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# Halogen Bonding-Mediated Controlled Cationic Polymerization of Isobutyl Vinyl Ether: Expanding the Catalytic Scope of 2-Iodoimidazolium Salts

Koji Takagi,\* Koji Yamauchi, and Hiroto Murakata

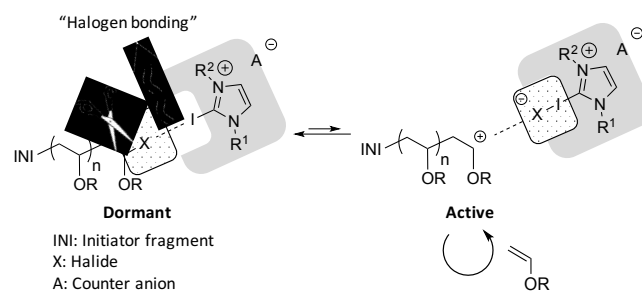
**Abstract:** Metal-free initiating systems for living cationic polymerizations are desirable from the viewpoint of environmentally benign polymer synthesis. We herein describe the development of a halogen bonding-mediated controlled cationic polymerization of isobutyl vinyl ether (IBVE) for the first time using 2-iodoimidazolium salts as an organocatalyst. Due to the ionic nature of the catalysts, the polymerization should be performed in  $\text{CH}_2\text{Cl}_2$ . The  $\text{HCl}$  adduct of IBVE was the most suitable initiator, and the polymerization was carried out at  $-10^\circ\text{C}$  under the catalyst concentration of 10 mM to suppress alcohol elimination from the polymer chain. The addition of a small amount of  $n\text{Bu}_4\text{NCl}$  (0.02 equivalent) was effective to accomplish the controlled cationic polymerization to obtain polyIBVE having the molecular weight distribution below 1.3.

Controlled or living polymerization is doubtlessly the most powerful tool for obtaining well-defined polymers with predictable molecular weights, narrow molecular weight distributions, functionalized chain ends, and block architectures. The living cationic polymerization has a long history since Higashimura et al found the novel initiating system ( $\text{HI}/\text{I}_2$ ) for isobutyl vinyl ether (IBVE) in 1984.<sup>[1]</sup> The subsequent discovery of new initiating systems enabled the living cationic polymerization for other vinyl ethers, under milder conditions, and with better controllability.<sup>[2,3]</sup> The key point for the successful polymerization is the reversible activation of dormant species by Lewis acids.<sup>[4–7]</sup> Metal halides are reliable candidates for Lewis acids that reversibly cleave the carbon-heteroatom bond in dormant species existing as the transient resting state.<sup>[8,9]</sup> The success or failure of this method based on the “atom-transfer mechanism” depends on the proper choice of the Lewis acid. Sophisticated living cationic polymerizations catalyzed by designed metal-based Lewis acids have been delivered in the new millennium, which include the stereoregulation by the bulky  $\text{TiCl}_2(\text{OAr})_2$  catalyst,<sup>[10]</sup> ultrafast polymerization by mixed  $\text{SnCl}_4/\text{EtAlCl}_2$  system,<sup>[11]</sup> and utility of heterogeneous and recyclable  $\text{Fe}_2\text{O}_3$  catalyst.<sup>[12]</sup>

On the other hand, metal impurities that may be responsible for the degradation and coloration of polymers should be reduced or removed to produce high-quality materials commercially. In light of this, the development of metal-free initiating system for the living cationic polymerization is highly demanded and is a state-of-the-art research topic in the community of precision polymer synthesis. The cationic polymerization of vinyl ethers without metal halides were actually investigated by Nuyken et al and Deffieux et al in the early 1990s.<sup>[13–15]</sup>

