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Reverse ATRP Process of Methacrylonitrile in [C4mim][PF6]

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In this original experiment, an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]), was used as the reaction media for reverse atom transfer radical polymerization of methacrylonitrile (MAN) initiated by azobisisobutyronitrile (AIBN) with $FeCl_3$ and isophthalic acid (IA) as catalyst and ligand. The polymerization in [C_4mim][PF_6] proceeded in a well-controlled manner as evidenced by kinetic studies. Compared with the polymerization in *N*, *N*-dimethylformamide (DMF), the polymerization in [C_4mim][PF_6] not only showed better control of molecular weight and narrower molecular weight distribution but also provided more rapid reaction rate with the ratio of [MAN]:[AIBN]:[$FeCl_3$]:[IA] at 300:1:2:4. The block copolymer PMAN-b-PSt was obtained via a conventional ATRP process in [C_4mim][PF_6] by using the resulting PMAN as macroinitiator. [C_4mim][PF_6] and $FeCl_3$/IA could be easily recycled and reused and had no effect on the living nature of reverse atom transfer radical polymerization of MAN.

Keywords: Block polymerization, living polymerization, reverse atom transfer radical polymerization, ionic liquid, methacrylonitrile

1 Introduction

Well-defined Polymethacrylonitrile (PMAN) and their block copolymers have attracted many interests due to their potential applications (1). However, PMAN is usually prepared by radical polymerization without control over molecular dimension and structure (2, 3). In order to satisfy the requirements for high performance PMAN, living/controlled free radical polymerization techniques, as it combines the advantage of radical polymerization and living polymerization techniques, could be employed to prepare polymers with predictable molecular weight, high polydispersity and well-defined architecture (4, 5). Atom transfer radical polymerization (ATRP) (6–8) and reverse ATRP (9–12) are the most powerful, versatile, simple and inexpensive methods in living/controlled free radical polymerization. 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 (13–19). 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.

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 (20–27).

Carmichael et al. (28) 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 (29) discussed the ATRP of MMA in ionic liquids containing different counterions, and Kubisa (30) studied effects of different substituents on ATRP of acrylates in [C_4mim][PF_6]. The other studies in this field have been done (31–38). Reverse ATRPs of MMA were firstly approached by Wan (39, 40) and his coworkers in three ionic liquids, [C_4mim][PF_6], 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4mim][BF_4]) and 1-dodecyl-3-methylimidazolium tetrafluoroborate ([C_{12}mim][BF_4]), respectively. Lu et al. (41) reported reverse ATRPs of MMA in [C_8mim][PF_6], [C_6mim][BF_4], [C_8mim][BF_4], and [C_{12}mim][BF_4].

To the best of our knowledge, neither ATRP nor reverse ATRP of MAN has been approached, except our group. A detailed study for the optimization of the reaction conditions to prepare well-defined PMAN by reverse ATRP was the starting point of this original research. Novel reaction media and new catalytic systems were developed. Acids

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were generally believed to deactivate the metal organic catalyst, resulting in poor control of the polymerization. However, isophthalic acid (IA), which are inexpensive and nontoxic, complex more easily with iron and may therefore, act as a ligand.

Keeping all these points in mind, $[C_4mim][PF_6]$ was chosen to be the reaction media due to its higher solvating power for transition metal salts, $FeCl_3$ and IA were selected to be catalyst and ligand, and AIBN was used as the initiator. The successful approach of the well-controlled reverse ATRP of MAN in ionic liquid was described for the first time. We found that this initiator and catalyst system could promote reverse ATRP of MAN with the desired characteristics of living/controlled radical polymerization in $[C_4mim][PF_6]$. Compared with reverse ATRP of MAN in DMF, the polymerization in $[C_4mim][PF_6]$ not only showed better control of molecular weight and narrower molecular weight distribution but also provided more rapid reaction rate. Block polymerization of styrene using PMAN as macroinitiator via a conventional ATRP process in $[C_4mim][PF_6]$ was also attempted. $[C_4mim][PF_6]$ and the catalyst system could be easily recycled and reused after simple purification.

