



Novel ionic liquids as reaction medium for ATRP of acrylonitrile in the absence of any ligand

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ABSTRACT

Atom transfer radical polymerization (ATRP) of acrylonitrile (AN) with ethyl 2-bromoisobutyrate (EBiB) as the initiator was firstly approached in the absence of any ligand in three novel ionic liquids, 1-methylimidazolium acetate ([mim][AT]), 1-methylimidazolium valerate ([mim][VT]) and 1-methylimidazolium caproate ([mim][CT]), respectively. All the polymerizations in the ionic liquids proceeded in a well-controlled manner. The polymerization in [mim][AT] not only showed the best control of molecular weight and its distribution but also provided a rather rapid reaction rate with the molar ratio of [AN]:[FeBr₂]:[EBiB] at 200:2:1. The resulting polyacrylonitrile was successfully used as the macroinitiator to proceed the chain extension polymerization in [mim][AT]. After simple purification, all the ionic liquids and FeBr₂ could be recycled and reused and had no effect on the living nature of polymerization.

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1. Introduction

Ionic liquids are either molten organic salts or mixtures of salts that are liquid at room or near room temperature and have been considered and used as a new generation of green solvents for a number of organic reactions and polymerizations as they are non-volatile, non-flammable, recyclable, and have good solubility to many organic and inorganic compounds [1–3].

Controlled radical polymerization is attracting growing attention, as it combines the advantage of radical polymerization and living polymerization techniques. Controlled radical polymerizations give polymers with predictable molecular weight, narrow polydispersity, and well-defined architecture. Atom transfer radical polymerization (ATRP) is one of the most widely used methods in the controlled radical polymerization. ATRP process involves an equilibrium reversible redox reaction between a transition metal complex and the halogen containing initiator, or dormant species forming a radical and the metal halide in a higher oxidation state [4–13].

ATRP of methyl methacrylate (MMA) was first carried out by Carmichael et al. [14] in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim][PF₆]). The rate of reaction was increased and the copper(II) contamination of resultant

polymers was reduced due to the good solubility of catalyst in [C₄mim][PF₆]. Matyjaszewski and Sarbu [15] and Kubisa and Biedron [16] also discussed ATRP of acrylates in [C₄mim][PF₆]. The other studies in this field have been done systematically [17–25]. However, the anions of these ionic liquids were mainly PF₆⁻ or BF₄⁻, and the transition metal to form the catalyst complex was mainly copper.

Acrylonitrile polymers are important materials and have found wide applications in textile, rubbers, fiber and plastic industries [26]. ATRP and reverse ATRP of acrylonitrile (AN) have been studied systematically to obtain polyacrylonitrile (PAN) with high molecular weight and narrow polydispersity. The new catalytic systems and new ligands have been developed [27–30]. To the best of our knowledge, ionic liquids as reaction media for ATRP of AN have never been approached.

Keeping all these points in mind, a novel series of ionic liquids, 1-methylimidazolium acetate ([mim][AT]), 1-methylimidazolium valerate ([mim][VT]) and 1-methylimidazolium caproate ([mim][CT]), were firstly applied as reaction media for ATRP of AN in this study. Acids are generally believed to deactivate the metallo-organic catalyst in copper-mediated ATRP. However, acids complex more easily with iron than with copper. The first successful attempt of the well-controlled ATRP of AN with only FeBr₂ as the catalyst system in the absence of any ligand, ethyl 2-bromoisobutyrate (EBiB) as the initiator, was described. The recycling and reuse of the ionic liquid were also attempted.

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2. Experimental

2.1. Materials

Acrylonitrile (AN, analytical-reagent-grade) was obtained from Shanghai Chemical Reagents Co. (Shanghai, China) and the inhibitor was removed by passing through an alumina column. Ethyl 2-bromoisobutyrate (EBiB, Aldrich) was used as an initiator. Anhydrous FeBr_2 (Shanghai Chemical Reagents Co., AR grade) was washed with the analytical-reagent-grade ethanol and dried under vacuum at 60°C before use. 1-Methylimidazolium acetate ([mim][AT]), 1-methylimidazolium valerate ([mim][VT]), 1-methylimidazolium caproate ([mim][CT]) were prepared following the literature method [31].

2.2. Polymerization

FeBr_2 and the ionic liquid were added into a dry glass tube under stirring. Three cycles of vacuum nitrogen were applied to remove oxygen. AN with EBiB dissolved in advance was added via an argon-washed syringe. The tube was degassed in vacuum and charged with N_2 (3 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 certain time, the polymerization was terminated by cooling the flask in ice water. The polymerization product was diluted with *N,N*-dimethylformamide (DMF). The resultant mixture was then poured into a large amount of methanol for precipitation, washed with methanol several times and dried at 50°C under vacuum, and PAN was obtained.