The addition of ammonium salts affected the polymerizations, and the optimization of the counter anion resulted in living polymerizations. Because volatile and unstable HI is essential in these methodologies, there is sufficient reason for developing new initiating systems. Aoshima et al have developed the binary initiating system composed of  $\text{CF}_3\text{SO}_3\text{H}$  and  $n\text{Bu}_4\text{NX}$  ( $\text{X} = \text{I}, \text{Br}, \text{or Cl}$ ), which can generate hydrogen halide (HX) that instantly reacts with vinyl ethers to form the 1:1 adduct.<sup>[16]</sup> Subsequent chain propagation assisted by the interaction with excess  $n\text{Bu}_4\text{NX}$  resulted in the living cationic polymerization of vinyl ethers using an appropriate X. In the past few years, metal-free living cationic polymerizations have been revisited and many evolutionary changes have been realized. In addition to the method relying on “atom-transfer mechanism” described above, two additional methods based on the “dissociation-combination mechanism” and “degenerative chain transfer mechanism” are available for this purpose.<sup>[17]</sup> As the former example, Webster<sup>[18]</sup> and Sugihara<sup>[19]</sup> have revealed the effectiveness of sulfide and ether additives to achieve the living cationic polymerization. The latter one is achieved by the application of reversible addition-fragmentation chain transfer (RAFT) agents such as thiocarbonylthio and thioether compounds.<sup>[20–22]</sup> The polymer molecular weights could be regulated by the feed ratio of IBVE relative to RAFT agent, and the amount of  $\text{CF}_3\text{SO}_3\text{H}$  could be greatly reduced.

We have developed a novel controlled cationic polymerization of IBVE mediated by halogen bonding (Figure 1). Halogen bonding is the non-covalent interaction similar to hydrogen bonding, which is defined by IUPAC in 2013 as the charge transfer interaction between electrophilic halogen substituents and Lewis bases.<sup>[23]</sup> Although halogen bonding interactions have been often studied in the condensed state, recent progress has offered a new avenue for the utility in organic reactions in solution.<sup>[24–27]</sup> Particularly, the halide-abstraction reaction of bromodiphenylmethane (**1**) and 1-chloroisochroman (**2**),<sup>[28,29]</sup> Diels-Alder reaction,<sup>[30,31]</sup> and hydrogen transfer reduction<sup>[32]</sup> have been well-investigated using 2-iodoimidazolium derivatives as the halogen bonding organocatalyst. However, to the best of our knowledge, the application of the halogen bonding to the metal-free polymer synthesis is only limited to the ring-opening polymerization of L-lactide by  $\text{ICl}_3$ .<sup>[33]</sup>



**Figure 1.** Schematic illustration of the halogen bonding-mediated halide transfer equilibrium at the propagating end.

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In this contribution, we expand the potential utility of the halogen bonding organocatalyst by demonstrating 1) whether halides reversibly transfer between the propagating end and the catalyst, 2) what is competing side reactions in the polymerization process, and 3) how to suppress these side reactions to accomplish the controlled cationic polymerization. We envisaged that the catalytic activity of 2-iodoimidazolium derivatives can be finely tuned by the adaptable molecular design of the cation and anion components.

The chemical structure of potential organocatalysts along with reference compounds are shown in Chart 1. Five compounds (**BisIm-OTf**, **BisIm\*-OTf**, **BisIm**, **MonoIm-OTf**, and **MonoBIm-OTf**) were synthesized according to the previous papers.<sup>[28,29]</sup> The octyl group was installed on the nitrogen atom to ensure the solubility of catalysts in the polymerization solvent. **BisIm-Cl** having the Cl anion instead of the trifluoromethanesulfonate (TfO) anion was prepared by the anion exchange reaction (See Supporting Information, SI, for detail). In addition to the commercially available **1**, **2** and the HCl adduct of IBVE (IBVE-HCl, **3**) were examined as initiators.

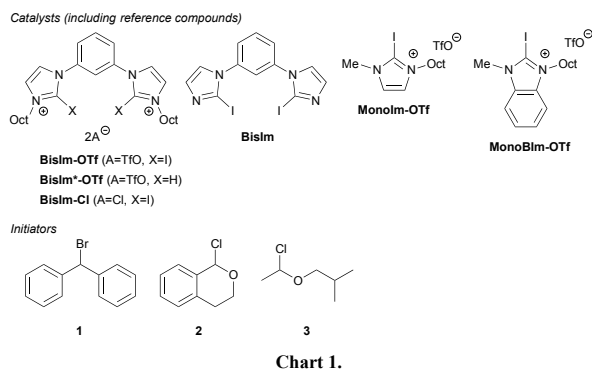


Chart 1.

