

# ARGET ATRP of Acrylonitrile with Ionic Liquid as Reaction Medium and FeBr<sub>3</sub>/Isophthalic Acid as Catalyst System

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**ABSTRACT:** Atom transfer radical polymerization using activators regenerated by electron transfer (ARGET ATRP) of acrylonitrile with FeBr<sub>3</sub> and isophthalic acid (IA) as catalyst and ligand, ascorbic acid (VC) as reducing agent, and ethyl 2-bromoisobutyrate as initiator was approached for the first time in the presence of air in 1-dodecyl-3-methylimidazolium tetrafluoroborate ([C<sub>12</sub>mim][BF<sub>4</sub>]), 1-octyl-3-methylimidazolium tetrafluoroborate ([C<sub>8</sub>mim][BF<sub>4</sub>]), and 1-butyl-3-methylimidazolium tetrafluoroborate ([C<sub>4</sub>mim][BF<sub>4</sub>]). The rate of polymerization in [C<sub>12</sub>mim][BF<sub>4</sub>] was considerably faster than in [C<sub>8</sub>mim][BF<sub>4</sub>] and [C<sub>4</sub>mim][BF<sub>4</sub>]. With an increase of VC concentration, both the monomer conversion and the molecular weight distribution showed a trend of

increase. Polyacrylonitrile (PAN) with higher molecular weight at 166,250 and broader distribution at 1.34 was successfully prepared with PAN as macroinitiator via ARGET ATRP in [C<sub>12</sub>mim][BF<sub>4</sub>] in the presence of air. The resultant polyacrylonitrile fibers were obtained with the fineness at 1.15 dtex and the tenacity at 6.24 cN dtex<sup>-1</sup>. Additionally, it was shown that [C<sub>12</sub>mim][BF<sub>4</sub>] could be recycled and reused after simple purification and had no effect on the living nature of polymerization. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3298–3302, 2011

**Key words:** ARGET ATRP; ionic liquid; living polymerization; kinetics

## INTRODUCTION

Polyacrylonitrile (PAN) precursors for high performance carbon-based materials must possess high molecular weight and well-controlled architecture.<sup>1</sup> Atom transfer radical polymerization (ATRP) can be used as an alternative to prepare polymers with predictable molecular weight, narrow polydispersity, and well-defined architecture.<sup>2–4</sup> Use of conventional radical initiators in the presence of complexes of transition metals in their higher oxidation state to overcome the oxidation of low-oxidation transition metal catalyst in ATRP has been reported and referred to as reverse ATRP by Matyjaszewski and coworkers.<sup>5–7</sup> ATRP and reverse ATRP of acrylonitrile (AN) have been studied systemically.<sup>8–11</sup> It is

obvious that a large amount of catalyst and higher solubility of catalyst in reaction media are ordinarily needed to achieve a higher polymerization rate in ATRP and reverse ATRP. Novel reaction media are being developed. Ionic liquids have been used as a new generation of green solvents for a number of polymerizations and have good solubility to many organic and inorganic compounds.<sup>12–14</sup> Carmichael et al.<sup>15</sup> first reported the successful use of 1-butyl-3-methylimidazolium hexafluorophosphate ([C<sub>4</sub>mim][PF<sub>6</sub>]) as a solvent for ATRP of methyl methacrylate (MMA). Sarbu and Matyjaszewski<sup>16</sup> discussed ATRP of MMA in ionic liquids containing different counterions. Biedron and Kubisa<sup>17</sup> studied effects of different substituents on ATRP of acrylates in [C<sub>4</sub>mim][PF<sub>6</sub>]. The other studies in this field have been done systemically.<sup>18–25</sup> Reverse ATRP of MMA in ionic liquids were first approached by Wan and coworkers.<sup>26,27</sup> Lu and coworkers<sup>28</sup> reported reverse ATRP of MMA in 1-octyl-3-methylimidazolium hexafluorophosphate [C<sub>8</sub>mim][PF<sub>6</sub>] was best controlled. Reverse ATRP of methacrylonitrile in ionic liquids has been achieved by our group.<sup>29,30</sup>

However, it is clear that catalyst concentration can not be independently reduced in ATRP and reverse ATRP. An improved ATRP technique, activators regenerated by electron transfer ATRP (ARGET ATRP) was developed by Matyjaszewski and coworkers.<sup>31</sup> This method allows an ATRP process to be conducted with a catalyst in a high oxidation

