Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 3965–3972 **3965**
DOI: 10.1021/ma900116s

Major Progress in Catalysts for Living Cationic Polymerization of Isobutyl Vinyl Ether: Effectiveness of a Variety of Conventional Metal Halides

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Received January 19, 2009; Revised Manuscript Received April 27, 2009

ABSTRACT: Cationic polymerization of isobutyl vinyl ether (IBVE) was examined using a variety of metal halides. In the presence of an appropriate added base, ester or ether, the living polymerization of IBVE proceeded for almost all Lewis acids (MCl_n; M: Fe, Ga, Sn, In, Zn, Al, Hf, Zr, Bi, Ti, Si, Ge, Sb) used in conjunction with an IBVE−HCl adduct in toluene at 0 °C. The difference in the polymerization activity of these Lewis acids was significant. As examples, polymerization with some acids, such as $FeCl_3$, proceeded in the order of seconds, whereas it took more than a few weeks with others such as $SiCl_4$ and $GeCl_4$. The difference in activity is based on the strength of the interaction between the Lewis acid and the propagating end chloride anion and/or the basic carbonyl (or ether) oxygen atom of the added base, that is, the chlorophilic or oxophilic nature of each metal halide is a decisive factor. In addition, a suitable combination of a Lewis acid and an additive was indispensable for living polymerization. With metal pentachlorides, $NbCl_5$ and $TaCl_5$, addition of a salt ($n$$Bu_4NCl$) resulted in superior control of the reaction over that for addition of a base. Lewis acids for living cationic polymerization of vinyl ether were categorized into groups depending on the preferences for these additives.

Introduction

Living cationic polymerization has been achieved by such methods as the use of an externally added weak Lewis base (ester or ether), an added salt (tetraalkylammonium halide), or a nucleophilic counteranion derived from a weak Lewis acid (I_2, ZnX_2, BCl_3, TiX_4 etc.).[1−4] These methods attain livingness invariably by keeping the concentration of the active species much lower than that of the dormant species. This is because the propagating carbocation is unstable, and frequently causes undesired reactions such as chain transfer. In an initiating system with an added base, for example, the ester or ether plays an important role not only in suppressing the surplus production of the active species by interacting with the Lewis acid, but also in stabilizing the carbocation produced and the counteranion, as shown in Scheme 1.[4,5] From the mechanism, slow reaction was considered inevitable for living cationic polymerization systems. However, recently fast living cationic polymerization systems that completed in seconds were obtained using IBEA-Et_xAlCl_{3-x}/$SnCl_4$/base or IBVE−HCl/$FeCl_3$/cyclic ether combinations.[6−8] The polymerization rates were thousands of times larger than that using $EtAlCl_2$ alone, a catalyst commonly used for an added base system, and were also significantly larger than those of other initiating systems. The balance between the acidity of the Lewis acid and the basicity of the added base is the key to achieving such acceleration without loss of the livingness. The high reactivity of the polymerization using $SnCl_4$ or $FeCl_3$ corresponds to the strength of chloride anion (Cl^-) extraction from a chloroalkane in a carbonyl compound solution ($FeCl_3 > SnCl_4 > AlCl_3$).[9]

Metal halides have been used as Lewis acid catalysts for a variety of organic syntheses, such as Friedel−Crafts reactions. There has also been much research regarding the acidity of metal halides. For example, examination of the activity of various metal halides in Friedel−Crafts benzylation using benzyl chloride,[10] and the classification of metal halides based on the strength and selectivity toward oxygen or nitrogen atoms in addition reactions of silyl enol ether with aldehyde or aldimine have been reported.[11] In addition, spectroscopic methods have provided various examples, such as NMR or IR analyses regarding the interaction between metal halides and ether,[12] aldehyde,[13] or ketone,[14] and UV−vis measurements to determine the amounts of carbocation produced by reaction between metal halides and chloroalkane where the cation generated has strong absorbance in the UV−vis region.[9] The principle of hard and soft acids and bases (HSAB) is well-known as a theoretical method.[15] Metal halide chemistry is still a vital field in both organic and inorganic chemistry for the development of catalysts in organic synthesis, and for the investigation of acidity.