In dry  $\text{CD}_2\text{Cl}_2$ , the  $^{13}\text{C}$ -NMR signal of the iodine-carrying carbon atom of **BisIm-OTf** at 102.4 ppm was shifted to 103.5 ppm by adding an equimolar amount of **1** (Figure S3 in SI).<sup>[28]</sup> Because the addition of  $n\text{Bu}_4\text{NBr}$  having the free Br anion induced a pronounced downfield shift to 110.8 ppm, the halogen bonding between **BisIm-OTf** and **1** is relatively weak but actually formed to activate the carbon-bromine bond in  $\text{CD}_2\text{Cl}_2$ .<sup>[34]</sup> With this result in hand, the cationic polymerization of IBVE was carried out using **1** and **BisIm-OTf** as an initiator and halogen bonding catalyst, respectively, in  $\text{CH}_2\text{Cl}_2$  (Scheme 1).  $\text{CH}_2\text{Cl}_2$  was selected as the polymerization solvent so as to thoroughly dissolve **BisIm-OTf**. We also prepared 1,4-bis(2-iodo-3-octyl-1H-imidazolium)benzene bis(trifluoromethanesulfonate) carrying two imidazolium units at the *para*-position of the benzene ring, but this compound was eliminated as a candidate target because of its low solubility in  $\text{CH}_2\text{Cl}_2$ . The polymerization was initially carried out at  $-20^\circ\text{C}$  with  $[\text{BisIm-OTf}]:[\text{1}]:[\text{IBVE}] = 10:10:150$  in mM concentrations (Entry 1 in Table 1). The complete conversion of IBVE was confirmed after 240 min and polyIBVE having the number-averaged molecular weight ( $M_n$ ) of 1600 was obtained. No polymer was obtained without **1** indicating that the polymerization definitely starts from the initiator (Entry 2 in Table 1). The control experiments using **BisIm\*-OTf** and **BisIm** did not bring about monomer consumption (Entries 3 and 4 in Table 1), which suggest that the 2-iodoimidazolium component is prerequisite for the catalyst. On the other hand, the monomer conversion was low in the polymerization at  $20^\circ\text{C}$  and polyIBVE with a much lower molecular weight ( $M_n = 570$ ) was obtained (Entry 5 in Table 1). The solution color of the polymerization system gradually turned brown with

time. After the polymerization, the catalyst was recovered a hexane-insoluble fraction and was analyzed by electrospray ionization mass spectroscopy (ESI-MS). It was found that partial degradation of **BisIm-OTf** occurred as evidenced by the peak at  $m/z = 711.2035$  (Figure S4), which is likely stemmed from the cleavage of carbon-iodine bond at the 2-position of imidazole and the formation of carbene intermediate (Scheme S1).<sup>[35]</sup> In the  $^1\text{H}$ -NMR spectrum of recovered **BisIm-OTf**, several minor signals were detected in addition to the signals of original **BisIm-OTf** (Figure S5). In the downfield region, a singlet signal was observed at 9.81 ppm that is most likely derived from the acidic proton at the 2-position of the decomposed imidazolium species. Complicated proton signals were also observed in the aromatic region between 7.5 ppm and 8.3 ppm. Although the detailed assignment of all signals was difficult, the stability/decomposition of the halogen bonding catalyst was roughly evaluated by comparing the integral ratio of a triplet signal at 4.33 ppm that is probably ascribed to the decomposed imidazolium species with that at 4.23 ppm assignable to the original **BisIm-OTf**. As a result, approximately 15% of 2-iodoimidazolium unit was supposed to degrade during the polymerization performed at  $20^\circ\text{C}$ . In contrast, the  $^1\text{H}$ -NMR spectrum of recovered **BisIm-OTf** after the polymerization at  $-20^\circ\text{C}$  indicated no detectable catalyst decomposition.

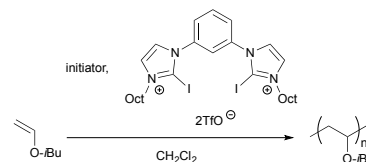
Scheme 1. Cationic polymerization of IBVE using **BisIm-OTf** as a halogen bonding catalyst.