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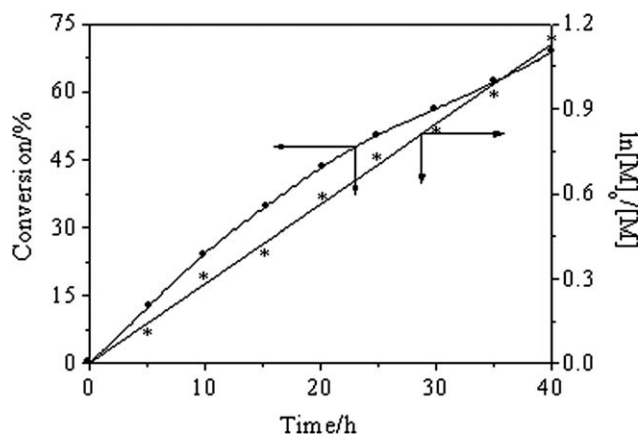
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state in a tiny amount in the presence of a sufficiently large excess of reducing agent. The universal characters of ARGET ATRP were demonstrated by many researchers.<sup>32,33</sup> ARGET ATRP of AN using in ethylene carbonate and dimethyl sulfoxide (DMSO) in the absence of oxygen has been reported by Matyjaszewski.<sup>34</sup> ARGET ATRP of AN has been approached in our group in 1-methylimidazolium acetate ([mim][AT]), 1-methylimidazolium propionate([mim][PT]), and 1-methylimidazolium butyrate ([mim][BT]) without any additional ligand.<sup>35</sup> Our group have also reported ARGET ATRP of AN in the presence of air in 1-dodecyl-3-methylimidazolium tetrafluoroborate ( $[C_{12}mim][BF_4]$ ), 1-octyl-3-methylimidazolium tetrafluoroborate ( $[C_8mim][BF_4]$ ), and 1-butyl-3-methylimidazolium tetrafluoroborate ( $[C_4mim][BF_4]$ ) with 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) as both ligand and reducing agent,  $CuBr_2$  as catalyst.<sup>36</sup>

Nontoxic isophthalic acid (IA), which can complex easily with iron, has been successfully used as a ligand in ATRP.<sup>37–40</sup> ARGET ATRP of AN catalyzed by  $FeCl_3/IA$  in the presence of air in *N,N*-dimethylformamide (DMF) was also reported by our group.<sup>41</sup> In this original experiment, ionic liquid,  $[C_{12}mim][BF_4]$ ,  $[C_8mim][BF_4]$ , and  $[C_4mim][BF_4]$  were applied as reaction media,  $FeBr_3/IA$  was selected to be catalyst system.

## EXPERIMENTAL

Analytical-reagent-grade acrylonitrile (AN) was obtained from Shanghai Chemical Reagents (Shanghai, China) and the inhibitor was removed by passing through an alumina column.<sup>42</sup> Anhydrous  $FeBr_3$  (A. R. grade, Shanghai Chemical Reagents) was washed with analytical-reagent-grade ethanol and dried under vacuum at 60°C before use. Ethyl 2-bromoisobutyrate (EBiB, 98%, Acros) was used as received. Analytical-reagent-grade IA (Shanghai Chemical Reagents, Shanghai, China) was used as received without purification. The 1-dodecyl-3-methylimidazolium tetrafluoroborate ( $[C_{12}mim][BF_4]$ ), 1-octyl-3-methylimidazolium tetrafluoroborate ( $[C_8mim][BF_4]$ ), and 1-butyl-3-methylimidazolium tetrafluoroborate ( $[C_4mim][BF_4]$ ) were prepared following the literature method.<sup>43</sup> A typical example of the general procedure in the presence of air was as follows.  $FeBr_3$ , IA, VC, AN, EBiB, and ionic liquid were added into a dry glass flask under stirring. The flask 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 resultant mixture was then poured into a large amount of methanol for precipitation, washed with methanol several times, and dried at 60°C under vacuum. The conversion of the mono-