2 Experimental

2.1 Materials

MAN (Xinhua Ruowei Chemical Co. Ltd, Hunan, China) were freed from inhibitor by washing with 5% NaOH and then with water several times. After drying over Na_2SO_4, they were distilled under reduced pressure. Anhydrous $FeCl_3$ (A. R. grade, Shanghai Chemical Reagents Co.) was washed with analytical-reagent-grade ethanol and dried under vacuum at 60°C before use. Isophthalic acid (IA, A. R. grade, Shanghai Chemical Reagents Co., Shanghai, China) was used as received without purification. 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. $[C_4mim][PF_6]$ was prepared following the literature method (42). DMF (A. R. grade, Tianjin Ruijinte Chemical Co. Ltd, Tianjin, China) was distilled at reduced pressure and stored over type4-Å molecular sieves before use.

2.2 Polymerization

A typical example of the general procedure was as follows. $FeCl_3$, IA and $[C_4mim][PF_6]$ were added into a dry glass tube under stirring. Three cycles of vacuum nitrogen were applied to remove oxygen. MAN with AIBN 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 definite time, the polymerization was terminated by cooling the flask in the ice water. The polymerization product was diluted with DMF. 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.

2.3 Characterization

The conversion of the monomer was determined gravimetrically. The molecular weight (M_n) and polydispersity index (PDI) of PMAN were measured by gel permeation chromatography (GPC). GPC was performed with a Waters 1515 solvent delivery system (Milford, MA) at a flow rate of $1.0\ mL\cdot min^{-1}$ 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 (43),

$$M_{th} = \frac{[MAN]}{2[AIBN]} \times M_{wMAN} \times \text{Conversion}$$

Where M_{WMAN} is the molecular weight of MAN.

3 Results and Discussion

3.1 Reverse ATRP of MAN in $[C_4mim][PF_6]$ and DMF

Reverse ATRP of MAN catalyzed by $FeCl_3$/IA was carried out at 75°C in $[C_4mim][PF_6]$ and DMF, respectively. Figure 1 shows the relationship between the monomer conversion and the reaction time in $[C_4mim][PF_6]$ and DMF. The monomer conversions increased with the reaction time, and the conversion in $[C_4mim][PF_6]$ was higher than in DMF. The monomer conversion reached about 66.7% within 180 min and the monomer conversion only

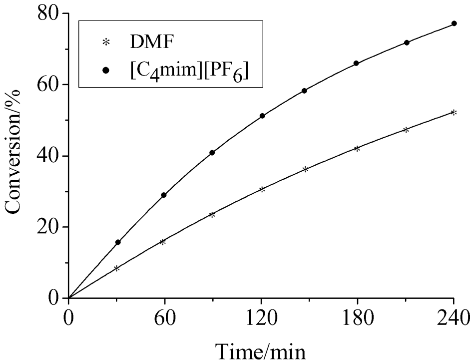

Fig. 1. Conversion dependence on the reaction time in $[C_4mim][PF_6]$ and DMF with MAN = 0.50 g, $[C_4mim][PF_6]$ = 1.5 g and $[MAN]:[AIBN]:[FeCl_3]:[IA] = 300:1:2:4$

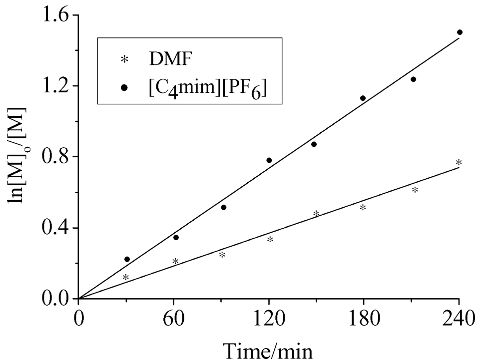

Fig. 2. Kinetics of reverse ATRP of MAN in $[C_4mim][PF_6]$ and DMF with MAN = 0.50 g, $[C_4mim][PF_6]$ = 1.5 g and $[MAN]:[AIBN]:[FeCl_3]:[IA] = 300:1:2:4$.