In contrast with the diversity in organic chemistry, only some metal halides (Et_xAlCl_{3-x}, $SnCl_4$, $TiCl_4$, $ZnCl_2$, BCl_3, etc.) have been used for living cationic polymerization.[3,4] The development of novel initiating systems using a variety of metal halides could be a key step for overcoming challenges such as the controlled polymerization of monomers that are difficult to polymerize in a living fashion or even in a conventional way, and the precision synthesis of various specifically shaped polymers by utilizing the characteristics of each metal. In addition, a novel index of Lewis acidity for various metal halides can also be obtained, based on differences in the polymerization rates and the polymerization behavior in the presence of certain functional groups.

In this study, the possibility of living cationic polymerization of isobutyl vinyl ether (IBVE) in conjunction with a variety of metal halides was investigated. By combining various metal halides with an added base of suitable type and basicity, the living polymerization of IBVE proceeded. For some metal halides, a salt was much superior to a base for control of the polymerization; therefore, the importance of appropriate combinations of Lewis acid and additives to realize living cationic polymerization are also described.

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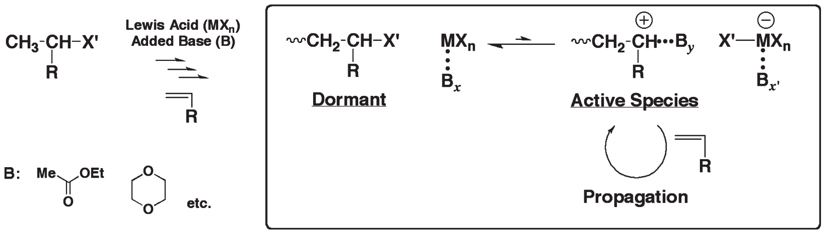
Scheme 1. Living Cationic Polymerization in the Presence of an Added Base



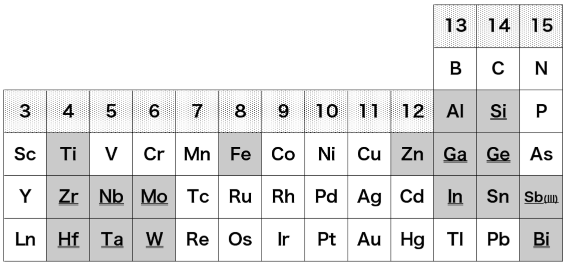
Experimental Section

Marterials. IBVE (TCI; >99.0%), ethyl acetate (Wako; >99.5%), and dichloromethane (Nacalai Tesque; 99%) were distilled twice over calcium hydride before use. Diethyl ether (Wako; >99.5%), 1,4-dioxane (Wako; >99.5%), and tetrahydrofuran (THF; Wako; >99.5%) were distilled over calcium hydride and then lithium aluminum hydride. Toluene (Wako; 99.5%) and hexane (Wako; >96.0%) were dried using solvent purification columns (Glass Contour). The adduct of IBVE with HCl (IBVE−HCl) was prepared from the addition reaction of IBVE with HCl.[16] Commercially available $SnCl_4$ (Aldrich; 1.0 M solution in dichloromethane), $ZnCl_2$ (Aldrich; 1.0 M solution in diethyl ether), $EtAlCl_2$ (Wako; 1.0 M solution in hexane), $TiCl_4$ (Aldrich; 1.0 M solution in toluene), and $SiCl_4$ (Aldrich; 1.0 M solution in dichloromethane) were used without further purification. For $FeCl_3$ and $FeBr_3$, stock solutions in diethyl ether were prepared from anhydrous $FeCl_3$ (Aldrich; 99.99%) and $FeBr_3$ (Strem; 99.9%). For $GaCl_3$, stock solution in hexane was prepared from anhydrous $GaCl_3$ (Aldrich; >99.999%). For $InCl_3$, $AlCl_3$, $HfCl_4$, $ZrCl_4$, $BiCl_3$, and $TaCl_5$, stock solutions in ethyl acetate were prepared from anhydrous $InCl_3$ (Strem; 99.999%), $AlCl_3$ (Aldrich; 99%), $HfCl_4$ (Strem; >99.9%), $ZrCl_4$ (Aldrich; 99.99%), $BiCl_3$ (Aldrich; 99.999%), and $TaCl_5$ (Strem; >99.99%). For $GeCl_4$ and $SbCl_3$, stock solutions in dichloromethane were prepared from anhydrous $GeCl_4$ (Wako; 99.99%) and $SbCl_3$ (Alfa Aesar; 99.999%). For $NbCl_5$, stock solution in a mixture of dichloromethane and ethyl acetate was prepared from anhydrous $NbCl_5$ (Strem; 99.99%). Pure solid $MoCl_5$ (Aldrich; 99.99%) and WCl_6 (Strem; 99.9%) were not dissolved completely in 1,2-dichloroethane, so that the heterogeneous solutions were used for polymerization. For nBu$_4$NCl, stock solution in dichloromethane was prepared from anhydrous nBu$_4$NCl (Fluka; >99.0%). All chemicals except for dichloromethane, toluene, and hexane were stored in brown ampules under dry nitrogen.