2.3. Characterization

The molecular weight (M_n) and polydispersity index (PDI) of PAN were measured by gel permeation chromatography (GPC). GPC was performed with a Waters model 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 model 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 [32]

$$M_{th} = \frac{[\text{AN}]}{[\text{EBiB}]} \times M_{WAN} \times \text{Conversion} \quad (1)$$

where M_{WAN} is the molecular weight of AN.

The monomer conversion was determined gravimetrically.

3. Results and discussion

3.1. Polymerization of AN in ionic liquids

ATRP of AN induced by EBiB/ FeBr_2 at 70°C was carried out in [mim][AT], [mim][VT], and [mim][CT], respectively. Under these conditions, all the reagents, including EBiB, FeBr_2 , AN, and the resulting PAN were soluble in all ionic liquids, and the polymerization system remained homogeneous throughout the polymerization. Fig. 1 shows kinetic plots of $\ln[M]_0/[M]$ versus time. The linearity of the plot indicated that the polymerization was approximately first-order with respect to the monomer concentration. The slope of the kinetic plots indicated that in the polymerization process, the number of active species was constant. The monomer conversion reached about 63.3% in [mim][AT], 39.8% in [mim][VT]

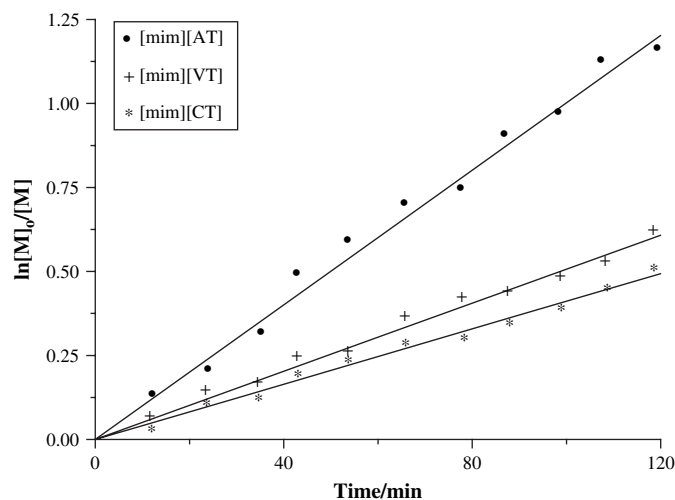


Fig. 1. First-order kinetic plot of monomer consumption as a function of time in ionic liquids during ATRP of AN with $[\text{AN}]:[\text{ionic liquid}](\text{volume ratio}) = 1:1$ and $[\text{AN}]:[\text{FeBr}_2]:[\text{EBiB}](\text{molar ratio}) = 200:2:1$ at 70°C .

and 33.7% in [mim][CT] within 100 min. The corresponding value of the rate coefficient of polymerization (k_p) calculated from the kinetic plot was $16.7 \times 10^{-5}\text{ s}^{-1}$, $8.45 \times 10^{-5}\text{ s}^{-1}$ and $6.86 \times 10^{-5}\text{ s}^{-1}$. The sequence of the rate coefficients of polymerization was $k_p([\text{mim}][\text{AT}]) > k_p([\text{mim}][\text{VT}]) > k_p([\text{mim}][\text{CT}])$, which indicated a strong dependence of the reaction rate on the length of the substituted groups of the counter ions in ionic liquids. A similar phenomenon was observed by Lai and co-workers [33] for ATRP of MMA with the initiation system EBiB/CuBr.

Fig. 2 represents M_n of the resulting PAN increasing linearly with conversion. The values of M_n determined by GPC agreed well with those of M_{th} when [mim][AT] was used as the reaction medium. When [mim][VT] and [mim][CT] were used as the reaction media, the plots of the molecular weights showed a little curvature. The values of PDI of PAN are shown in Fig. 3. The polydispersity in all ionic liquids was narrow when the conversion increased from 15% to 60% and the value of PDI of PAN could reach 1.16 when [mim][AT] was used as the reaction medium. The higher molecular weight and the broader polydispersity at conversion less than 15% indicated that there was some termination or side reaction at the beginning

