co-worker [31] discussed the ATRP of MMA in ionic liquids containing different counterions, and Kubisa and co-worker [32] studied the effects of different substituents on ATRP of acrylates in [C_4mim][PF_6]. The other studies in this field have been done systemically [33–40]. Reverse ATRPs of MMA in ionic liquids were firstly approached by Wan and co-workers [41,42]. Lu et al. [43] also reported reverse ATRPs of MMA in ionic liquids and found that the polymerization in [C_8mim][PF_6] was best controlled.

To the best of our knowledge, neither ATRP nor reverse ATRP of EA in ionic liquid has been approached. A detailed study for the optimization of the reaction conditions to prepare well-defined PEA by reverse ATRP was the starting point of this original research. In this original experiment, ionic liquids, [C_{12}mim][BF_4], [C_8mim][BF_4] and [C_4mim][BF_4] were applied as reaction media for the first time, $CuBr_2$ and *N*,*N*,*N*′,*N*″,*N*″-pentamethyl diethylene triamine (PMDETA) were selected to be catalyst and ligand, and AIBN was used as the initiator. Effects of $CuBr_2$ content on the polymerization were studied. Block polymerization of styrene using PEA as

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macroinitiator via a conventional ATRP process in [C_{12}mim][BF_4] was also attempted. Recycling and reuse of [C_{12}mim][BF_4] and the catalyst system were discussed.

2. Experimental

2.1. Materials

EA (Beijing Chemical Reagent Co. Ltd., Beijing, China) was washed with 5% NaOH and then with distilled water twice. After drying over sodium carbonate, they were distilled under reduced pressure over calcium hydride. Anhydrous $CuBr_2$ (Shanghai Chemical Reagents Co., AR grade) was washed with analytical-reagent-grade ethanol and dried under vacuum at 60 °C before use. Azobisisobutyronitrile (AIBN, Shanghai Chemical Reagents Co., Shanghai, China) was used as an initiator and recrystallized from analytical-reagent-grade ethanol and dried in a desiccator. PMDETA (Aldrich) was used as received. Ionic liquids, [C_{12}mim][BF_4], [C_8mim][BF_4] and [C_4mim][BF_4], were prepared according to the literature method [44]. *N*,*N*-Dimethylformamide (DMF, AR grade, Tianjin Ruijinte Chemical Co. Ltd., Tianjin, China) was distilled at reduced pressure and stored over type 4-Å molecular sieves before use.

2.2. Polymerization

A typical example of the general procedure was as follows. $CuBr_2$, PMDETA and ionic liquid were added into a dry glass tube under stirring. Three cycles of vacuum nitrogen were applied to remove oxygen. EA and AIBN were added via an argon-washed syringe. The tube was degassed in vacuum and charged with N_2 (three times) and was sealed under N_2. The tube was then immersed in an oil bath at the desired temperature maintained by a thermostat. After a definite time, the polymerization was terminated by cooling the flask in the ice water. The final crude product was passed through a short column of neutral alumina oxide to remove catalyst, precipitated in methanol and dried under vacuum at room temperature.

2.3. Characterization

The conversion of the monomer was determined gravimetrically.

The molecular weight (M_n) and polydispersity index (PDI) of PEA were measured by gel permeation chromatography (GPC). GPC was performed with a Waters 1515 solvent delivery system (Milford, MA) at a flow rate of 1.0 mL min^{-1} through a combination of Waters HT3, HT4, and HT5 styragel columns. Poly(methyl methacrylate) standards were used to calibrate the columns. The analysis was undertaken at 35 °C with purified high-performance-liquid-chromatography-grade DMF as an eluent. A Waters 2414 differential refractometer was used as the detector.

According to the characteristics of living polymerization, the theoretical molecular weight (M_{th}) could be calculated from the following equation [45]:

$$M_{th} = \frac{[EA]}{2[AIBN]} \times M_{wEA} \times \text{conversion}$$

where M_{WEA} is the molecular weight of EA.