Characterization. The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C with three polystyrene gel columns [Tosoh; TSK gel G-4000H$_{XL}$, G-3000H$_{XL}$, and G-2000H$_{XL}$; exclusion limit molecular weight = 4×10^5, 6×10^4, and 1×10^4, respectively; bead size = 5 μm; column size = 7.8 mm (internal diameter) × 300 mm; flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive-index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from the chromatographs with respect to 16 polystyrene standards (Tosoh; M_n = 577−1.09×10^6, $M_w/M_n \leq 1.1$). NMR spectra were recorded using a JEOL JNM-LA 500 spectrometer (500.00 MHz for ^1H and 125.65 MHz for ^{13}C). MALDI−TOF−MS spectra were recorded using a Shimadzu/Kratos AXIMA-CFR spectrometer (linear mode) using dithranol as the matrix and sodium trifluoroacetate as the ion source.[17]

Polymerization Procedures. The following is a typical polymerization procedure (the $FeCl_3$/1,4-dioxane system as an example). A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki; PJ-206A; the blow temperature ~ 450 °C) under dry nitrogen. Toluene (3.05 mL), 1,4-dioxane (0.45 mL; 5.3 mmol), IBVE (0.50 mL; 3.8 mmol), and 40 mM IBVE−HCl solution in toluene (0.50 mL; 2.0×10^{-2} mmol) were added into the tube using dry syringes, successively. The polymerization was started by the addition of a prechilled 50 mM $FeCl_3$ solution in toluene/diethyl ether (3/1, v/v; 0.50 mL; 2.5×10^{-2} mmol) at 0 °C. After 15 s, the reaction was terminated with prechilled methanol (3 mL) containing a small amount of aqueous ammonia solution (0.1%). The quenched mixture was washed with dilute hydrochloric acid, an aqueous NaOH solution, and then water to remove the initiator residues. The volatiles were then removed under reduced pressure at 50 °C, and the residue was vacuum-dried for more than six hours at room temperature to yield a colorless, gummy polymer (0.370 g; conversion = 96%). The monomer conversion was determined by gravimetry [for some reactions, the monomer conversion was determined by gas chromatography using heptane (5 vol%) as an internal standard]. The GPC analysis data was as follows: M_n = 18200; M_w/M_n = 1.06.

Chart 1. Central Metals of the Metal Halides Used for Cationic Polymerization (Shaded Elements, Examined in This Paper; Underlined, Living Polymerization Has Not Been Reported Yet)



										13	14	15
										B	C	N
3	4	5	6	7	8	9	10	11	12	Al	Si	P
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb(III)
Ln	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi