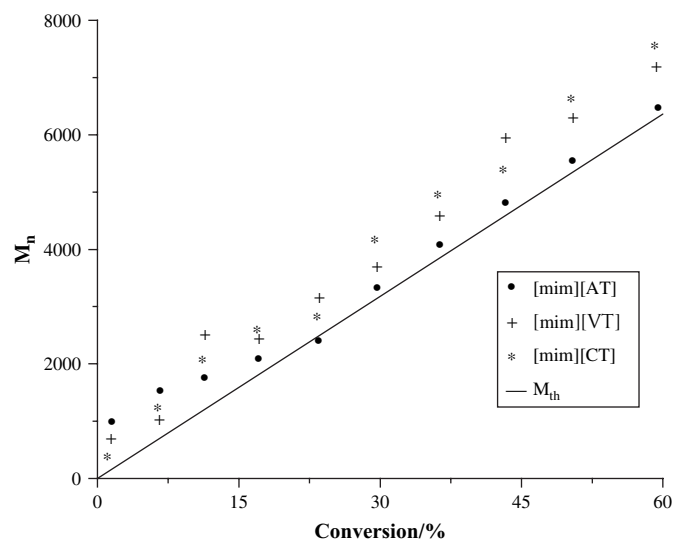


Fig. 2. Dependence of M_n on the monomer conversion in ionic liquids during ATRP of AN with $[\text{AN}]:[\text{ionic liquid}](\text{volume ratio}) = 1:1$ and $[\text{AN}]:[\text{FeBr}_2]:[\text{EBiB}](\text{molar ratio}) = 200:2:1$ at 70°C .

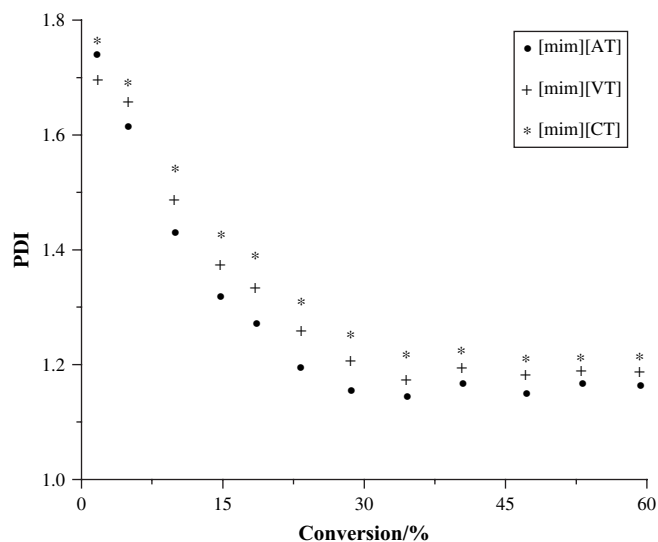


Fig. 3. Dependence of PDI on the monomer conversion in ionic liquids during ATRP of AN with [AN]:[ionic liquid](volume ratio)=1:1 and [AN]:[FeBr₂]:[EBiB](molar ratio)=200:2:1 at 70 °C.

of the reaction because the radicals were not immediately deactivated.

To compare with the polymerization behavior of ATRP of AN induced by EBiB/FeBr₂ in the absence of any ligand in [mim][AT], ATRP of AN induced by EBiB/FeBr₂ with succinic acid as the ligand at 70 °C was carried out in *N,N*-dimethylformamide (DMF). The results are summarized in Table 1. The monomer conversion reached about 57.4% in DMF within 100 min. The corresponding value of k_p calculated from the kinetic plot was $14.2 \times 10^{-5} \text{ s}^{-1}$. This implied that the rate of polymerization showed a trend of increase in [mim][AT] and the polymerization was well-controlled in ionic liquids as well as in DMF.

3.2. Chain extension of PAN

According to the polymerization mechanism of ATRP, the well-defined PAN with bromine atom end groups was obtained. Another method to verify the living functionality of resulting PAN was its use as a macroinitiator for the same or other monomers [34]. In this study, [mim][AT] was used as the solvent to enable the formation of high molar mass AN polymers. The extension polymerization of the resulting PAN ($M_{th}=6710$, $M_n=7370$, PDI=1.16) with AN was carried out in [mim][AT] at 75 °C in the presence of FeBr₂. AN polymers obtained had $M_{th}=30150$, $M_n=34560$ and PDI=1.21. It clearly demonstrated that the chain extension of PAN took place.

3.3. Recycling and reuse of ionic liquids

The probability of separation from other reagents and resultant polymers, recycling and reuse of [mim][AT], [mim][VT] and [mim][CT] were also discussed in this study. The polymerization was terminated after a certain time. The polymerization product was diluted with DMF. The resultant mixture was then poured into a large amount of methanol for precipitation, and washed with

