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Cationic Polymerization of Isobutyl Vinyl Ether in an Imidazole-Based Ionic Liquid: Characteristics and Mechanism

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Abstract:

Cationic polymerizations of isobutyl vinyl ether (IBVE) in an ionic liquid 1-octyl-3-methylimidazolium tetrafluoroborate ([omim][BF_4]) were thoroughly examined at 0 ^{o}C. A variety of coinitiators was used in conjunction with IBVE-HCl adduct as a cationogen. Compared with those in organic solvents, the cationic polymerization of IBVE in [omim][BF_4] proceeded in a milder exothermic manner, yielding polymers with higher molecular weight, and giving a higher monomer conversion. Although the polymerization reaction in [omim][BF_4] could not be controlled due to the presence of β-proton

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elimination, the monomer addition experiments confirmed the existence of long-lived species. Introducing a small amount of 2,6-di-*tert*-butylpyridine (DTBP) into the system may lead to a controlled polymerization. The corresponding elementary reactions and stabilization mechanism of propagating carbocation in [omim][BF_4] were also proposed.

Keywords: Cationic polymerization; Isobutyl vinyl ether; Ionic liquid; Controlled/living polymerization

Introduction

Controlled/living cationic polymerization, which was discovered by Higashimura and Kennedy groups in middle of the 1980s[1,2], represents an attractive technique for the synthesis of well-defined polymers. Controlled/living cationic polymerization usually has been achieved by using initiator/coinitiator system in an organic solvent under strictly anhydrous circumstance [3-8]. High polarity of organic solvent favors the controlling of a cationic polymerization, because the equilibrium between active and dormant species can be easily maintained [9-12]. However, polar solvents especially chlorinated solvents can cause environmental pollution due to their toxic, volatile and corrosive nature, and therefore they should be replaced. In addition, it is difficult to separate the Lewis acid catalyst from the reaction products, and reuse/disposal of the catalyst constitutes also a challenge to industry [13].

In recent years, room temperature ionic liquids have been extensively investigated as clean solvents for a variety of chemical reactions. The interests in ionic liquids include negligible vapor (non-contaminating “green” solvents), high thermal stability, and their ability to dissolve several inorganic and organ metallic compounds allowing several catalytic processes to be carried out under homogeneous conditions. The use of ionic liquids as solvents in polymerization reactions has been recently reported for radical polymerization[14-15], atom-transfer radical polymerization[16], polycondensation[17], ring-opening polymerization[18], and anionic polymerization[19-20].

Due to the ionic nature, ionic liquids are regarded as highly polar but non-coordinating solvents, enabling them as ideal solvents for cationic polymerization. Early applications of ionic liquids as reaction media for cationic polymerization were mainly described in the patents[21], involved those containing haloaluminate anions ($AlCl_4^-$ frequently in conjunction with R_nAlCl_{3-n}). Those water-sensitive acidic ionic liquids were used as both solvents and initiators for the cationic oligomerization of alkenes because they can be hydrolyzed easily. More recently, developed air- and water-stable ionic liquids (for instance, 1-butyl-3-methylimidazoliumhexafluorophospate ([BMIM][PF_6])[22-25] and trihexyltetradecylphosphonium bis(trifluoromethanesulfonyl)-amide ([$P_{6,6,6,14}$][NTf_2])[26]) have been applied in cationic polymerization. Moreover, cationic polymerization of styrene in *N*-butyl-*N*-methylpyrrolidiniumbis-(trifluoromethanesulfonyl)amide ([P_{14}][tf_2N])[27] ionic liquid with organoborate acids as initiators indicates some living/controlled characteristics.

Vinyl ethers are among the most reactive monomers in cationic polymerization, even more reactive than styrene and its derivatives[28,29]. However, surprisingly, there is no research activity concerning the application of ionic liquids as solvents for vinyl ethers cationic polymerization, despite the fact that ionic liquids are considered ideal solvents for any process that involves a charge separation. The main objective of the present work is to compare the polymerization characteristics of isobutyl vinyl ether (IBVE) in ionic liquids with those in organic solvents. Furthermore, the corresponding polymerization mechanism will be proposed. To the best of our knowledge, it is the first report on controlled/living cationic polymerization of IBVE in air- and water-stable ionic liquids.

Experimental Part

Materials

Ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6], >99.0%), 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF_6], >99.0%), 1-octyl-3-methylimidazolium hexafluorophosphate ([omim][PF_6], >99.0%), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4], >99.0%), 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF_4], >99.0%), 1-octyl-3-methylimidazolium tetrafluoroborate ([omim][BF_4], >99.0%), were purchased from Sigma-Aldrich. They were dried and degassed under vacuum at 60 ^{o}C for a few days to remove moisture. Karl-Fisher analysis of the ionic liquid indicated that the water content was reduced to less than 40ppm. IBVE (TCI; >99.0%), ethyl acetate (Wako; >99.5), and dichloromethane (Beijing Chemical Co., 99.9%) were distilled twice over calcium hydride before use. 2,6-Di-*tert*-butylpyridine (DTBP; Aldrich; 97+%) was distilled twice over calcium hydride under reduced pressure. 1,4-Dioxane (Wako; >99.5) was distilled over calcium hydride and then lithium aluminum hydride. Commercially available ethylaluminium sesquichloride ($Al_2Cl_3Et_3$, Aldrich, 0.4M solution in hexane) and stannic chloride ($SnCl_4$ Aldrich; 1.0M solution in dichloromethane) were used as received. IBVE-HCl was prepared from the addition reaction of IBVE with HCl[30]. IBVE-HCl adduct was synthesized by bubbling dry HCl gas through a solution of IBVE in hexane (1.0 M) at $0^{o}C$. HCl was generated by dropping concentrated sulfuric acid into powdery sodium chloride and dried by passing it through a column packed with calcium chloride. After 30min, excess HCl in solution was removed by bubbling dry nitrogen at $0^{o}C$ for 30 min, and the clean and quantitative formation of IBVE-HCl adduct was confirmed by ^{1}H NMR spectroscopy.