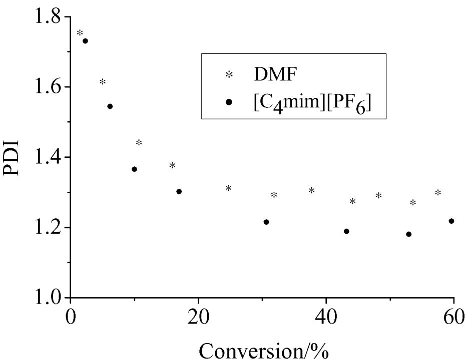

Fig. 4. Dependence of PDI on monomer conversion for reverse ATRP of MAN in $[C_4mim][PF_6]$ and DMF with MAN = 0.50 g, $[C_4mim][PF_6]$ = 1.5 g and $[MAN]:[AIBN]:[FeCl_3]:[IA] = 300:1:2:4$.

reached 42.6% in DMF. This clearly demonstrates that the rate of polymerization in $[C_4mim][PF_6]$ was considerably faster than in DMF.

In order to prove the living nature of reverse ATRP of MAN in $[C_4mim][PF_6]$ and DMF, kinetic studies were performed. Figure 2 shows the kinetic plots of $\ln([M]_0/[M])$ versus time for reverse ATRP of MAN. 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}) was calculated. The k_p^{app} in $[C_4mim][PF_6]$ ($10.2 \times 10^{-5} s^{-1}$) was much higher than in DMF ($5.14 \times 10^{-5} s^{-1}$). A similar result was reported by Kubisa et al. (44) for ATRP of acrylates in $[C_4mim][PF_6]$. They reported that either instantaneous concentration of radicals or the propagation-rate constant was higher in ionic liquids.

Figure 3 indicates that the molecular weights of the resulting polymers obtained in $[C_4mim][PF_6]$ and DMF increased linearly with conversion, and the molecular weights agreed reasonably well with the theoretical molecular weight at conversion beyond 10%. In contrast with the resulting PMAN in DMF, M_n of the resulting PMAN in $[C_4mim][PF_6]$ agreed better with those of the theoretical molecular weight (M_{th}). The higher molecular weight at conversion less than 10% indicates the incomplete decomposition of AIBN at the beginning of the reaction resulting small amount of the polymer chain.

The values of PDI of polymethacrylonitrile in $[C_4mim][PF_6]$ and DMF are shown in Figure 4. The molecular weight distribution were narrower (PDI = 1.19) in $[C_4mim][PF_6]$ than in DMF(PDI = 1.23) when the conversion was from 10 to 60%. The broader PDI at conversion less than 10% suggested there was some termination or side reaction at the beginning of the reaction because the radicals were not immediately deactivated. First-order kinetics of the polymerization rate with respect to the monomer concentration, linear increase of the molecular weight with monomer conversion and high polydispersity were indicatives of living/controlled radical polymerization. Reverse ATRP of MAN with $FeCl_3$/IA as catalyst complex in $[C_4mim][PF_6]$ was more controlled than in DMF because of good solubility of AIBN and $FeCl_3$/IA in $[C_4mim][PF_6]$.

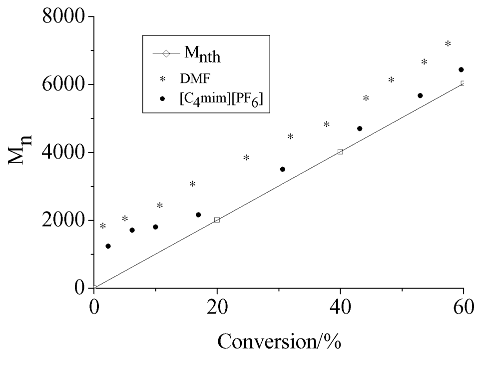

Fig. 3. Dependence of M_n on monomer conversion for reverse ATRP of MAN in $[C_4mim][PF_6]$ and DMF with MAN = 0.50 g, $[C_4mim][PF_6]$ = 1.5 g and $[MAN]:[AIBN]:[FeCl_3]:[IA] = 300:1:2:4$.