Results and Discussion

1. Living Cationic Polymerization of Isobutyl Vinyl Ether Using Various Metal Halides in the Presence of an Added Base. *(a) Polymerization Results.* Cationic polymerization of IBVE was performed using a variety of metal halides (Chart 1) in conjunction with IBVE−HCl as a cationogen in toluene at 0 °C ([IBVE]$_0$ = 0.76 M, [IBVE−HCl]$_0$ = 4.0 mM, [metal halide]$_0$ = 5.0 mM). As shown in Table 1, polymers with broad MWDs were produced with almost all the metal halides used, which indicate uncontrolled polymerization. With $SiCl_4$ or $GeCl_4$, the reactions were not controlled, and similarly produced polymers with broad MWDs (entries 8 and 9), although the time taken to complete polymerization was more than a few days, in contrast to the instant reactions with the other Lewis acids. With $SbCl_3$, polymers with bimodal MWDs were obtained and their lower molecular weight parts were shifted to the higher molecular weight region, which indicates the production of long-lived species (entry 10). $ZnCl_2$ induced a controlled reaction to produce polymers with narrow MWDs (entry 5), as previously reported.[18]

Table 1. Cationic Polymerization of Isobutyl Vinyl Ether (IBVE) in the Absence of an Added Base[a]

entry	metal halide	time	convn (%)	$M_n \times 10^{-3}$ (calcd)	$M_n \times 10^{-3}$[b]	M_w/M_n[b]
1	$FeBr_3$[c]	1 s	98	18.6	9.9	2.30
2	$GaCl_3$	1 s	98	18.6	12.3	2.89
3	$FeCl_3$[c]	1 s	100	19.0	12.0	2.19
4	$SnCl_4$	1 s	99	18.8	10.1	1.59
5	$ZnCl_2$[c]	20 s	87	16.5	12.5	1.19
6	$EtAlCl_2$	1 s	99	18.8	36.7	2.47
7	$TiCl_4$	1 s	100	19.0	11.4	1.42
8	$SiCl_4$	91 h	60	11.4	32.3	2.03
9	$GeCl_4$	48 h	65	12.2	35.5	1.83
10	$SbCl_3$	23 h	19	3.6	8.5 (1.1)[d]	11.97 (1.06)[d]
11	$MoCl_5$	5 s	98	18.6	11.3	2.61
12	WCl_6	5 s	94	17.8	8.6	2.37

[a] $[IBVE]_0$ = 0.76 M, $[IBVE-HCl]_0$ = 4.0 mM, $[\text{metal halide}]_0$ = 5.0 mM, in toluene at 0 °C. [b] M_n: number-average molecular weight, M_w/M_n: polydispersity ratio (weight-average molecular weight/number-average molecular weight), by GPC (polystyrene calibration). [c] Containing diethyl ether ($FeBr_3$, 400 mM; $FeCl_3$, 250 mM; $ZnCl_2$, 50 mM). [d] For a main peak.

Table 2. Cationic Polymerization of Isobutyl Vinyl Ether (IBVE) in the Presence of an Added Base[a]