Polymerizations

All cationic polymerizations were carried out under a dry nitrogen atmosphere in MBraun 150-M glovebox. The moisture (<5ppm) and oxygen content (<10ppm) were monitored. 50 mL screw-cap vials were used as polymerization reactors with an IKA-MS3 vortex stirrer. A typical cationic polymerization was carried out in [omim][BF_4] at $0^{o}C$ using the following concentration: [IBVE-HCl]=0.003M, [$Al_2Cl_3Et_3$]=0.048M, [IBVE]=1.04M. Into a 50mL screw-cap vial 10mL of [omim][BF_4], 2mL of IBVE, 1mL of IBVE-HCl stock solution in dichloromethane (0.045mol/L) were added and mixed thoroughly at $0^{o}C$. The polymerization was started by addition of 1.8mL of $Al_2Cl_3Et_3$ stock solution (0.4M, in hexane) at $0^{o}C$. In controlled cationic polymerization of IBVE, 1mL of DTBP stock solution in dichloromethane (0.03mol/L) should be added in above mentioned polymerization system before initiating reaction. After a predetermined time, the polymerization was quenched with 10 mL prechilled ethanol. The quenched reaction mixtures were washed with ethanol to remove the ionic liquid. The polymer products were dried in a vacuum oven at 40 °C to a constant weight overnight. The monomer conversion was determined gravimetrically.

Measurements

The number-average molecular weight (M_n) and molecular weight distribution (MWD; i.e., M_w/M_n) of the polymers were determined with a Waters 515-2410 gel permeation chromatography (GPC) system equipped with four Waters styragel columns connected in the following series: 500, 10^3, 10^4, and 10^5 at 30 °C. THF was used as solvent of poly(IBVE) with a concentration of 20 mg of poly(IBVE)/10 mL of THF and was also used as mobile phase at a flow rate of 1.0 $mL\cdot min^{-1}$. The calibration of molecular weight was based on polystyrene standards.

NMR spectroscopy of the polymers was performed on a Bruker AV600 MHz spectrometer using $CDCl_3$ as a solvent at 25 °C. ^{1}H-NMR spectra of solutions in $CDCl_3$ were calibrated to tetramethylsilane as internal standard ($\delta_H = 0.00$).

The cloud point of solutions of IBVE in ionic liquids was measured by a polarized optical microscope (Olympus BHSP, Tokyo, Japan) equipped with a temperature controlling stage (Linkam THMS 600, London, UK) under parallel polarizer.

Viscosity of ionic liquids and IBVE solutions of ionic liquid was measured at 25 ^{o}C by using a Brookfield viscometer (Model DV-II+, Stoughton, MA, USA) with cone spindle.

Computational Method

All calculations were carried out with the software package Gaussian 03. Geometry optimizations and frequency calculations were performed by the density functional theory (DFT) BP86: Becke's 1988 exchange functional[31] with Perdew's correlation functional[32] using 6-31G$*$ basis sets for C, H, Cl, O, B, F, and the relativistic effective core potential with the LANL2DZ basis sets for Ti.

Results and Discussion

1. Selection of Ionic Liquids

The replacement of traditional organic solvents is one of the most promising areas for industrial applications of ionic liquids. However, the solubility issue of the reagents in ionic liquids often plagues the efficiency of the reaction. For this reason, prior to polymerizations, the IBVE solubility in ionic liquids was first examined. In order to meet the requirements of low temperature for cationic polymerization, we mainly focused on the low-melting-point ionic liquids. In Table 1, the melting point, viscosity, and the solubility data were presented, in which [omim][BF_4] possessed the highest solubility for IBVE. Although [omim][BF_4] itself had a high viscosity, the IBVE solution viscosity in [omim][BF_4] decreased significantly with increasing solubility of IBVE, which was in favor to diffusion of the monomer in the polymerization process.

Table 1 Data of melting point, viscosity of ionic liquids, IBVE solubility and viscosity of IBVE solution

Entry	Ionic liquid	Melting Point/ °C	Viscosity of ionic liquid/CP	Solubility in ionic liquid/wt%	Viscosity of IBVE Solution/CP
1	[bmim][PF_6]	-8	366	5.63	295
2	[hmim][PF_6]	-61	586	7.97	410
3	[omim][PF_6]	-76	699	9.98	521
4	[bmim][BF_4]	-81	140	4.12	109
5	[hmim][BF_4]	-81	266	10.27	190
6	[omim][BF_4]	-80	415	19.45	188

The viscosity was tested at 25 °C.

In order to determine the lowest reaction temperature, the effect of temperature on IBVE solubility was studied. As shown in Figure 1, compared with in other ionic liquids, [omim][BF_4] possessed the highest solubility of IBVE at different temperatures. Below 0°C, the IBVE solubility in [omim][BF_4] decreased rapidly with decreasing temperature. Above 0°C, the IBVE solubility in [omim][BF_4] did not change significantly with temperature. As a result, [omim][BF_4] was selected to investigate the feature of IBVE cationic polymerization at 0°C.