3. Results and discussion

3.1. Reverse ATRP of EA in ionic liquids

Reverse ATRP of EA catalyzed by $CuBr_2$/PMDETA was carried out at 85 °C in [C_{12}mim][BF_4], [C_8mim][BF_4] and [C_4mim][BF_4]. Fig. 1 shows the relationship between the monomer conversion and the reaction time. The monomer conversions increased with the reaction time. The monomer conversion reached about 74.9%, 61.8% and 49.4% within 120 min in [C_{12}mim][BF_4], [C_8mim][BF_4] and [C_4mim][BF_4], respectively. This clearly demonstrates that the rate of polymerization in [C_{12}mim][BF_4] was considerably faster than in [C_4mim][BF_4] and [C_8mim][BF_4].

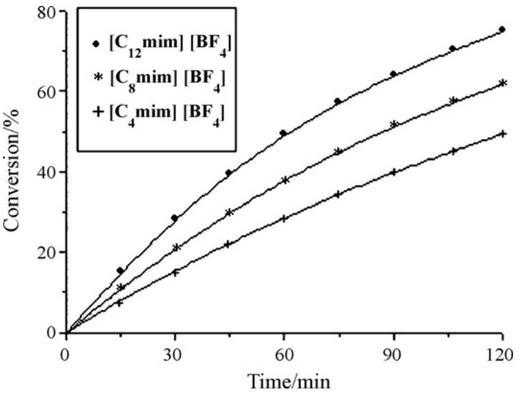

Fig. 1. Conversion dependence on the reaction time in ionic liquids during reverse ATRP of EA with [EA]:[ionic liquid](volume ratio) = 1:1 and [EA]:[$CuBr_2$]:[AIBN]:[PMDETA](molar ratio) = 400:1:3:4 at 85 °C.

In order to prove the living nature of reverse ATRP of EA in ionic liquids, kinetic studies was performed. Fig. 2 shows the kinetic plots of ln($[M]_0/[M]$) versus time for reverse ATRP of EA. The linearity of the plot indicates that the polymerization was approximately first order with respect to the monomer concentration. The slope of the kinetic plots indicates that the number of active species was constant and the termination reactions could be neglected throughout the polymerization process. According to the slopes of the kinetic plots, the apparent rate constant (k_p^{app}) were calculated. The k_p^{app} was $19.2 \times 10^{-5}\,s^{-1}$, $13.4 \times 10^{-5}\,s^{-1}$ and $9.45 \times 10^{-5}\,s^{-1}$ in [C_{12}mim][BF_4], [C_8mim][BF_4] and [C_4mim][BF_4], respectively. The sequence of the rate coefficients of polymerization was k_p^{app}([C_{12}mim][BF_4] > k_p^{app}([C_8mim][BF_4]) > k_p^{app}([C_4mim][BF_4]). It means that either the instantaneous concentration of radicals or the propagation-rate constant was higher in [C_{12}mim][BF_4] than in [C_4mim][BF_4] and [C_8mim][BF_4].

Fig. 3 indicates that the molecular weights of the resulting polymers measured by GPC in ionic liquids increased linearly with conversion. The molecular weights in [C_{12}mim][BF_4] agreed reasonably well with the theoretical molecular weights as conversion beyond 15%. The values of M_n were higher than their theoretical molecular weights when [C_8mim][BF_4] and [C_4mim][BF_4] were

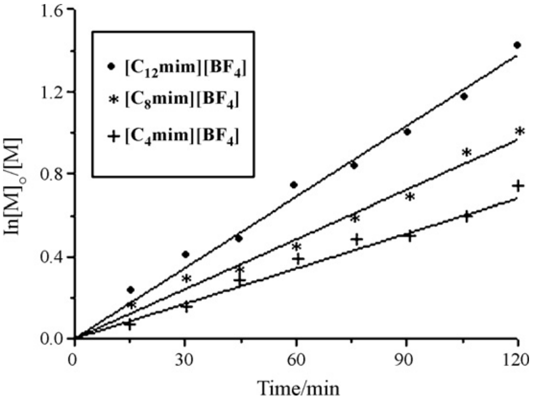

Fig. 2. First-order kinetic plot of monomer consumption as a function of time in ionic liquids during reverse ATRP of EA with [EA]:[ionic liquid](volume ratio) = 1:1 and [EA]:[$CuBr_2$]:[AIBN]:[PMDETA](molar ratio) = 400:1:3:4 at 85 °C.