entry	metal halide	added base[b]	time	convn (%)	$M_n \times 10^{-3}$ (calcd)	$M_n \times 10^{-3}$[c]	M_w/M_n[c]
1	$FeBr_3$	EA[d]	1 s	96	18.3	8.0	1.71
2		DO[d]	1 s	100	19.0	7.2	1.82
3		THF[d]	30 min	95	18.0	18.6	1.09
4	$GaCl_3$	EA	1 s	80	15.2	11.0	1.38
5		DO	6 s	97	18.5	11.4	1.32
6		THF	35 min	93	17.7	19.1	1.08
7	$FeCl_3$	EA[d]	1 s	96	18.3	18.2	1.34
8		DO[d]	15 s	96	18.2	18.2	1.06
9	$SnCl_4$	EA	90 s	94	17.8	18.0	1.04
10		DO	70 s	93	17.6	17.8	1.07
11	$InCl_3$	EA	7 min	92	17.5	19.0	1.03
12		DO[e]	5 min	12	2.3	2.3	1.08
13	$ZnCl_2$	EA[d]	25 min	96	18.3	18.1	1.04
14		DO[d]	80 min	75	14.2	14.7	1.04
15	$AlCl_3$	EA	5 h	96	18.2	18.0	1.10
16		DO[e]	90 min	69	13.2	12.8	1.17
17	$HfCl_4$	EA	7 h	97	18.4	15.8	1.09
18		DO[e]	15 min	88	16.7	21.4	2.16
19	$ZrCl_4$	EA	6 h	92	17.5	12.7	1.06
20		DO[e]	30 min	98	18.5	14.7	1.46
21	$EtAlCl_2$	EA	22 h	93	17.7	18.9	1.06
22		DO	6 h	93	17.7	19.4 (17.8)[f]	1.38 (1.03)[f]
23	$BiCl_3$	EA	32 h	94	17.9	14.3	1.08
24	$TiCl_4$	EA	120 h	97	18.4	12.6	1.02
25		DO	12 h	76	14.3	12.1 (9.7)[f]	4.66 (1.03)[f]
26	$SiCl_4$	EA	336 h	30	5.7	3.9	1.26
27		DO	336 h	66	12.5	8.9 (8.2)[f]	1.43 (1.06)[f]
28	$GeCl_4$	EA	336 h	8	1.4	2.2	2.15
29		DO	336 h	46	8.7	6.5	1.04
30	$SbCl_3$	EA	336 h	24	4.5	3.9	1.17
31		DO	336 h	15	2.8	2.2	1.19
32	$NbCl_5$	EA	20 min	95	18.0	13.9	1.37
33		DO[e]	9 min	94	17.9	13.9	1.33
34		THF[e]	8 h	66	12.6	9.9	1.55
35	$TaCl_5$	EA	2.5 min	62	11.7	33.6	1.99
36		DO[e]	2.5 min	84	15.9	35.1	2.27
37		THF[e]	45 min	49	9.3	32.6	2.36
38	$MoCl_5$	EA	5 s	96	18.3	15.8	3.80
39		DO	5 s	98	18.5	14.5	3.19
40		THF	15 s	87	16.5	29.1	2.06
41	WCl_6	EA	10 s	96	18.3	8.2	2.26
42		DO	5 s	96	18.2	8.9	1.95
43		THF	10 s	69	13.1	8.0	1.99

[a] $[IBVE]_0$ = 0.76 M, $[IBVE-HCl]_0$ = 4.0 mM, $[\text{metal halide}]_0$ = 5.0 mM, [added base] = 1.0 M, in toluene at 0 °C. [b] EA: ethyl acetate. DO: 1,4-dioxane. [c] M_n: number-average molecular weight, M_w/M_n: polydispersity ratio (weight-average molecular weight/number-average molecular weight), by GPC (polystyrene calibration). [d] Containing diethyl ether ($FeBr_3$, 400 mM; $FeCl_3$, 250 mM; $ZnCl_2$, 50 mM). [e] Containing ethyl acetate ($InCl_3$, 500 mM; $AlCl_3$, 100 mM; $HfCl_4$, 500 mM; $ZrCl_4$, 100 mM; $NbCl_5$, 10 mM; $TaCl_5$, 200 mM). [f] For a main peak.

Polymerization was then examined in the presence of an added base under similar conditions. When metal halides were hardly soluble in toluene, the halides were dissolved in the base (diethyl ether for $FeBr_3$, $FeCl_3$, and $ZnCl_2$; ethyl acetate for $InCl_3$, $AlCl_3$, $HfCl_4$, $ZrCl_4$, $NbCl_5$, and $TaCl_5$) to be added to the monomer solution, and the reaction mixtures were homogeneous. Polymerization in the presence of ethyl acetate or 1,4-dioxane showed quite different behavior compared to that without a base, as shown in Table 2. Living polymerization proceeded with almost all the metal halides examined in this study. With ethyl acetate, polymerization was controlled well to produce polymers with very narrow MWDs in conjunction with $SnCl_4$, $InCl_3$, $ZnCl_2$, $AlCl_3$, $HfCl_4$, $ZrCl_4$, $EtAlCl_2$, $BiCl_3$, $TiCl_4$, or $SbCl_3$ (entries 9, 11, 13, 15, 17, 19, 21, 23, 24, and 30). In these polymerizations, the M_n values increased in direct proportion to the monomer conversion, which supports the occurrence of living polymerization (Supporting Information). With $SnCl_4$, $InCl_3$, and $ZnCl_2$, living polymerization also proceeded in the presence of 1,4-dioxane (entries 10, 12, and 14). $FeCl_3$ and $GeCl_4$ induced living polymerization when 1,4-dioxane was used instead of ethyl acetate (entries 8 and 29). Although long-lived species were produced with $EtAlCl_2$, $TiCl_4$, or $SiCl_4$ in conjunction with 1,4-dioxane, a small amount of uncontrolled polymers were observed in the higher molecular weight region (entries 22, 25, and 27). Since these uncontrolled polymers of high molecular weight were produced in the early stage of polymerization, it is likely that some side reactions occurred during the initiating step, possibly by the initiation from some protic impurities such as adventitious water. Although the reactivity of $FeBr_3$ or $GaCl_3$ was too high to control the polymerization in the presence of ethyl acetate or 1,4-dioxane, a more basic cyclic ether, THF, could moderate their activity to induce living polymerization (entries 3 and 6). Monomer addition experiments were also conducted with some Lewis acids to confirm the living nature of the polymerization. As shown in Figure 1, peaks of the GPC curves shifted toward the higher molecular weight region after the addition of a fresh feed of the monomer.[19] The results indicate that the variety of metal halides examined could induce living polymerization by addition of a base of suitable type and basicity. Addition of the base is considered to contribute to the adjustment of Lewis acidity for control of the equilibrium between the dormant and the active species, stabilization of the propagating carbocations, and the formation of monomeric complexed Lewis acids.[4]