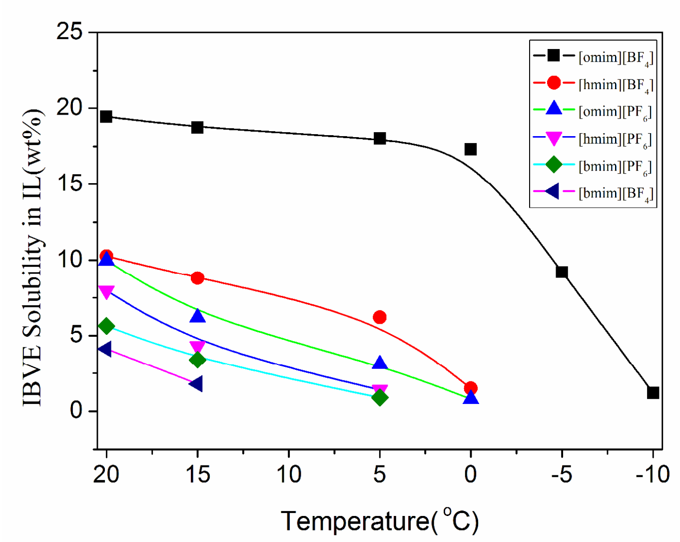


Figure 1 Effect of temperature on IBVE solubility in ionic liquids

2. Characteristics of IBVE cationic polymerization in [omim][BF_4]

IBVE cationic polymerizations were performed using a variety of coinitiators in conjunction with a cationogen IBVE-HCl in [omim][BF_4] at 0 °C. In the experiments phenomena, a high monomer conversion (~80%) was observed for homogeneous IBVE polymerization in [omim][BF_4]. This was interesting since polymer solubility in ionic liquids was often very low. Long-chain alkane substituents of imidazolium cation may contribute to improve the solubility of polymer in ionic liquid. According to Figure 2, the plots of the monomer conversion versus the polymerization time indicated that the monomer conversion gradually increased with prolonging polymerization time. The first-order plots of ln([M$_0$]/[M]) versus time were not linear for all coinitiators used, indicating that the concentration of active species in the polymerization system kept decreasing over time. The obtained polymers exhibited broad MWDs (Figure 3), which also indicated the polymerization was not well controlled. Some side reactions may occur during the polymerization, possibly from *β*-proton or some protic impurities such as adventitious water.

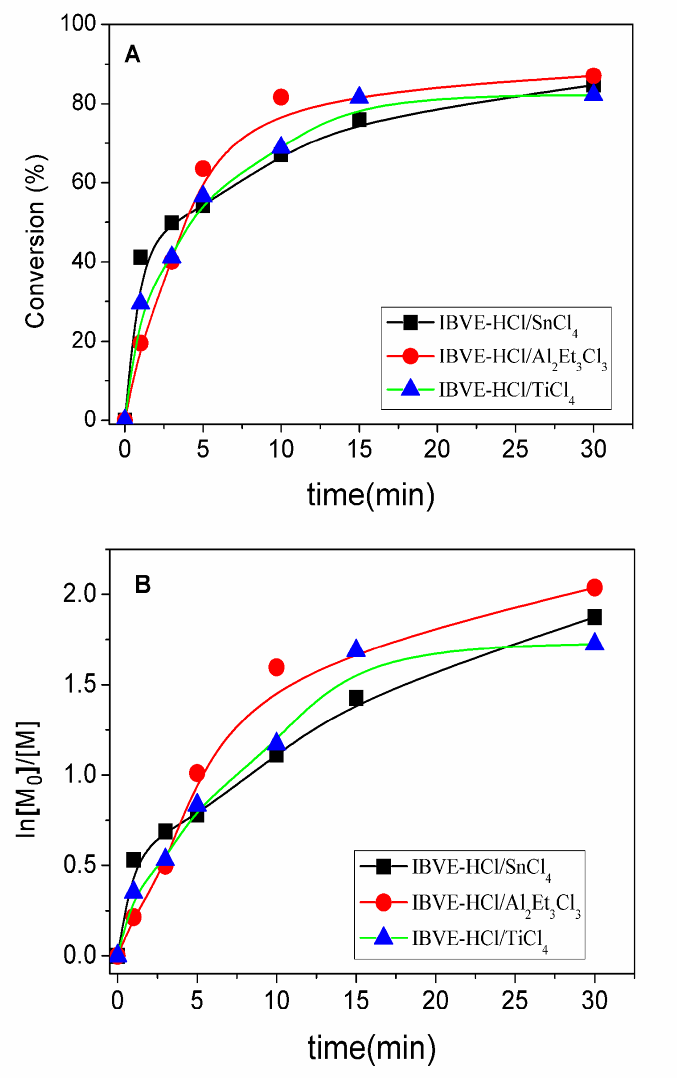


Figure 2 Kinetic plots of IBVE polymerization in [omim][BF$_4$]: (A)conversion vs. time; (B) ln([M$_0$]/[M]) vs. time. [IBVE-HCl]=0.003M, [IBVE]=1.04M, the molar ratio of coinitiator to IBVE-HCl =16, T=0 ^{o}C.

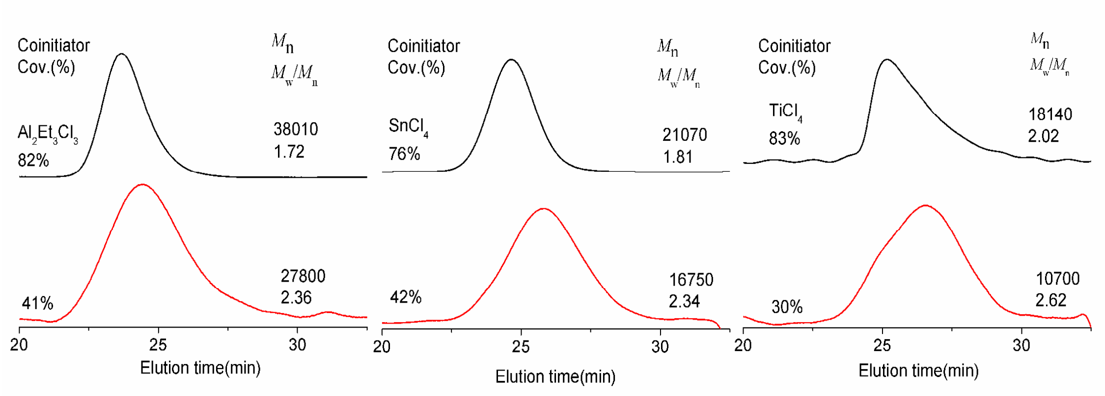


Figure 3 Representative GPC curve of poly(IBVE)s obtained in [omim][BF$_4$] using various coinitiators.