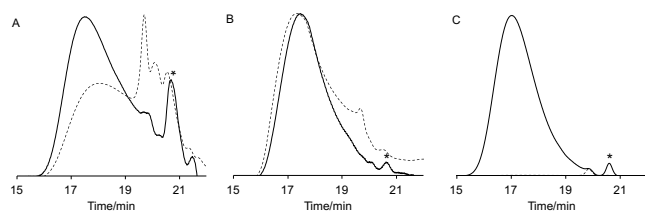
Table 1. Polymerization conditions and results.

Entry	Init.	Cat.	Temp. / $^\circ\text{C}$	Time /min	Conc. /mM <sup>[a]</sup>	$M_n$ ( $M_w/M_n$ ) <sup>[b]</sup>
1	<b>1</b>	<b>BisIm-OTf</b>	$-20$	240	10:10:150	1600 (2.91)
2	-	<b>BisIm-OTf</b>	$-20$	240	10:0:150	NP
3	<b>1</b>	<b>BisIm*-OTf</b>	$-20$	240	10:10:150	NP
4	<b>1</b>	<b>BisIm</b>	$-20$	240	10:10:150	NP
5	<b>1</b>	<b>BisIm-OTf</b>	20	240	10:10:150	570 (5.61)
6	<b>1</b>	<b>BisIm-OTf</b>	$-10$	240	10:10:500	3610 (3.23)
7	<b>2</b>	<b>BisIm-OTf</b>	$-10$	240	10:10:500	2490 (2.21)
8	<b>3</b>	<b>BisIm-OTf</b>	$-10$	5	10:10:500	4660 (1.77)
9	<b>3</b>	<b>BisIm-OTf</b>	$-10$	5	5:10:500	5040 (1.52)
10	<b>3</b>	<b>BisIm-OTf</b>	20	5	10:10:500	3580 (2.39)
11	<b>3</b>	<b>BisIm-OTf</b>	$-40$	360	2:2:100	2840 (2.04)
12	<b>3</b>	<b>BisIm-OTf</b>	$-10$	240	5:5:250	4300 (1.79)
13	<b>3</b>	<b>BisIm-OTf</b>	$-10$	240	2:2:100	2670 (1.96)
14	<b>3</b>	<b>BisIm-OTf</b>	$-10$	240	1:1:50	1580 (2.05)

[a] [Cat.]:[Init.]:[IBVE]. [b] Estimated by GPC (THF, PSt standard samples). NP denotes no polymerization.

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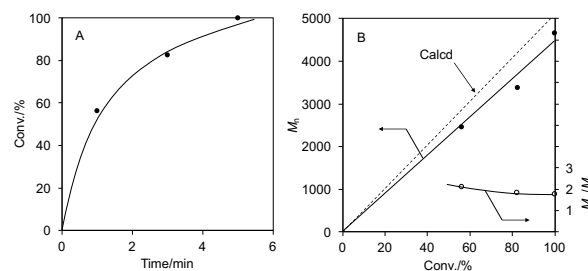
Accordingly, the temperature was found to be an important factor in performing the cationic polymerization of IBVE catalyzed by **BisIm-OTf**. When the polymerization was carried out at -10 °C under the concentrations of  $[\text{BisIm-OTf}]:[\text{1}]:[\text{IBVE}] = 10:10:500$  in mM, polyIBVE having  $M_n$  of 3610 and the molecular weight distribution ( $M_w/M_n$ ) of 3.23 was obtained (Entry 6 in Table 1). The carbocation generated from **1** is resonance-stabilized by the benzene ring and is presumed to have a different characteristic from the carbocation at the propagating end that is resonance-stabilized by the oxygen atom. Because this variance might result in the broad molecular weight distribution of polyIBVE, **2** and **3** giving rise to the carbocation stabilized by the neighboring oxygen atom were subsequently examined as an initiator. According to a previous paper, the Cl anion forms a weaker halogen bonding with 2-iodoimidazolium salts in comparison with the Br anion.<sup>[36]</sup> We have conceived that the halide transfer equilibrium at the propagating end shifts to the dormant species (Figure 1) and the mild polymerization likely proceeds using **2** and **3** having the chlorine atom. The polymerization using **2** gave polyIBVE having  $M_n$  of 2490 and a narrower molecular weight distribution ( $M_w/M_n = 2.21$ ; Entry 7 in Table 1). As indicated in Figure 2, the gel permeation chromatography (GPC) peaks monitored by the ultraviolet (UV) and refractive index (RI) detectors overlap each other suggesting that side reactions can be suppressed in contrast to the polymerization using **1**. Actually, in the polymerization under the concentrations of  $[\text{BisIm-OTf}]:[\text{2}]:[\text{IBVE}] = 10:10:1000$  in mM,  $M_n$  of polyIBVE increased to 7230 while keeping a narrow molecular weight distribution ( $M_w/M_n = 2.05$ ).