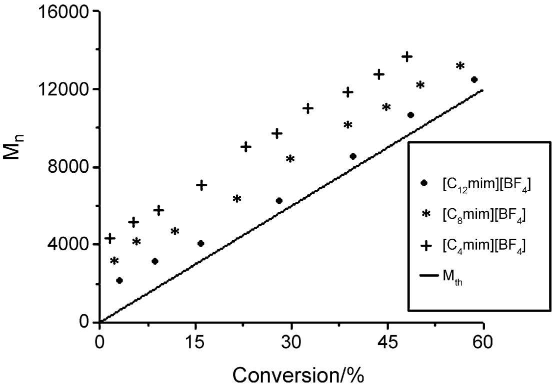

Fig. 3. Dependence of M_n on the monomer conversion in ionic liquids during reverse ATRP of EA with [EA]:[ionic liquid](volume ratio) = 1:1 and [EA]:$[CuBr_2]$:[AIBN]:[PMDETA](molar ratio) = 400:1:3:4 at 85 °C.

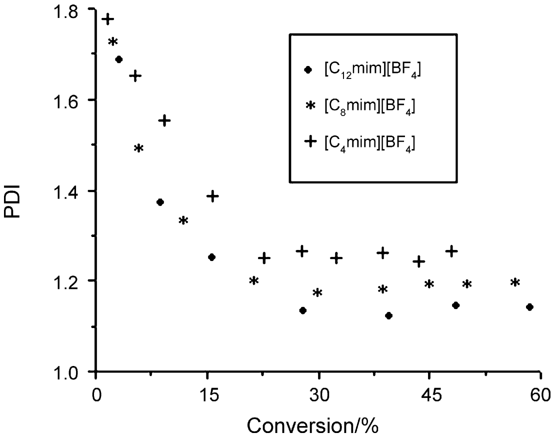

Fig. 4. Dependence of PDI on the monomer conversion in ionic liquids during reverse ATRP of EA with [EA]:[ionic liquid](volume ratio) = 1:1 and [EA]:$[CuBr_2]$:[AIBN]:[PMDETA](molar ratio) = 400:1:3:4 at 85 °C.

used as the reaction media. It may be caused by the cage effect of high viscous ionic liquid, which lead to more coupling reaction of primary and the relatively lower solubility of PEA in $[C_8mim][BF_4]$ and $[C_4mim][BF_4]$.

The values of PDI of PEA in ionic liquids are shown in Fig. 4. The polydispersity was narrower in $[C_{12}mim][BF_4]$ than in $[C_8mim][BF_4]$ and $[C_4mim][BF_4]$ when the conversion was from 15 to 60%. The higher molecular weight and the broader PDI at conversion less than 15% suggested that there was some termination or side reaction at the beginning of the reaction because the radicals were not immediately deactivated.

The activity of the catalyst in reverse ATRP depends dramatically on its solubility in the polymerization media. Better the solvating power of ionic liquid is, better the polymerization could be controlled. The solvating power for transition metal salts and PEA in ionic liquids is $[C_{12}mim][BF_4] > [C_8mim][BF_4] > [C_4mim][BF_4]$. As a result, reverse ATRP of EA with $CuBr_2$/PMDETA as catalyst complex in $[C_{12}mim][BF_4]$ should be better controlled than in $[C_8mim][BF_4]$ and $[C_4mim][BF_4]$, which should more similarities with the experimental result of polymerization.