3.2 Effect of $FeCl_3$ Content on Reverse ATRP of MAN in $[C_4mim][PF_6]$ and DMF

The catalyst $FeCl_3$ plays an important role in reverse ATRP of MAN. To further discuss effects of $FeCl_3$ content on reverse ATRP of MAN, a series of experiments were carried out in $[C_4mim][PF_6]$ and DMF. The results have been summarized in Table 1. If $FeCl_3$ was not enough (entries 1, 2, 7–9), the polymerization in $[C_4mim][PF_6]$ and DMF proceeded in an uncontrolled manner. When the ratio of $[FeCl_3]/[IA]$ increased from 2:4 to 4:4(entries 4–6, 10–12), the molecular weight distribution of polymers became narrower and narrower, and the rate of polymerization decreased prominently. $FeCl_3$ itself was an effective catalyst

Table 1. Data for reverse ATRP of MAN in [C_4mim][PF_6] and DMF at 75°C with MAN = 0.50 g, [C_4mim][PF_6] = 1.5 g and [MAN]:[AIBN] = 300:1

Entry	*[AIBN]:[FeCl$_3$]:[IA]*	*Reaction media*	*Reaction time/min*	*Conversion/%*	M_{th}	M_n	*PDI*
1	1:0:4	[C_4mim][PF_6]	180	84.5	8492	54850	2.78
2	1:1:4	[C_4mim][PF_6]	180	79.8	8020	32540	2.09
3	1:1.5:4	[C_4mim][PF_6]	180	70.5	7085	7960	1.23
4	1:2:4	[C_4mim][PF_6]	180	66.7	6703	7420	1.19
5	1:3:4	[C_4mim][PF_6]	180	58.7	5899	6430	1.17
6	1:4:4	[C_4mim][PF_6]	180	52.4	5266	5590	1.13
7	1:0:4	DMF	180	81.4	8181	49690	3.05
8	1:1:4	DMF	180	78.1	7849	42560	2.62
9	1:1.5:4	DMF	180	74.4	7477	36780	2.37
10	1:2:4	DMF	180	42.6	4281	5160	1.23
11	1:3:4	DMF	180	36.7	3688	4680	1.20
12	1:4:4	DMF	180	32.9	3306	3640	1.18

in reverse ATRP, but excess $FeCl_3$ would not only slow the polymerization rate significantly but also could contaminate the resultant polymers. As shown in Table 1, another interesting phenomenon was that only less amount of $FeCl_3$ (entries 3) was needed to gain well control over the polymerization in [C_4mim][PF_6] than DMF (entries 10). The main reason might be the good solubility of $FeCl_3$ in [C_4mim][PF_6].

3.3 Block Copolymerization with Styrene

According to the mechanism polymerization of reverse ATRP, the well-defined PMAN with an ω-chlorine atom end groups was obtained in reverse ATRP of MAN using AIBN/$FeCl_3$/IA system in [C_4mim][PF_6]. Another method to verify the living functionality of obtained PMAN is its use as a macroinitiator for the same or other monomers (45). In this study, block polymerization of styrene (St) using PMAN (M_n =7420, PDI = 1.19) as macroinitiator was carried out at 85°C in the presence of the $FeCl_2$/IA catalyst system via a conventional ATRP process. [C_4mim][PF_6] was used as the solvent to enable the formation of higher molecular weight PMAN-b-PSt copolymers. When MAN = 1.0 g, [C_4mim][PF_6] = 3.0 g and [St]:[PMAN]:[$FeCl_2$]:[IA] = 300:1:2:4, block copolymer PMAN-b-PSt was obtained with M_n =43560, PDI = 1.31. It was clearly verified that the block polymerization of PMAN did take place.