**Figure 2.** GPC profiles of polyIBVE obtained with **BisIm-OTf** using (A) **1**, (B) **2**, and (C) **3** as an initiator (solid line: RI detector, broken line: UV detector). Asterisk is the signal attributed to the stabilizer in THF.

Although the advantage of **2** over **1** was demonstrated as discussed above, the purification of **2** required a skillful technique and the polymerization results varied from batch to batch unless the greatest care was exercised. We therefore changed the initiator from **2** to **3** that has been frequently applied in many living cationic polymerizations of IBVE. When the polymerization was carried out at -10 °C under the concentrations of  $[\text{BisIm-OTf}]:[\text{3}]:[\text{IBVE}] = 10:10:500$  in mM, polyIBVE of  $M_n$  4660, almost in agreement with the theoretical value (5000), and  $M_w/M_n$  of 1.77 was obtained (Entry 8 in Table 1). Because proton signals derived from the decomposed halogen bonding catalyst were not evident in the <sup>1</sup>H-NMR spectra, the decomposition of **BisIm-OTf** did not basically take place at -10 °C. Nevertheless, the broad molecular weight distribution might be originated from a trace amount of HI generated by the slight decomposition of **BisIm-OTf**.<sup>[37]</sup> In that case, the halide at the propagating end is not chloride but iodide. We have independently confirmed that 2-iodoimidazolium compounds form a strong halogen bonding with I<sub>2</sub> (not shown here), and therefore less controlled polymerization possibly occurs to result in the broad

molecular weight distribution. In addition, the halide transfer equilibrium (the equilibrium constants and kinetics) at the propagating end should be carefully controlled by designing the steric and electronic environments of the halogen bonding catalyst as well as the leaving group other than simple halide anions, which is now undertaken in our laboratory. No GPC peak as monitored by UV detection was seen implying again that the polymerization starts not from the catalyst but from the initiator (Figure 2C). The polymerization was completed in 5 min, and the  $M_n$  value increased with monomer conversion in a linear relationship and exhibited a Poisson distribution (Table S1 and Figure 3). It is to be emphasized that a similar polymerization under the concentrations of  $[\text{BisIm-OTf}]:[\text{3}]:[\text{IBVE}] = 5:10:500$  in mM gave polyIBVE having  $M_n$  of 5040 (Entry 9 in Table 1). The molecular weight is thus determined by the molar ratio of  $[\text{3}]:[\text{IBVE}]$ , which strongly suggests that **BisIm-OTf** is not a simple carbocation generator from **3** but acts as the catalyst in the truest sense. Namely, the Cl anion goes back and forth between the propagating end and the catalyst as illustrated in Figure 1, and **BisIm-OTf** can activate the carbon-chlorine bond at numerous polymer chain ends repeatedly. On the basis of the first-order kinetic equation  $-d[\text{IBVE}]/dt = k_{\text{obs}}[\text{BisIm-OTf}][\text{IBVE}]$ , the kinetic coefficient ( $k_{\text{obs}}$ ) was calculated as 0.45 min<sup>-1</sup>. From the <sup>13</sup>C-NMR spectrum, the dyad distribution was determined from the peak intensity of the main chain methylene carbon signals at around 40 ppm (Figure S6).<sup>[10]</sup> As a result, the meso dyad was calculated to be approximately 52% in accordance with the conventional cationic polymerization.