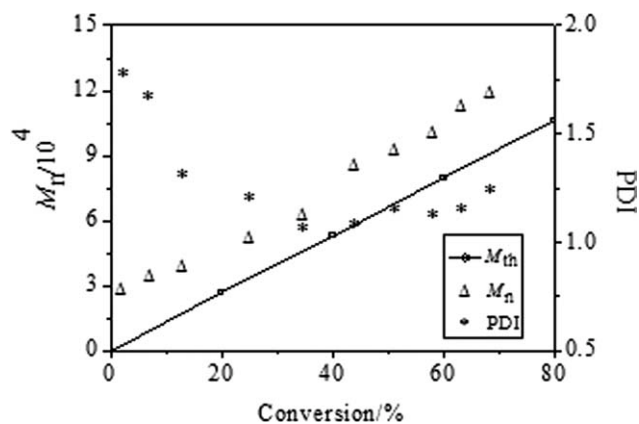
**Figure 1** Kinetic plot for ARGET ATRP of AN at 70°C in  $[C_{12}mim][BF_4]$  with  $[AN]_0:[ionic\ liquid]_0$ (volume ratio) = 1 : 1,  $[AN]_0 = 7.5M$  and  $[AN]_0 : [EBiB]_0 : [FeBr_3]_0 : [IA]_0 : [VC]_0 = 2500 : 1 : 0.1 : 1 : 1$ .

mer was determined gravimetrically. The molecular weight ( $M_n$ ) and polydispersity index (PDI) of PAN 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.

## RESULTS AND DISCUSSION

### ARGET ATRP of an in ionic liquids

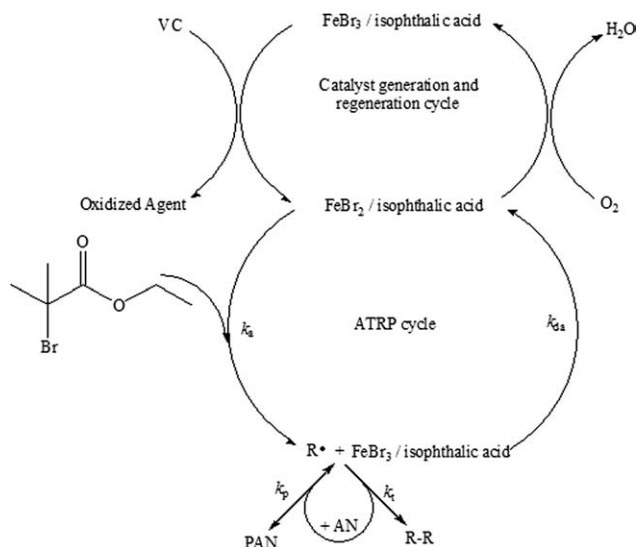
ARGET ATRP of AN catalyzed by  $FeBr_3/IA$  in the presence of air were carried out at 70°C in  $[C_{12}mim][BF_4]$  with volume ratio of  $[AN]_0:[ionic\ liquid]_0$  at 1 : 1 and molar ratio of  $[AN]_0 : [EBiB]_0 : [FeBr_3]_0 : [IA]_0 : [VC]_0$  at 2500 : 1 : 0.1 : 1 : 1 with  $[AN]_0 = 7.5M$ . Figure 1 shows kinetic plots of monomer conversion and  $\ln([M]_0/[M])$  versus reaction time for ARGET ATRP of AN with 40 ppm of Fe versus monomer. The monomer conversion reached about 68.6% within 40 h. The linearity of the plot of  $\ln([M]_0/[M])$  versus reaction time indicates that the polymerization was approximately first-order with respect to monomer concentration. The slope of the kinetic plots indicates that in the polymerization process, the number of active species was constant, and the termination reactions could be neglected. According to the slopes of the kinetic plots, the apparent rate constant ( $k_p^{app}$ ) was calculated to be  $7.83 \times 10^{-6} s^{-1}$ . Figure 2 indicates that values of molecular weight and polydispersity index (PDI) of the resulting polymers measured by gel permeation



**Figure 2** Dependence of  $M_n$  and PDI on monomer conversion for ARGET ATRP of AN at 70°C in  $[C_{12}mim][BF_4]$  with  $[AN]_0 : [ionic\ liquid]_0 (volume\ ratio) = 1 : 1$ ,  $[AN]_0 = 7.5M$  and  $[AN]_0 : [EBiB]_0 : [FeBr_3]_0 : [IA]_0 : [VC]_0 = 2500 : 1 : 0.1 : 1 : 1$ .

chromatography (GPC). The values of molecular weight increased linearly with conversion. The polydispersities were narrow and in the range of 1.18–1.26 when the conversion was in the range of 20–70%. The higher molecular weight and the broader polydispersity at conversion less than 20% could be ascribed to the lower amount of Fe species and relatively slow deactivation in viscous ionic liquid. The proposed mechanism for ARGET ATRP of AN in the presence of air was shown in Scheme 1.