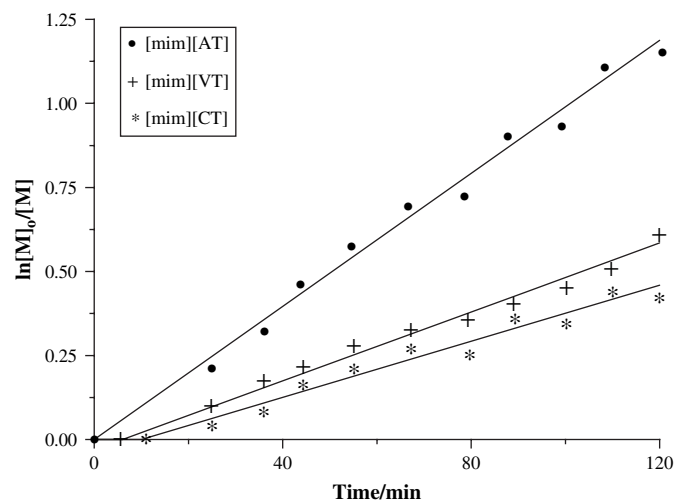


Fig. 4. Kinetics of ATRP of AN in recovered ionic liquids and FeBr₂ with [AN]:[recovered ionic liquid](volume ratio)=1:1 and [AN]:[recovered FeBr₂]:[EBiB](molar ratio)=200:2:1 at 70 °C.

methanol several times. The precipitated PAN was obtained. After the evaporation of methanol, DMF and the residue AN, ATRP of AN was carried out again in recovered [mim][AT], [mim][VT], [mim][CT] and FeBr₂ by introducing EBiB and AN, respectively. Fig. 4 shows the plot of $\ln([M]_0/[M])$ versus time for ATRP of AN. The linearity of the plot indicates that polymerization was approximately first-order with respect to the monomer concentration. The number of active species was constant throughout the polymerization process. The rate coefficient of polymerization was also calculated. The values of k_p in recovered [mim][AT], [mim][VT] and [mim][CT] were calculated to be $16.5 \times 10^{-5} \text{ s}^{-1}$, $8.55 \times 10^{-5} \text{ s}^{-1}$ and $6.96 \times 10^{-5} \text{ s}^{-1}$, which were almost same with in [mim][AT], [mim][VT] and [mim][CT], respectively. But the induction periods for ATRP of AN were found in recovered [mim][VT] and [mim][CT]. The induction period was longer in recovered [mim][VT] (6 min) than that in recovered [mim][CT] (10 min). The induction period was perhaps caused by the slow formation of the catalytic center and by the presence of oxygen and impurities [35]. Table 2 displays dependence of M_n and PDI on the monomer conversion for ATRP of AN in recovered ionic liquids and FeBr₂. M_n of PAN increased linearly with conversion and PDI remained relatively narrow in recovered ionic liquids and FeBr₂.

4. Conclusions

Three novel ionic liquids, [mim][AT], [mim][VT] and [mim][CT], have been firstly demonstrated to be the excellent reaction media for ATRP of AN with ethyl 2-bromoisobutyrate (EBiB) as the initiator and FeBr₂ as the catalyst in the absence of any ligand. The sequence of the rate coefficients of polymerization was $k_p([\text{mim}][\text{AT}]) > k_p([\text{mim}][\text{VT}]) > k_p([\text{mim}][\text{CT}])$. AN polymers with a molecular weight of 34,560 and a narrow polydispersity as low as 1.21 were successfully prepared by using resulting PAN as a macroinitiator in [mim][AT]. All the ionic liquids and FeBr₂ could be easily recycled and reused after simple purification.

Table 1
Data for ATRP of AN in [mim][AT] and DMF

Reaction media	[AN]:[FeBr ₂]:[EBiB]:[succinic acid]	Reaction time/min	Conversion/%	$k_p \times 10^5/\text{s}^{-1}$	M_{th}	M_n	PDI
[mim][AT]	200:2:1:0	100	63.3	16.7	6710	7370	1.18
DMF	200:2:1:4		57.4	14.2	6084	6940	1.17

[AN]:[reaction media](volume ratio) = 1:1, $T = 70 \text{ }^\circ\text{C}$.

Table 2
Dependence of M_n and PDI on the monomer conversion for ATRP of AN in recovered ionic liquids and FeBr_2

Entry	Recovered ionic liquid	Reaction time/min	Conversion/%	M_{th}	M_n	PDI
1	[mim][AT]	50	39.1	4145	4560	1.18
2		80	54.7	5798	6380	1.17
3		100	62.8	6657	7340	1.19
4	[mim][VT]	50	20.3	2152	2460	1.35
5		80	31.5	3339	3820	1.29
6		100	38.2	4049	4610	1.21
7	[mim][CT]	50	17.9	1897	2140	1.42
8		80	27.3	2894	3330	1.36
9		100	32.5	3445	3970	1.24

[AN]:[recovered ionic liquid](volume ratio) = 1:1, [AN]:[recovered FeBr_2]:[EBiB] (molar ratio) = 200:2:1, $T = 70^\circ\text{C}$.

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