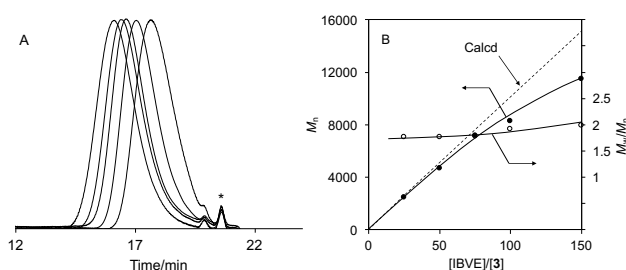
**Figure 3.** (A) Time vs monomer conversion plot and (B)  $M_n$  ( $M_w/M_n$ ) vs monomer conversion plot under the concentrations of  $[\text{BisIm-OTf}]:[\text{3}]:[\text{IBVE}] = 10:10:500$  in mM.

Subsequently, the influence of polymerization temperature was re-investigated (Figure S7). The polymerization using **3** at 20 °C gave polyIBVE having  $M_n$  of 3580 in contrast to the unsuccessful polymerization using **1** (Entry 10 in Table 1), which indicates that chain transfer reactions (Scheme S1) are relatively suppressed by introducing chloride at the propagating end to form a weaker halogen bonding. However, the molecular weight distribution ( $M_w/M_n = 2.39$ ) was still broad probably caused by the temperature of polymerization. On the other hand, polymerization at -40 °C surprisingly resulted in a lower molecular weight ( $M_n = 2840$ ) irrespective of the complete monomer conversion. A broad molecular weight distribution ( $M_w/M_n = 2.04$ ) was confirmed (Entry 11 in Table 1). Because the polymerization was performed in the catalyst concentration of 2 mM due to the limited solubility of **BisIm-OTf** at -40 °C, side reactions are likely predominant as compared to the ideal propagating reaction under the diluted concentration. Actually, the molecular weight appears to have been lowered due to the decreased polymerization concentrations (Entries 12–14 in Table 1 and Figure S8). In the <sup>1</sup>H-NMR spectrum of polyIBVE obtained after the polymerization in 5 min under the concentration of

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10:10:500 in mM concentrations (Entry 7 in Table 1), the methyne proton signal at the propagating end and the methyl proton signal at the initiating end were observed at 4.61 ppm and 1.14 ppm, respectively (Figure S9A). The integral ratio of two signals were in good accordance with the theoretical value (1:3). In addition, small signals were detected at 5.33 and 5.60 ppm, which can be ascribed to the main chain olefinic protons derived from the elimination of isobutyl alcohol.<sup>[16]</sup> These signals were more pronounced in the spectrum of polyIBVE obtained after the polymerization of 240 min under the concentrations of 1:1:50 in mM (Entry 14 in Table 1 and Figure S9B).<sup>[38]</sup> Accordingly, elimination of isobutyl alcohol and the associated chain transfer reaction are supposedly the origin of the low molecular weight under the diluted concentrations (Scheme S2). It was found that not only the polymerization concentration but also the polymerization time may have an influence on the elimination of isobutyl alcohol. The signal intensity of olefinic protons in Figure S9C were larger compared with those in Figure S9A when the time to quenching was extended from 5 min to 240 min.

The influence of the monomer feed ratio was then investigated at  $-10\text{ }^{\circ}\text{C}$  under the catalyst and initiator concentrations of 10 mM (Table S2). All polymerizations were quenched within 20 min. The GPC profiles all exhibited monomodal distributions (Figure 4A), but the molecular weight did not show a linear increase and the molecular weight distribution was broad at the higher monomer feed ratio (Figure 4B). The percentage of the isobutyl ether group in the repeating unit relative to the carbon-chlorine bond at the propagating end is large at the higher monomer feed ratio and with the larger molecular weight polymer. Therefore, elimination of isobutyl alcohol (Scheme S2) cannot be ignored resulting in the chain transfer reaction at the higher monomer feed ratio even if the polymerization is performed in the optimized temperatures and concentrations.



**Figure 4.** (A) GPC profiles of polyIBVE obtained by varying the monomer feed ratio. (B)  $M_n$  ( $M_w/M_n$ ) vs  $[\text{IBVE}]/[\mathbf{3}]$  plot. Asterisk is attributed to the stabilizer in THF.