In order to further understand the ion environment and its effect on cationic polymerization, we compared the characteristics of IBVE cationic polymerization in organic molecule medium. Table 2 showed the data of IBVE polymerization in dichloromethane in the same condition as [omim][BF$_4$]. All the reactions were quenched in a few minutes, resulting in polymers with broad MWDs. Moreover, the yields of poly(IBVE)s prepared in dichloromethane were lower (~30%) as compared with those in [omim][BF$_4$]. Apparently, more severe chain transfer and chain termination reactions took place in the dichoromethane system. The M_n of poly(IBVE)s obtained in [omim][BF$_4$] were much higher than those obtained in dichloromethane in the same conditions. It may be accounted for the relatively higher polarity of the ionic liquid. The

[omim][BF_4] had a considerably higher normalized solvent polarity E^N_T as compared to dichloromethane[33]. Generally, the higher the polarity of solvent gives, the higher the M_n of the resulted polymer[9]. Moreover, the polymerization in dichloromethane system proceeded in a highly exothermic manner. For example, in IBVE-HCl/$TiCl_4$ initiating system, the exothermic peak reached to 24°C. However, the exotherm in [omim][BF_4] was only 9°C with ~90% monomer conversion. The milder reactions in ionic liquid may be due to the relatively higher viscosity and higher heat capacity of the ionic liquid. The high viscosity of ionic liquid reduced the diffusion rate of monomer and thus slowed down the reaction rate. The relatively higher heat capacity of ionic liquid could absorb more heat during the polymerization and thus to reduce the chance of chain transfer reaction.

Table 2 Cationic polymerizations of IBVE using various coinitiators in ionic liquid and dichloromethane

Entry	Solvent	Coinitiator	Time (min)	Conv. (%)	M_n	M_w	M_w/M_n
1	dichloromethane	$Al_2Et_3Cl_3$	1.5	20	21880	40700	1.86
2	dichloromethane	$SnCl_4$	2.5	27	16490	31500	1.91
3	dichloromethane	$TiCl_4$	2.5	29	13200	24000	1.82
4	[omim][BF_4]	$Al_2Et_3Cl_3$	10.0	82	38010	65380	1.72
5	[omim][BF_4]	$SnCl_4$	15.0	76	21070	38140	1.81
6	[omim][BF_4]	$TiCl_4$	15.0	83	18140	36600	2.02

Conditions: Initiator:[IBVE-HCl]=0.003M, [IBVE]=1.04M, the molar ratio of coinitiator to IBVE-HCl =16, T=0 °C; $M_{n(theor)}$=34300g/mol.

Importantly, the long-lived species were observed in [omim][BF_4] system. Monomer addition experiments were carried out to confirm the existence long-lived species in [omim][BF_4] system. A fresh feed of monomer was added to the ionic liquid reaction mixture after the first feed was almost 85% exhausted. As shown in Figure 4, although the second stage of polymerization proceeded with bimodal MWD, the GPC curve of the polymer shifted toward higher molecular weights. Therefore, it was speculated that a part of propagating carbocations of poly(IBVE)s might be stabilized by the inherent molecular structure of [omim][BF_4].

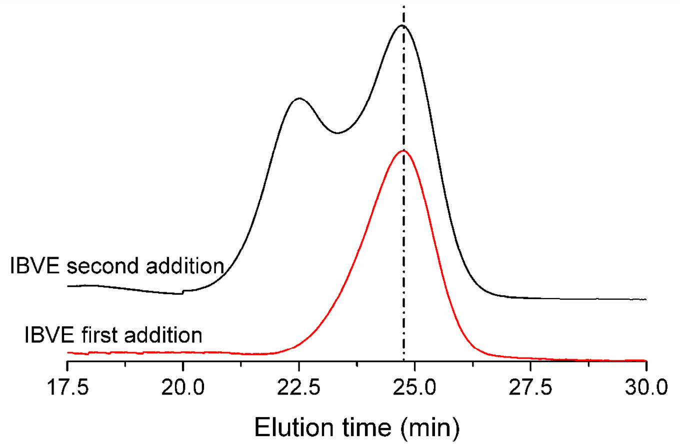


Figure 4 GPC curves of poly(IBVE)s obtained in [omim][BF_4] by monomer addition experiments. [IBVE-HCl]=0.003M, $[IBVE]_0$=$[IBVE]_{add}$=0.75M, [$Al_2Cl_3Et_3$]=0.048M, T=0 ^{o}C.

Stereoregularity of the product polymers was revealed from the peaks of methylene carbons of the main chains in the ^{13}C-NMR spectra recorded in $CDCl_3$[34-38]. The meso diad values of the polymers produced in [omim][BF_4] were in the range of 55-58% (in Figure 5), which were lower than those obtained in dichloromethane system (61-67%). It could be concluded that the propagating carbocation in [omim][BF_4] system was much less sterically hindered to restrict the direction of the insertion of monomer molecules into the propagating carbocation. Therefore, the ionic environment may affect the interaction between propagating carbocation and metal halide-based counterion.

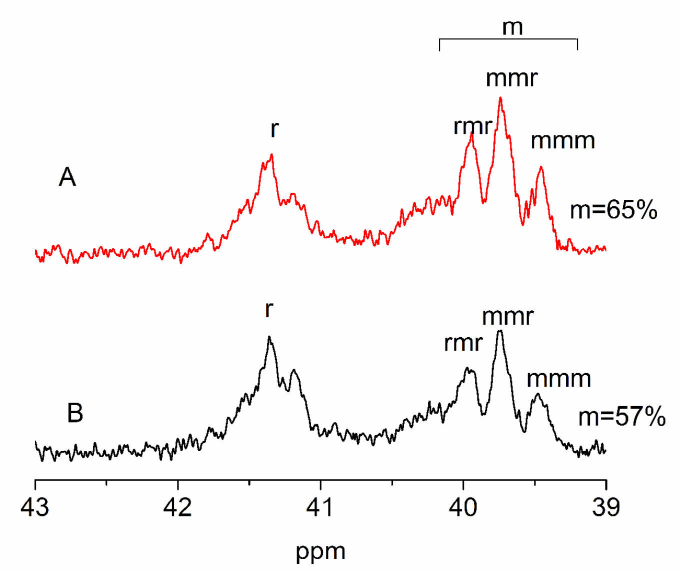


Figure 5 ^{13}C-NMR spectra around 39-43 ppm of poly(IBVE)s obtained in dichloromethane (A) and in [omim][BF_4] (B).