3.2. *Effect of $CuBr_2$ on reverse ATRP of EA in $[C_{12}mim][BF_4]$*

To further discuss the effects of $CuBr_2$ content on reverse ATRP of EA, a series of experiments were carried out in $[C_{12}mim][BF_4]$, $[C_8mim][BF_4]$ and $[C_4mim][BF_4]$. The results have been summarized in Table 1. If $CuBr_2$ was absent or not enough (entries 1, 7, 8, 13 and 14), the polymerization in ionic liquids proceeded in an uncontrolled manner. When the ratio of $[CuBr_2]$/[PMDETA] increased from 2:4 to 5:4 (entries 3, 4, 5, 6, 9, 10, 11,12, 15, 16, 17 and 18), the molecular weight distribution of polymers became narrower and narrower, and the rate of polymerization decreased prominently. $CuBr_2$ itself was an effective catalyst in reverse ATRP, but excess $CuBr_2$ would not only slow the polymerization rate significantly but could also contaminate the resultant polymers. As shown in Table 1, another interesting phenomenon was that only less amount of $CuBr_2$ (entry 2) was needed to gain well control over the polymerization in $[C_{12}mim][BF_4]$ than in $[C_8mim][BF_4]$ and $[C_4mim][BF_4]$ (entries 9 and 15). The main reason might be the good solubility of $CuBr_2$ in $[C_{12}mim][BF_4]$.

3.3. *Block copolymerization with styrene in $[C_{12}mim][BF_4]$*

According to the mechanism polymerization of reverse ATRP, the well-defined PEA with an ω-bromine atom end groups was obtained in reverse ATRP of EA using AIBN/$CuBr_2$/PMDETA system in $[C_{12}mim][BF_4]$. Another method to verify the living functionality of obtained PEA is its use as a macroinitiator for the same or other monomers [46]. In this study, block polymerization of styrene (St) using PEA (M_n = 16,850, PDI = 1.21) as macroinitiator was carried out at 90 °C in the presence of the CuBr/PMDETA catalyst system via a conventional ATRP process. $[C_{12}mim][BF_4]$ was used as the solvent to enable the formation of higher molecular weight PEA-b-PSt copolymers. When [EA]:[ionic liquid](volume ratio) = 1:1.5 and

Table 1
Data for reverse ATRP of EA in ionic liquids with [EA]:[ionic liquid](volume ratio) = 1:1 and [EA]:[AIBN](molar ratio) = 400:1 at 85 °C.

Entry	[AIBN]:$[CuBr_2]$:[PMDETA]	Reaction media	Reaction time/min	Conversion/%	M_{th}	M_n	PDI
1	1:0:4	$[C_{12}mim][BF_4]$	120	86.1	17,220	45,230	3.24
2	1:1:4			81.5	16,300	19,560	1.35
3	1:2:4			77.6	15,520	17,420	1.25
4	1:3:4			74.9	14,980	16,850	1.21
5	1:4:4			62.4	12,480	14,610	1.19
6	1:5:4			57.3	11,460	13,540	1.16
7	1:0:4	$[C_8mim][BF_4]$		82.5	16,500	51,230	3.35
8	1:1:4			73.7	14,740	46,580	2.64
9	1:2:4			69.1	13,820	16,520	1.42
10	1:3:4			61.8	12,360	14,520	1.25
11	1:4:4			53.6	10,720	12,590	1.21
12	1:5:4			49.9	9,980	11,270	1.17
13	1:0:4	$[C_4mim][BF_4]$		79.4	15,880	48,920	3.14
14	1:1:4			71.6	14,320	47,110	2.91
15	1:2:4			65.7	13,140	16,780	1.51
16	1:3:4			49.4	9,880	11,230	1.28
17	1:4:4			40.3	8,060	10,450	1.24
18	1:5:4			34.6	6,920	9,420	1.21

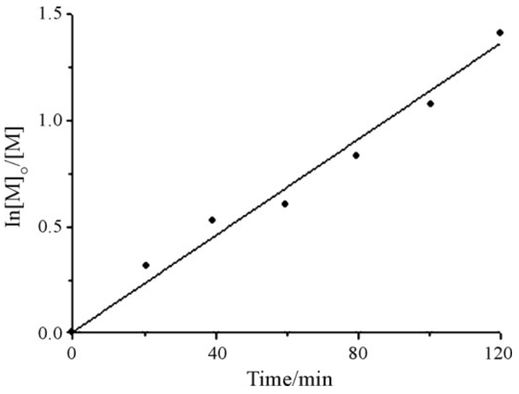

Fig. 5. Kinetics of reverse ATRP of EA in recovered [C_{12}mim][BF_4], $CuBr_2$ and PMDETA with [EA]:(recovered [C_{12}mim][BF_4])(volume ratio) = 1:1 and [EA]:[recovered $CuBr_2$]:[AIBN]:[recovered PMDETA](molar ratio) = 400:1:3:4 at 85 °C.