ARGET ATRP of AN catalyzed by  $FeBr_3/IA$  in the presence of air were also carried out in  $[C_8mim][BF_4]$  and  $[C_4mim][BF_4]$  with  $[AN]_0 = 7.5M$  at 70°C. Kinetic data for ARGET ATRP of AN were shown in Table I. It was obvious that the rate of polymerization in  $[C_{12}mim][BF_4]$  was considerably faster than in  $[C_4mim][BF_4]$  and  $[C_8mim][BF_4]$ . The  $k_p^{app}$  was  $6.01 \times 10^{-6}$  and  $4.99 \times 10^{-6} s^{-1}$  in  $[C_8mim][BF_4]$  and  $[C_4mim][BF_4]$ , respectively. The sequence of the rate coefficients of polymerization was  $k_p^{app}([C_{12}mim][BF_4]) > k_p^{app}([C_8mim][BF_4]) > k_p^{app}([C_4mim][BF_4])$ . The



**Scheme 1** Proposed mechanism for ARGET ATRP of AN in the presence of air.

activity of catalyst in ARGET ATRP depends dramatically on its solubility in the polymerization medium. The solvating power for transition metal salts and PAN in ionic liquids is  $[C_{12}mim][BF_4] > [C_8mim][BF_4] > [C_4mim][BF_4]$ . Thus, ARGET ATRP of AN catalyzed by  $FeBr_3/IA$  in the presence of air in  $[C_{12}mim][BF_4]$  were better controlled than in  $[C_8mim][BF_4]$  and  $[C_4mim][BF_4]$ .

#### Effect of VC on ARGET ATRP of AN

In ARGET ATRP of AN, VC reduces the stable  $Fe(III)/IA$  precursor to the active  $Fe(II)/IA$  complex. Effect of VC content on ARGET ATRP of AN in the presence of air in  $[C_{12}mim][BF_4]$  were summarized in Table II. The monomer conversion increased from 41.3 to 67.1% with increasing VC concentration, and the molecular weight distribution increased from 1.14 to 1.38. Increasing the amount of VC resulted in

**TABLE I**  
Data for ARGET ATRP of AN at 70°C in Different Ionic Liquids

Entry	Reaction medium	Reaction time $h^{-1}$	Conversion/%	$k_p^{app} \times 10^6 s^{-1}$	$M_{th}$	$M_n$	PDI
1	$[C_{12}mim][BF_4]$	10	24.9	7.83	32,993	47,560	1.25
2		20	43.4		57,505	87,650	1.18
3		30	56.2		74,465	104,220	1.19
4		40	68.6		90,895	123,450	1.26
5	$[C_8mim][BF_4]$	10	19.5	6.01	25,838	40,140	1.31
6		20	35.8		47,435	79,430	1.21
7		30	48.4		64,130	89,560	1.19
8		40	58.5		77,513	110,680	1.22
9	$[C_4mim][BF_4]$	10	16.4	4.99	21,730	38,970	1.33
10		20	30.9		40,943	68,320	1.25
11		30	42.1		55,783	77,540	1.22
12		40	52.3		69,298	99,430	1.26

$[AN]_0 : [ionic\ liquid]_0 (volume\ ratio) = 1 : 1$ ,  $[AN]_0 = 7.5M$ ,  $[AN]_0 : [EBiB]_0 : [FeBr_3]_0 : [IA]_0 : [VC]_0 = 2500 : 1 : 0.1 : 1 : 1$ .

**TABLE II**  
Effect of VC Content on ARGET ATRP of AN at 70°C in [C<sub>12</sub>mim][BF<sub>4</sub>]

Entry	[FeBr <sub>3</sub> ] <sub>0</sub> : [VC] <sub>0</sub>	Conversion/%	M <sub>th</sub>	M <sub>n</sub>	PDI
1	0.1 : 0.3	41.3	54,723	70,560	1.14
2	0.1 : 0.4	50.5	66,913	81,230	1.17
3	0.1 : 1.0	56.2	74,465	104,220	1.19
4	0.1 : 1.1	60.1	79,633	110,200	1.27
5	0.1 : 1.2	67.1	88,908	123,340	1.38

[AN]<sub>0</sub> : [C<sub>12</sub>mim][BF<sub>4</sub>]<sub>0</sub>(volume ratio) = 1 : 1, [AN]<sub>0</sub> = 7.5M, [AN]<sub>0</sub> : [EBiB]<sub>0</sub> : [FeBr<sub>3</sub>]<sub>0</sub> : [IA]<sub>0</sub> = 2500 : 1 : 0.1 : 1, t = 30 h.

the higher concentration of Fe(II)/IA produced by the reduction of Fe(III)/IA complex, and then increased concentrations of the propagating radicals in the polymerization system, resulting in the increase of polymerization rate.