3. Controlled cationic polymerization of IBVE in [omim][BF_4]

To achieve the controlled cationic polymerization of IBVE, addition of bases, such as 1,4-dioxane or ethyl acetate in polymerization system was essential for organic solvent. Polymerization in the presence of ethyl acetate or 1,4-dioxane showed quite different behavior compared to the default system(see Supporting Information). With ethyl acetate or 1,4-dioxane, polymerization was controlled well to produce polymers with very narrow MWDs. The M_n increased in direct proportion to the monomer conversion, which was consistent with those in literatures[34,39]. Generally, addition of bases could control the equilibrium between the dormant and the active species, and thus stabilizing the propagating carbocations in organic solvent[34]. Thus, 1,4-dioxane and ethyl acetate were tried in ionic liquid system. Unfortunately, the obtained poly(IBVE) had a broad MWD, and M_n almost did not vary linearly with monomer conversion. This meant that the cationic polymerization of IBVE in [omim][BF_4] could not be controlled by addition of 1,4-dioxane or ethyl acetate. Obviously, the role of the bases in ionic liquid was different from that in organic solvent.

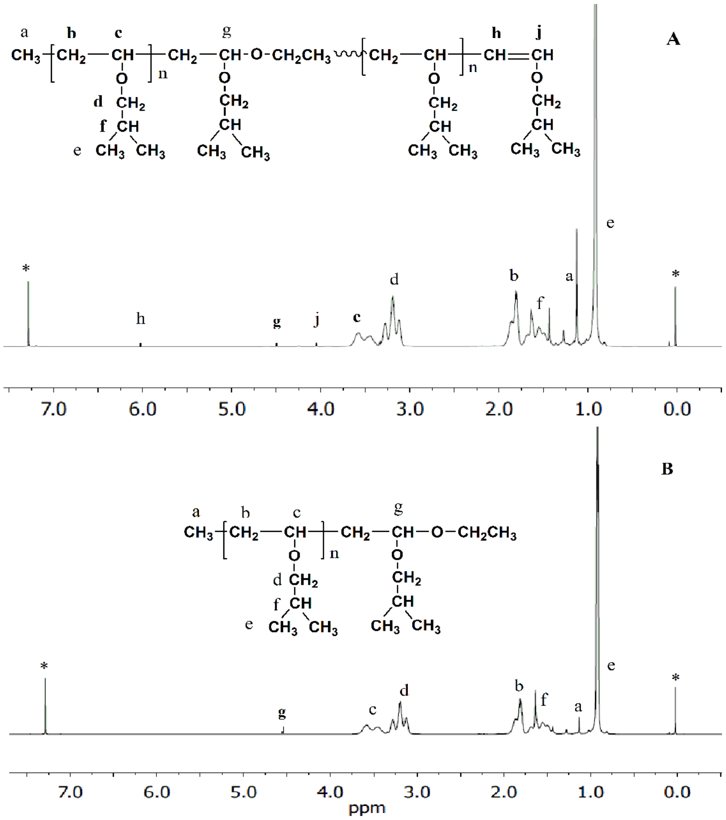


Figure 6 ^{1}H-NMR spectra of poly(IBVE)s obtained in [omim][BF_4] (A) and in dichloromethane (B) .

To further find the reasons for uncontrolled polymerization in ionic liquid media, the elementary reactions and chain end structures of synthesized poly(IBVE) were analyzed by means of ^{1}H-NMR spectroscopy. Typical spectra of polymers obtained in [omim][BF_4] and dichloromethane were compared in Figure 6. The characteristic resonances at δ=0.96

ppm (peak e), δ=1.98 ppm (peak b), and δ=3.77 ppm (peak c) were assigned to methyl, methane, and methylene groups of IBVE, respectively. Poly(IBVE) with $–CH_3$ head group (δ =1.15 ppm, peak a) indicated that the IBVE cationic polymerization was initiated from IBVE-HCl adduct. As shown in Figure 6A, the polymer chains terminated by adding ethanol gave a characteristic resonance of $–CH–O–CH_2CH_3$ (δ =4.56 ppm, peak g), which was similar to that in poly(IBVE) obtained in dichloromethane (Figure 6B). However, compared with Figure 6B, there was a signal (δ =6.1 ppm, peak h) in Figure 6A, which was assigned to the structure of –CH=C*H*–O*i*Bu due to β-proton elimination, the content of which was determined to be 26%. From this one may conclude that, as generally considering, the polymerization reaction in ionic liquid could not be controlled due to the presence of β-proton elimination.

In order to realize the control of the polymerization in ionic liquid, another reagent, DTBP, was tried. DTBP possessed two bulky substituents around the basic nitrogen atom and thus had an ability to trap protic impurities such as β-proton or adventitious water to prevent unintended initiation reactions in living cationic polymerization [39]. As shown in Figure 7, when DTBP was introduced into [omim][BF_4] system, M_n increased in direct proportion to monomer conversion and was close to the theoretical values at later stage of polymerization. The M_n at the early stage of polymerization was higher than the theoretical one; this may be attributed to slow initiation due to the slow diffusion of initiator in viscous ionic liquid. The linear first-order plots showed that the concentration of growing centers remained constant. The absence of termination also confirmed the living nature of the polymerization. Moreover, relatively narrow MWDs (i.e. M_w/M_n~1.2-1.5) were obtained.