[St]:[PEA]:[CuBr]:[PMDETA] = 300:1:2:4, block copolymer PEA-b-PSt was obtained with M_n = 54,730, PDI = 1.33. It was clearly verified that the block polymerization of PEA took place.

3.4. Recycling and reuse of [C_{12}mim][BF_4]

Recycling and reuse of [C_{12}mim][BF_4] were also attempted in this work. After a certain time, the polymerization was stopped. The polymerization product was diluted with DMF. The resultant mixture was then poured into a large amount of methanol for precipitation, and washed with methanol several times. The precipitated PEA was obtained. After the evaporation of methanol, DMF and the residue EA, recovered [C_{12}mim][BF_4], $CuBr_2$ and PMDETA were obtained. Reverse ATRP of EA was carried out again in recovered [C_{12}mim][BF_4], $CuBr_2$ and PMDETA by introducing AIBN and EA. Fig. 5 shows the plot $\ln([M]_0/[M])$ versus time for reverse ATRP of EA. The linearity of the plot indicates that the polymerization was approximately first order with respect to the monomer concentration. The number of active species was constant throughout the polymerization process. The apparent rate constant (k_p^{app}) was also calculated. The k_p^{app} in recovered [C_{12}mim][BF_4], $CuBr_2$ and PMDETA was calculated to be $18.9 \times 10^{-5}\,s^{-1}$, which was almost the same in [C_{12}mim][BF_4]. Fig. 6 displays the plot of the molecular weight (M_n) and polydispersity index (PDI) versus monomer conversion. M_n of EA polymers in recovered [C_{12}mim][BF_4], $CuBr_2$ and PMDETA increased linearly with conversion and PDI remained relatively narrow. This indicated a well-controlled polymerization process.

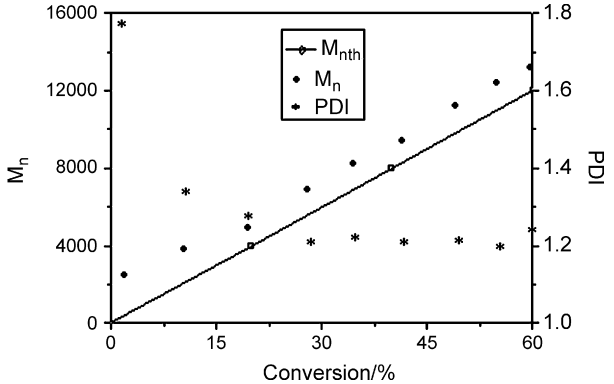

Fig. 6. Dependence of M_n and PDI on monomer conversion in recovered [C_{12}mim][BF_4], $CuBr_2$ and PMDETA with [EA]:(recovered [C_{12}mim][BF_4])(volume ratio) = 1:1 and [EA]:[recovered $CuBr_2$]:[AIBN]:[recovered PMDETA](molar ratio) = 400:1:3:4 at 85 °C.

4. Conclusions

Reverse ATRP of EA with AIBN/$CuBr_2$/PMDETA as the catalyst system was first approached in ionic liquids, [C_{12}mim][BF_4], [C_8mim][BF_4] and [C_4mim][BF_4]. The polymerization in [C_{12}mim][BF_4] proceeded in a best-controlled manner as evidenced by kinetic studies and the monomer conversion in [C_{12}mim][BF_4] was highest under the same experimental conditions. As more $CuBr_2$ was added, the monomer conversion decreased, and the molecular weight distributions became narrower and narrower. The block copolymer PEA-b-PSt with a molecular weight at 54,730 and a narrow polydispersity as low as 1.33 were successfully prepared by using obtained PEA as a macroinitiator via a conventional ATRP process in [C_{12}mim][BF_4]. The kinetic study of reverse ATRP of EA in recovered [C_{12}mim][BF_4], $CuBr_2$ and PMDETA indicates that [C_{12}mim][BF_4] and the catalyst system could be reused after simple purification.

Acknowledgments

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