3.4 Recycling and Reuse of [C_4mim][PF_6]

Recycling and reuse of [C_4mim][PF_6] 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, washed with methanol several times. The precipitated PMAN was obtained. After the evaporation of methanol, DMF and the residue MAN, recovered [C_4mim][PF_6], $FeCl_3$ and IA were obtained. Reverse ATRP of MAN was carried out again in recovered [C_4mim][PF_6], $FeCl_3$ and IA by introducing AIBN and MAN. Figure 5 shows the plot $\ln([M]_0/[M])$ versus time for reverse ATRP of MAN. 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_4mim][PF_6], $FeCl_3$ and IA was calculated to be $9.9 \times 10^{-5} s^{-1}$, which was almost same with in [C_4mim][PF_6]. But an induction period (10 min) was observed for reverse ATRP of MAN in recovered [C_4mim][PF_6], $FeCl_3$ and IA. The longer induction period was perhaps caused by the presence of oxygen and impurities and slow decomposition of AIBN at the early stages of the polymerization. The primary radicals generated form AIBN completely reacted with $FeCl_3$ to form the dormant species and the propagation of PMAN chains was retarded.

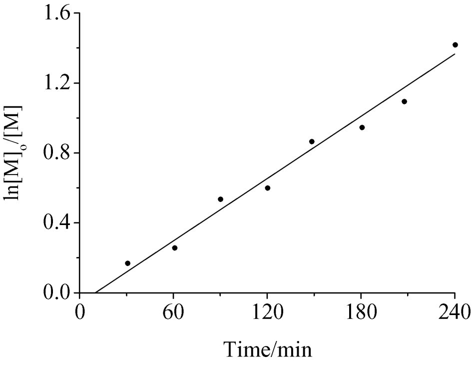

Fig. 5. Kinetics of reverse ATRP of MAN in recovered [C_4mim][PF_6], $FeCl_3$ and IA at 75°C with AN = 0.50 g, [C_4mim][PF_6] = 1.5 g and [MAN]:[AIBN]:[$FeCl_3$]:[IA] = 300:1:2:4

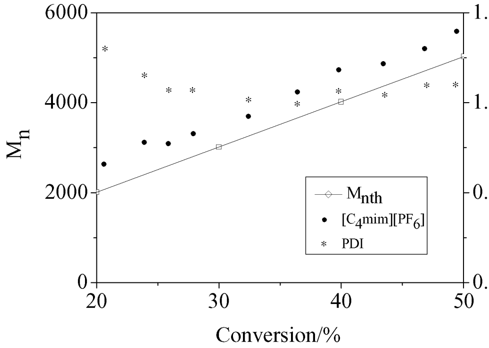

Fig. 6. Dependence of M_n and PDI on monomer conversion in recovered $[C_4mim][PF_6]$, $FeCl_3$ and IA at 75°C with AN = 0.50 g, $[C_4mim][PF_6] = 1.5$ g and $[MAN]:[AIBN]:[FeCl_3]:[IA] = 300:1:2:4$.

Figure 6 displays the plot of the molecular weight (M_n) and polydispersity index (PDI) vs. monomer conversion. M_n of MAN polymers in recovered $[C_4mim][PF_6]$, $FeCl_3$ and IA increased linearly with conversion and the molecular weight distribution remained relatively narrow. This indicated a well-controlled polymerization process.

4 Conclusions

Reverse ATRP of MAN with $AIBN/FeCl_3/IA$ as the catalyst system was first approached in the ionic liquid, $[C_4mim][PF_6]$. The monomer conversion in $[C_4mim][PF_6]$ was higher than in DMF under the same experimental conditions. As more $FeCl_3$ was added, the monomer conversion decreased, and the molecular weight distributions became narrower and narrower. The block copolymer PMAN-b-PSt with a molecular weight at 43560 and a high polydispersity as low as 1.31 were successfully prepared by using obtained PMAN as a macroinitiator via a conventional ATRP process in $[C_4mim][PF_6]$. The kinetic study of reverse ATRP of MAN in recovered $[C_4mim][PF_6]$, $FeCl_3$ and IA indicates that $[C_4mim][PF_6]$ and the catalyst system could be reused after simple purification.

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