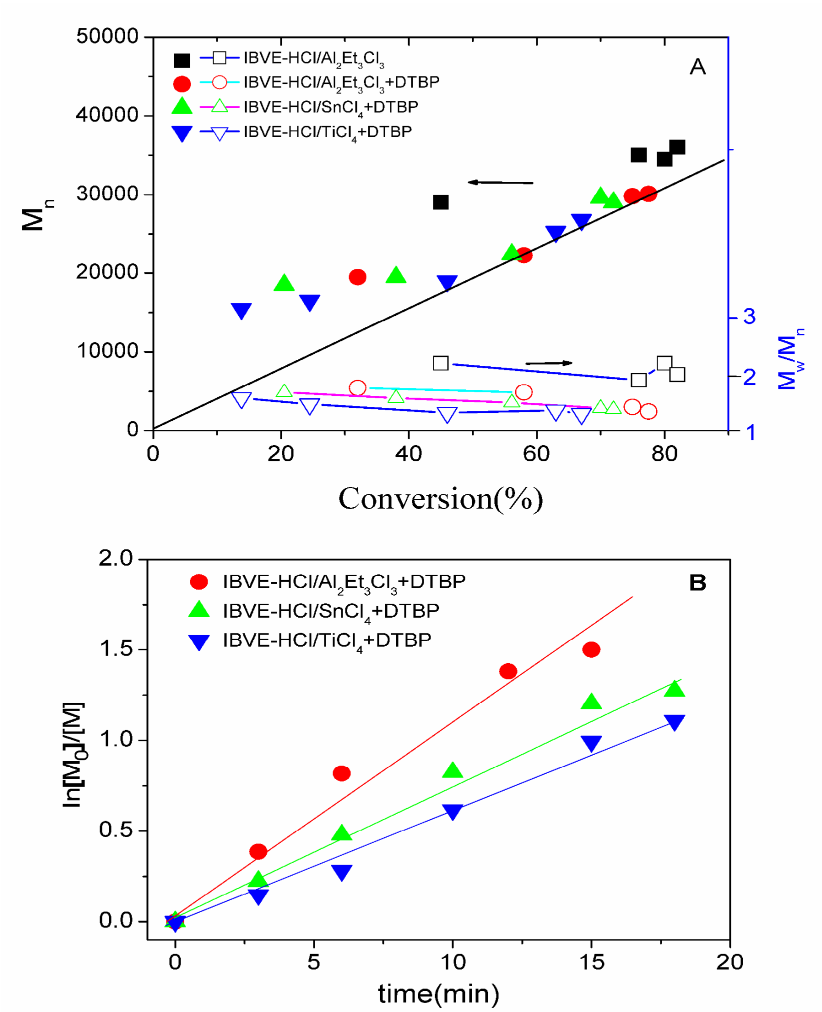


Figure 7 Kinetic plots of IBVE controlled polymerization in [omim][BF_4]: (A)conversion vs. M_n and M_w/M_n; (B) ln([M_0]/[M]) vs. time. (■□) IBVE-HCl/$Al_2Et_3Cl_3$, (●○)IBVE-HCl/$Al_2Et_3Cl_3$+DTBP, (▲△)IBVE-HCl/$SnCl_4$+DTBP (▼▽),IBVE-HCl/$TiCl_4$+DTBP. [IBVE-HCl]=0.003M, [IBVE]=0.97M, [DTBP]=0.002M, the molar ratio of coinitiator to IBVE-HCl=16, T=0 °C.

Figure 8 showed the M_n and MWDs of poly(IBVE)s obtained by addition of DTBP as a function of the feed ratio of IBVE to IBVE-HCl. The M_n increased linearly with increasing [IBVE]/[IBVE-HCl] ratio, and the MWDs remained narrow over the whole [IBVE]/[IBVE-HCl] range. Monomer addition experiments were also carried out to investigate the living nature of IBVE polymerization in [omim][BF_4](Figure 9). The M_n of the polymer product increased linearly even in second stage, and the GPC curve of the polymer shifted toward higher molecular weight, while the MWD remained narrow. This behavior confirmed that the molecular characteristics of the polymers were well controlled in the ionic liquid.

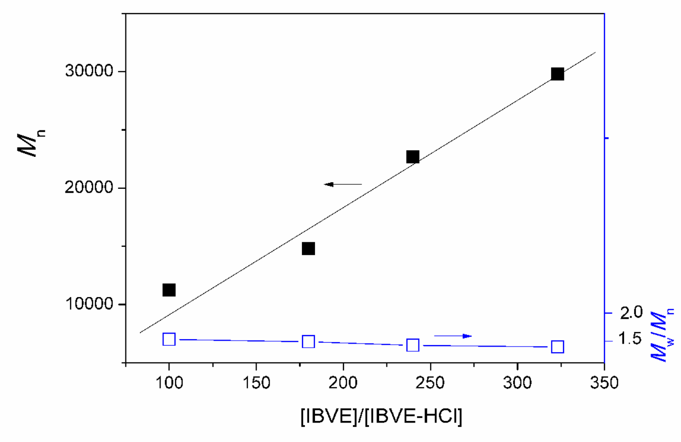


Figure 8 M_n and M_w/M_n values of poly(IBVE) obtained in IBVE-HCl/$Al_2Et_3Cl_3$/DTBP initiating system as a function of the feed ratio of IBVE to IBVE-HCl. [IBVE-HCl]=0.003M, [DTBP]=0.002M, $Al_2Et_3Cl_3$=0.048M, T=0 °C.

Complex formation with a Lewis acid catalyst and interaction with a carbocation were also reported as additional roles of DTBP in some studies[40,41], although others claimed there was no proof of this[42]. In this study, a large amount (1.0 M) of DTBP was used but little effect on the rate was observed, which indicated that DTBP did not interact with the propagating species derived from IBVE in [omim][BF_4] (see Supporting Information).