In order to clarify the catalytic performance of 2-iodoimidazolium derivatives, the cationic polymerizations of IBVE initiated by **3** were investigated with **MonoIm-OTf** and **MonoBIm-OTf** both with the mono imidazolium structure. The polymerizations were carried out at  $-10\text{ }^{\circ}\text{C}$  under the concentrations of  $[\text{catalyst}]:[\mathbf{3}]:[\text{IBVE}] = 10:10:500$  in mM. Although the polymerization with **MonoIm-OTf** after 20 min resulted in a 80% monomer conversion and gave polyIBVE having  $M_n$  of 5600 ( $M_w/M_n = 1.94$ ), further increase of monomer conversion was not confirmed even after the prolonged reaction time (Figure S10A). This result is also explicit in the plot of  $\ln([\text{IBVE}]_0/[\text{IBVE}])$  as a function of polymerization time, in which  $[\text{IBVE}]_0$  denotes the initial concentration of IBVE (Figure S10B). The curve is an upward convex, suggesting that **MonoIm-OTf** is gradually inactivated with increasing

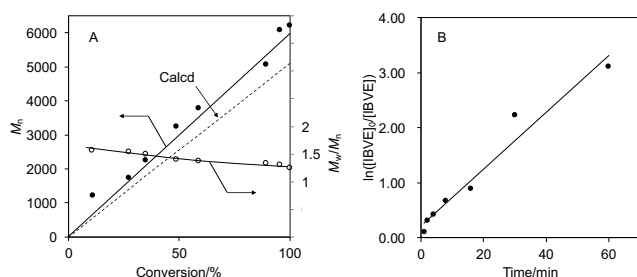
polymerization times. Although further experiments are required to reveal the origin of this curious phenomenon, the catalytic activity of **MonoIm-OTf** was evaluated on the basis of the first-order kinetic equation at the early stage of the polymerization. The kinetic coefficient ( $k_{\text{obs}}$ ) was calculated by the linear approximation as  $0.20\text{ min}^{-1}$ . In the previous report, Huber et al have demonstrated a higher catalytic activity of bidentate bis(imidazolium) salts as opposed to their monodentate imidazolium counterparts in the chloride abstraction reaction of **2**.<sup>[29]</sup> The binding mode of bis(imidazolium) salt with the halide anion is difficult to be anticipated.<sup>[29,39]</sup> In our polymerizations, the catalytic activity per one 2-iodoimidazolium unit was almost comparable between **BisIm-OTf** and **MonoIm-OTf**. However, the potential utility of **BisIm-OTf** was validated due to the complete monomer conversion and the narrower molecular weight distribution of polyIBVE at least below the molecular weight of 10000. Likewise, the polymerization with **MonoBIm-OTf** after 20 min resulted in complete monomer conversion and gave polyIBVE having  $M_n$  of 6110 ( $M_w/M_n = 1.89$ ). While the catalytic activity was slightly decreased at the last stage of the polymerization, the kinetic coefficient ( $k_{\text{obs}}$ ) was roughly calculated as  $0.28\text{ min}^{-1}$  (Figure S11). The improved catalytic activity of **MonoBIm-OTf** compared with **MonoIm-OTf** showed the same trend as that reported by Huber et al.<sup>[29]</sup>