Despite the wide diversity of Lewis acids for living polymerization, no metal pentachloride ($NbCl_5$, $TaCl_5$, and $MoCl_5$) or hexachloride (WCl_6) has mediated living polymerization in the presence of any added base. However, in the presence of ethyl acetate, the production of a long-lived species was confirmed with $NbCl_5$ by increase of the M_n with the procession of polymerization, and polymers with broad MWDs were obtained (entry 32). With $TaCl_5$, the same group analogue of $NbCl_5$, polymers with very high molecular weight were produced, regardless of their monomer conversion in the presence of ethyl acetate, 1,4-dioxane, or THF (entries 35−37). Very fast polymerization proceeded with group 6 element metal halides, $MoCl_5$ and WCl_6, to yield polymers with broad MWDs in the presence of each added base (entries 38−43). Thus, penta- and hexachlorides of group 5 and 6 elements exhibited quite different behavior from the others.

The stereoregularity of the polymers obtained by living polymerization was analyzed using the ^{13}C NMR method. However, no clear difference was observed among the Lewis acids used; the polymers were almost atactic ($[m]$ = 60−70%; Supporting Information).

(b) Role and Importance of an Added Base. A weak Lewis base is indispensable for controlling cationic polymerization of IBVE. As determined from the results with various Lewis acids, the base is considered to take the following roles: formation of monomeric complexed Lewis acids, adjustment of the Lewis acid acidity, and stabilization of the propagating carbocation and counteranion (for some acids), as shown in Scheme 1. Preferences for added bases (ester, ether, or both of them) were also shown with the Lewis acids. Thus, for control of the polymerization, it is important to select an added base of suitable type and basicity, based on the nature of each metal halide. For instance, the combination of THF (a stronger Lewis base) with $FeBr_3$ or $GaCl_3$ (stronger Lewis acids) resulted in controlled reactions. In these cases, the base acted to suitably adjust the active-dormant equilibrium as a result of the strong acid−base interaction. The basicity of the added base is a significantly important factor. The different role of the added base led to living polymerization with $SiCl_4$, $GeCl_4$, and $SbCl_3$. With these mild catalysts, very slow polymerization proceeded, even in the absence of an added base. Although the slow reaction resulted from the low concentration of the active species, uncontrolled reactions still occurred, indicating that the counteranions produced by these acids are insufficient to stabilize the propagating carbocation by themselves. An added base would be involved in the formation of a counteranion, which in turn interacts suitably with the propagating carbocations.