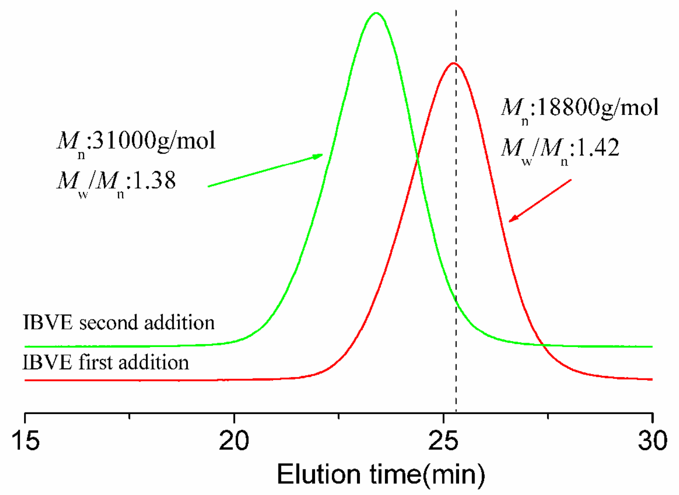
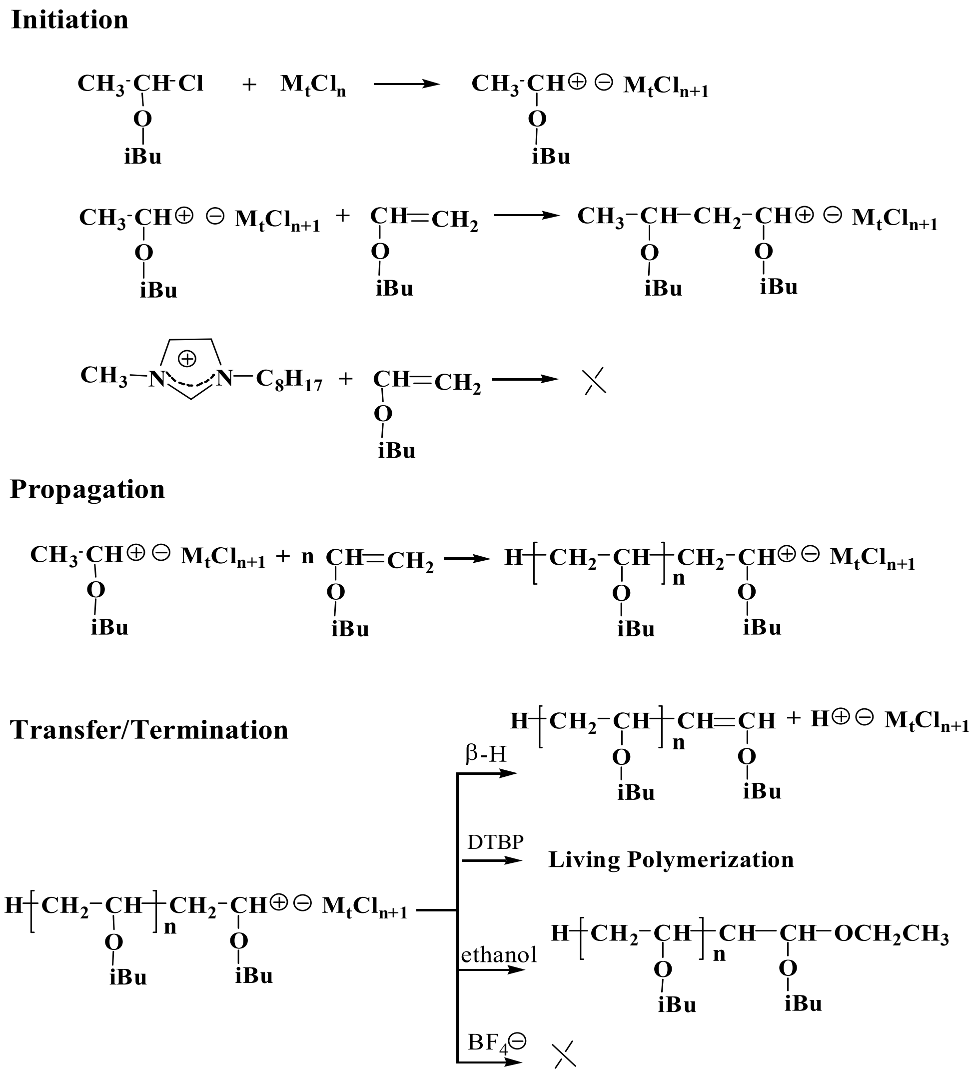


Figure 9 GPC curves of poly(IBVE)s obtained in monomer addition experiments by controlled cationic polymerization in IBVE-HCl/$Al_2Et_3Cl_3$/DTBP initiating system. Polymerization conditions: [IBVE-HCl]=0.003M, $[IBVE]_0=[IBVE]_{add}$=0.75M, $[Al_2Cl_3Et_3]$=0.048M, [DTBP]=0.002M, T=0 °C.

On the basis of above observation, we proposed the corresponding elementary reactions of IBVE cationic polymerization in $[omim][BF_4]$ system, as shown in scheme 1. In initiation reactions, Lewis acid metal halide abstracted a Cl atom form IBVE-HCl, producing a carboncation and a metal halide-based counterion. Comparing with $omim^+$ cation, the electrophilic carboncation was easier to attack the IBVE to initiate the polymerization. Since $BF_4^{\ominus}$ anion was very weakly nucleophilic species, halide-based counterion was likely to strongly interact with carbocationic growing species. Therefore, it was proposed that the chain termination reactions directly took place toward halide-based counterion rather than $BF_4^{\ominus}$ anion. The polymerization took place by chain-breaking via predominant β-proton elimination from $–CH_2–$ in the growing carbocation and then by protic reinitiation to create a new polymer chain, resulting in the formation of polymer chains with exo-olefin terminal group. Therefore, the counteranion, formed by the combination of Lewis acid with the anionic part ($Cl^{\ominus}$) from initiator, associated with the growing carbocation and thus influenced the cationicity of the growing ends and selective *β*-proton elimination from $-CH_2-$. Once DTBP was used; *β*-proton had been trapped. Thus, the polymerization in ionic liquid exhibited some characteristics of a living/controlled process.



Scheme 1 The elementary reactions of cationic polymerization of IBVE in ionic liquid.