#### Effect of FeBr<sub>3</sub> on ARGET ATRP of AN

Effects of FeBr<sub>3</sub> on ARGET ATRP of AN in the presence of air in [C<sub>12</sub>mim][BF<sub>4</sub>] were shown in Table III. When the ratio of [FeBr<sub>3</sub>]/[IA] increased from 0.08 : 1 to 0.15 : 1, the rate of polymerization decreased prominently with the molecular weight distribution of polymers remaining narrow.

#### Chain extension of PAN and preparation of fibers

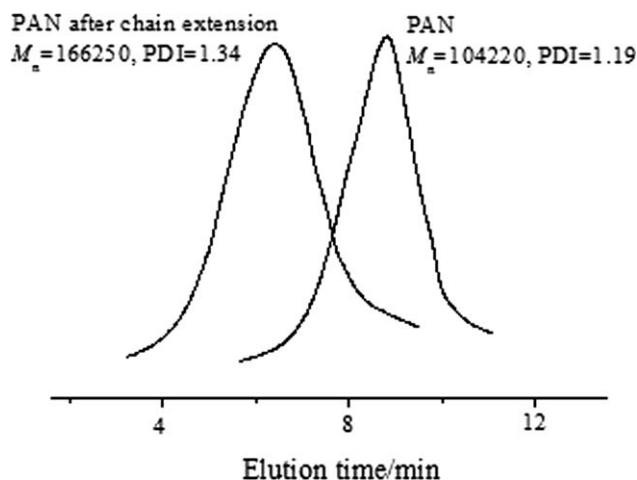
For further confirmation of the controlled radical polymerization, chain extension of PAN (*M<sub>n</sub>* = 104220, PDI = 1.19) was carried out at 70°C in [C<sub>12</sub>mim][BF<sub>4</sub>] with FeBr<sub>3</sub>/IA as catalyst system and using VC as a reducing agent by ARGET ATRP in the presence of air. To prepare PAN fibers, the same monomer AN was used as comonomer for chain extension of PAN. When [AN]<sub>0</sub> : [ionic liquid]<sub>0</sub>(volume ratio) was 1 : 1, [AN]<sub>0</sub> : [PAN]<sub>0</sub> : [FeBr<sub>3</sub>]<sub>0</sub> : [IA]<sub>0</sub> : [VC]<sub>0</sub> was 1000 : 1 : 0.1 : 1 : 1, and the resultant PAN was obtained with *M<sub>n</sub>* at 166,250 and PDI at 1.34, as shown in Figure 3.

According to the wet-spun process for acrylic fibers, the resultant PAN (*M<sub>n</sub>* = 166,250, PDI = 1.34)

**TABLE III**  
Effect of FeBr<sub>3</sub> on ARGET ATRP of AN at 70°C in [C<sub>12</sub>mim][BF<sub>4</sub>]

Entry	[FeBr <sub>3</sub> ] <sub>0</sub> : [IA] <sub>0</sub>	Conversion/%	M <sub>th</sub>	M <sub>n</sub>	PDI
1	0.08 : 1	60.1	79,633	116,870	1.22
2	0.10 : 1	56.2	74,465	104,220	1.19
3	0.12 : 1	52.9	70,093	96,950	1.18
4	0.15 : 1	50.4	66,780	87,460	1.24

[AN]<sub>0</sub> : [C<sub>12</sub>mim][BF<sub>4</sub>]<sub>0</sub>(volume ratio) = 1 : 1, [AN]<sub>0</sub> = 7.5M, [AN]<sub>0</sub> : [EBiB]<sub>0</sub> : [IA]<sub>0</sub> : [VC]<sub>0</sub> = 2500 : 1 : 1 : 1, t = 30 h.