Finally, the additive effect of ammonium salt was investigated for positive evidence of the formation of halogen bonding and control of the halide transfer equilibrium at the propagating end. Based on our working hypothesis in Figure 1, the added halide anion competitively coordinates to the catalytic center and decreases the concentration of active species, which eventually influences the polymerization rate as well as the molecular weight distribution of polyIBVE. The addition of  $n\text{Bu}_4\text{NCl}$  in 0.2 equivalent relative to **BisIm-OTf** dramatically decreases the catalytic activity, and the monomer conversion reached only 55% even after polymerization for 240 min. The molecular weight agreed with the value calculated from the monomer feed ratio and conversion, and a relatively narrow molecular weight distribution ( $M_w/M_n = 1.38$ ) was attained. The additive effect of  $n\text{Bu}_4\text{NCl}$  was further supported by the polymerization with **BisIm-Cl** having the Cl counter anion. In contrast to the less coordinating TfO anion, the Cl anion preferably coordinates to the 2-iodoimidazolium moiety. As a result, halogen bonding toward the propagating end was restricted and no polymerization occurred regardless of the polymerization temperature and time. In contrast, in the polymerization with a small amount of  $n\text{Bu}_4\text{NCl}$  (0.02 equivalent relative to **BisIm-OTf**), monomer was slowly consumed with time and polyIBVE was obtained after 120 min (Table S3). The molecular weight distribution became narrower compared with the polymerization without  $n\text{Bu}_4\text{NCl}$ . The  $^1\text{H-NMR}$  spectrum indicates that the elimination of isobutyl alcohol was considerably suppressed (Figure S12). As indicated in Figure 5A, the molecular weight values linearly increased in proportion to the monomer conversion and the molecular weight distributions decreased at higher monomer conversions. These facts absolutely suggest that the cationic polymerization of IBVE with **BisIm-OTf**/ $n\text{Bu}_4\text{NCl}$  system proceeds in a controlled manner. The first-order kinetic analysis was performed to estimate the kinetic coefficient ( $k_{\text{obs}}$ ) as  $0.05\text{ min}^{-1}$  (Figure S13 and Figure 6B). When the  $[\text{IBVE}]/[\mathbf{3}]$  ratio was increased to 100, polyIBVE having  $M_n$  of 10100 and  $M_w/M_n$  of 1.31 was obtained.

The matrix-assisted laser desorption/ionization-time of flight (MALDI-ToF) mass spectrum showed six series of peaks and five peaks

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could be completely assigned (Figure S14). The three major peaks are derived from the methoxy, isobutoxy, and aldehyde groups at the terminating end. For example, polyIBVE having a degree of polymerization of 35 and with hydrogen/methoxy ends is expected to produce a signal at  $m/z = 3558.1$ . The corresponding signal is actually observed at  $m/z = 3559.4$ . Because the aldehyde group was not detected in the  $^1\text{H-NMR}$  spectrum, this signal is probably generated by the hydrolysis of acetal terminal unit during the measurement of MALDI-ToF mass spectrum. The two minor peaks are indicative of the elimination of one isobutyl alcohol group per one polymer chain. Accordingly, the present polymerization system is well-controlled but does not proceed via a perfect living mechanism, and can be refined by the design of the halogen bonding catalyst.



**Figure 5.** (A)  $M_n$  ( $M_w/M_n$ ) vs monomer conversion plot and (B) first-order kinetic plot in the presence of small amount of  $n\text{Bu}_4\text{NCl}$ .

In conclusion, a metal-free cationic polymerization of isobutyl vinyl ether (IBVE) mediated by halogen bonding was developed. We found that the HCl adduct of IBVE (IBVE-HCl) is the most suitable initiator and a bis(2-iodoimidazolium) derivative having a less coordinating trifluoromethanesulfonate (TfO) anion exhibits catalytic activity to promote the controlled polymerization in  $\text{CH}_2\text{Cl}_2$  at  $-10^\circ\text{C}$  under the concentration of 10 mM. The molecular weight was predictable and narrow molecular weight distributions were attained, but the elimination of isobutyl alcohol brought about a chain transfer reaction at high monomer feed ratios. The polymerization rate was influenced by the catalyst structure. It is to be underlined that the addition of a small amount of  $n\text{Bu}_4\text{NCl}$  could regulate the halide transfer equilibrium at the propagating end to realize the better control of the polymerization.

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**Keywords:** controlled cationic polymerization • halogen bonding • organocatalyst

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## COMMUNICATION

## Entry for the Table of Contents

Layout 1:

## COMMUNICATION

**XB meets polymerization:** Metal-free controlled cationic polymerization of isobutyl vinyl ether (IBVE) was accomplished using halogen bonding (XB) organocatalysts. 2-Iodoimidazolium salts enabled the carbon-halide bond scission at the propagating end to give polyIBVE with narrow molecular weight distribution. The addition of a small amount of  $n\text{Bu}_4\text{NCl}$  was effective to realize a controlled polymerization.



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Catalytic Scope of 2-Iodoimidazolium  
Salts**