4. Possible interactions between ionic liquid and propagating carbocation

Although the [omim][BF_4] did not participate mostly in elementary reactions of IBVE cationic polymerization, it may affect the stability of propagating carbocation and interaction between propagating carbocation and metal halide-based counterion. It was observed from monomer addition experiments that the long-lived species existed in [omim][BF_4] system. It is crucial for the production of the long-lived species to stabilize the carbocation. In order to provide a theoretical basis for stabilization of propagating carbocation in ionic liquid, the density functional theory was used to study the interactions among propagating carbocation, halide-based counterion and $BF_4^{\ominus}$ anion. The ion pair models of CH_3-$CH^{\oplus}$-OiBu--$TiCl_5^{\ominus}$ and $BF_4^{\ominus}$--CH_3-$CH^{\oplus}$-OiBu--$TiCl_5^{\ominus}$ were proposed by using density functional theory at 6-31G* level where the conformations were optimized in bond length and bond angle so as to minimize strain energy. According to the geometry in Figure 10, the propagating carbocations of the poly(IBVE)s in [omim][BF_4] interacted with not only metal halide-based counterions, but also soft Lewis basic $BF_4^{\ominus}$ anions. It was also noted that the charge of carbocation (+0.275e) in model of $BF_4^{\ominus}$--CH_3-$CH^{\oplus}$-OiBu--$TiCl_5^{\ominus}$ was lower than corresponding carbocation(+0.469e) in model of CH_3-$CH^{\oplus}$-OiBu--$TiCl_5^{\ominus}$. As a result, the charge on the propagating carbocation in ionic liquid should be separated by its interaction with $BF_4^{\ominus}$ anion, leading to form relative stabilized propagating carboncation. However, these interactions were still insufficient to stabilize the propagating carboncation to achieving a controlled polymerization.

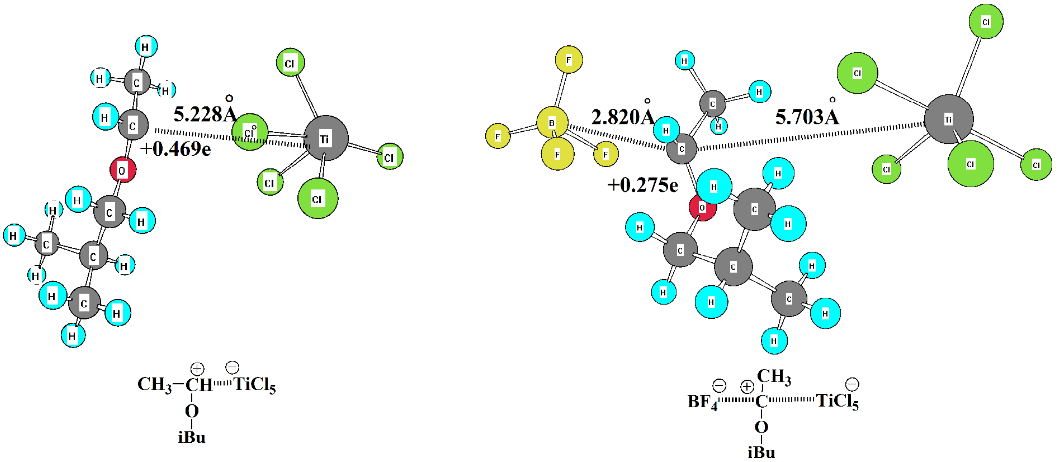


Figure 10 The optimized geometries of CH_3-$CH^{\oplus}$-OiBu--$TiCl_5^{\ominus}$ and $BF_4^{\ominus}$ --CH_3-$CH^{\oplus}$-OiBu--$TiCl_5^{\ominus}$ at the 6-31G∗ level.

According to elementary reactions in [omim][BF_4], despite the existence of interaction between growing carbocation with $BF_4^{\ominus}$ anion, the interaction between the growing carbocation and counteranion was still dominant. In general, the sterical hindrance of counteranion influenced the insertion of monomer molecules into the propagating carbocation. Thus, the interaction between propagating carbocation and metal halide-based counterion was directly responsible for stereoregulation[43]. It can be also seen from Figure 10 that the $C^{\oplus}\cdots$Ti distance (5.703Å) in model of $BF_4^{\ominus}$ --CH_3-$CH^{\oplus}$-OiBu--$TiCl_5^{\ominus}$ was longer than corresponding $C^{\oplus}\cdots$Ti bond in model of CH_3-$CH^{\oplus}$-OiBu--$TiCl_5^{\ominus}$ (5.228Å). The longer the distance of $C^{\oplus}\cdots$Ti, the lower the steric hindrance effect of the counteranion on growing carbocation. For this reason it could be speculated that due to the existence interaction between growing carbocation with $BF_4^{\ominus}$ anion in ionic liquid, the interaction between the growing carbocation and counteranion become weaker. Therefore, the model of $BF_4^{\ominus}$ --CH_3-$CH^{\oplus}$-OiBu--$TiCl_5^{\ominus}$ perfectly explained why the polymer obtained in [omim][BF_4] with a relatively low stereoregulation.

Conclusions

The poly(IBVE)s were successfully synthesized in an ionic liquid [omim][BF_4] using a variety of coinitiators at 0 °C. The yield, molecular weight, and exotherm of the polymerization were examined and compared with those in an organic solvent. It was found that the cationic polymerizations in [omim][BF_4] proceeded smoothly and there existed long-lived species in this system. The terminal structure of poly(IBVE)s analyzed by ^{1}H-NMR spectroscopy clearly indicated that β-proton elimination occurred in the ionic liquid during polymerization. The polymerization could proceed in a controlled fashion by addition of DTBP. Because of the interaction between ionic liquid and growing carbocation, the charge of growing carbocation was reduced, which contribute to the formation of the stabilized carbocation. Sterical hindrance of counteranion was reduced in [omim][BF_4] which led to lower stereoregulation.

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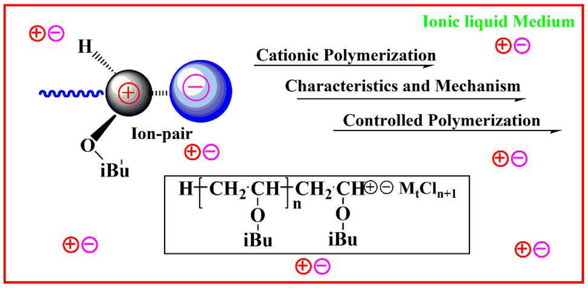
Table of content



Controlled cationic polymerizations of IBVE were successfully achieved in ionic liquid, and corresponding elementary reactions and mechanism were proposed.