**Figure 3** GPC curves of PAN before and after a chain extension reaction.

was spun into fibers. First, PAN resins was washed with methanol several times and dissolved in dimethylsulfoxide after drying under vacuum to get a clear dope, the obtained dope was deaerated, filtered, and then pumped through a spinneret to a coagulation bath. After a definite time, the coagulated protofibers were obtained. The wet-spun protofibers were washed and drawn in three steps in a water bath, and the filaments were then dried to collapse them, further drawn in steam, set, dried, and wound to fibers. The overall draw ratio was 14. The fibers were obtained with the fineness at 1.15 dtex and the tenacity at 6.24 cN dtex<sup>-1</sup>. The fibers satisfied the requirements for high performance PAN fibers.

#### Reuse of [C<sub>12</sub>mim][BF<sub>4</sub>]

Recycling and reuse of [C<sub>12</sub>mim][BF<sub>4</sub>] were also discussed. After a definite time, the polymerization was terminated and the resultant mixture was poured into a large amount of methanol for precipitation, and then washed with methanol several times. The precipitated PAN was obtained. After evaporation of methanol and the residual AN, ARGET ATRP of AN

**TABLE IV**  
Kinetic Data for ARGET ATRP of AN at 70°C in Recovered [C<sub>12</sub>mim][BF<sub>4</sub>]

Entry	Reaction time h <sup>-1</sup>	Conversion/%	M <sub>th</sub>	M <sub>n</sub>	PDI	<i>k<sub>p</sub></i> <sup>app</sup> × 10 <sup>6</sup> s <sup>-1</sup>
1	10	25.2	33,390	49,870	1.39	7.72
2	20	41.3	54,723	76,590	1.28	
3	30	58.1	76,983	108,650	1.22	
4	40	66.4	87,980	120,570	1.26	

[AN]<sub>0</sub> : (recovered [C<sub>12</sub>mim][BF<sub>4</sub>])<sub>0</sub> (volume ratio) = 1 : 1, [AN]<sub>0</sub> = 7.5M, [AN]<sub>0</sub> : [EBiB]<sub>0</sub> : [FeBr<sub>3</sub>]<sub>0</sub> : [IA]<sub>0</sub> : [VC]<sub>0</sub> = 2500 : 1 : 0.1 : 1 : 1.

was carried out again in the presence of air in recovered [C<sub>12</sub>mim][BF<sub>4</sub>], FeBr<sub>3</sub>, and IA by introducing EBiB, AN, and VC. The results were summarized in Table IV. The values of  $k_p^{\text{app}}$  in recovered [C<sub>12</sub>mim][BF<sub>4</sub>] were calculated to be  $7.72 \times 10^{-6} \text{ s}^{-1}$ , which was a little lower in that than in [C<sub>12</sub>mim][BF<sub>4</sub>]. Table IV also displayed dependence of  $M_n$  and PDI on the monomer conversion for ARGET ATRP of AN in recovered ionic liquids and FeBr<sub>3</sub> and IA. The molecular weight of PAN increased with the conversion and PDI remained relatively narrow in recovered ionic liquids. This means that [C<sub>12</sub>mim][BF<sub>4</sub>] could be recycled and reused after simple purification and had no effect on the living nature of polymerization.

### CONCLUSIONS

A new method for conducting ARGET ATRP of AN in ionic liquid with FeBr<sub>3</sub>/IA as catalyst system in the presence of air was first developed. First-order kinetics of polymerization with respect to the monomer concentration and linear increase of the molecular weight with monomer conversion indicate that ARGET ATRP of AN [C<sub>12</sub>mim][BF<sub>4</sub>] is the living/controlled radical polymerization. The sequence of the rate coefficients of polymerization was  $k_p^{\text{app}}([\text{C}_{12}\text{mim}][\text{BF}_4]) > k_p^{\text{app}}([\text{C}_8\text{mim}][\text{BF}_4]) > k_p^{\text{app}}([\text{C}_4\text{mim}][\text{BF}_4])$ . With an increase of VC concentration, both the monomer conversion and the molecular weight distribution showed a trend of increase. The polymerization rate showed a prominent trend of decrease with the increase in FeBr<sub>3</sub> content. The resultant PAN with molecular weight of 166,250 and distribution of 1.34 was successfully prepared with PAN as macroinitiator via ARGET ATRP in [C<sub>12</sub>mim][BF<sub>4</sub>]. The fibers obtained from PAN satisfy the requirements for high performance PAN fibers and could be used to prepare carbon fibers. [C<sub>12</sub>mim][BF<sub>4</sub>] could be recycled and reused after simple purification.

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