(c) Polymerization Rates in the Presence of an Added Base: Comparison with Other Studies and the Relationship with Lewis Acidity. The differences in polymerization activity

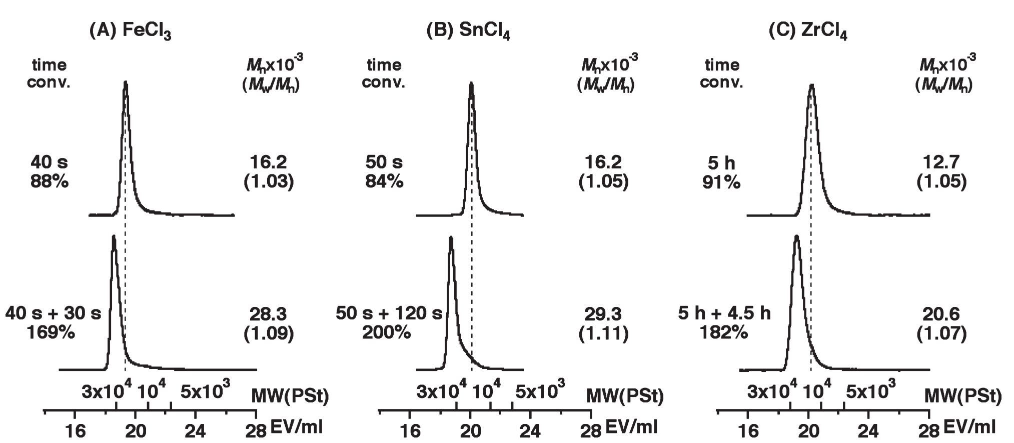


Figure 1. Molecular weight distribution curves for poly(isobutyl vinyl ether)s [poly(IBVE)s] in the monomer addition experiments {Polymerization conditions: $[IBVE]_0 = [IBVE]_{added} = 0.76$ M, $[IBVE{-}HCl]_0 = 4.0$ mM, $[\text{metal halide}]_0 = 2.0$ mM ($FeCl_3$) or 5.0 mM ($SnCl_4$ and $ZrCl_4$), [added base] = 1.0 M (1,4-dioxane for $FeCl_3$, ethyl acetate for $SnCl_4$ and $ZrCl_4$), in toluene at 0 °C; M_n: number-average molecular weight, M_w/M_n: polydispersity ratio (weight-average molecular weight/number-average molecular weight), by GPC (polystyrene calibration)}.

were quite significant for all the metal halides examined in this study. The order of polymerization rate in the presence of ethyl acetate was as follows:

$$\mathrm{GaCl_3} \sim \mathrm{FeCl_3} > \mathrm{SnCl_4} > \mathrm{InCl_3} > \mathrm{ZnCl_2} > \mathrm{AlCl_3} \sim \mathrm{HfCl_4} \sim \mathrm{ZrCl_4} > \mathrm{EtAlCl_2} > \mathrm{BiCl_3} > \mathrm{TiCl_4} \gg \mathrm{SiCl_4} \sim \mathrm{GeCl_4} \sim \mathrm{SbCl_3}$$

In this polymerization system, metal halides are considered to interact with both the carbonyl (or ether) oxygen atom of the added base and the chlorine atom of the propagating chain end. It has been reported that the strength of metal halides for extraction of the chloride anion from trityl chloride in a carbonyl compound, PhCOCl, decreased in the following order:[9]

$$\mathrm{FeCl_3} > \mathrm{SnCl_4} > \mathrm{ZnCl_2} > \mathrm{TiCl_4} > \mathrm{AlCl_3} \quad \text{(in PhCOCl, ref 9)}$$

This order corresponds to the polymerization rates obtained in this study. These results are also consistent with the amounts of cations generated from trityl chloride with some metal halides in the presence of ethyl acetate (Supporting Information):

$$\mathrm{FeCl_3} \sim \mathrm{GaCl_3} > \mathrm{InCl_3} > \mathrm{AlCl_3}$$

On the other hand, ^{13}C NMR investigation (Supporting Information) of the interaction between the metal halides and ethyl acetate (equivalent amount) revealed almost no relationship with the order of polymerization rate, although there was a vague correspondence for some metal halides; stronger interactions resulted in slower polymerization rates.

$$\mathrm{GaCl_3} > \mathrm{TiCl_4} > \mathrm{EtAlCl_2} > \mathrm{SnCl_4} > \mathrm{ZnCl_2} > \mathrm{GeCl_4} \sim \mathrm{SiCl_4}$$

From these results, some metal halides such as $SnCl_4$ and $ZnCl_2$ are more likely to interact strongly with a chlorine atom (chloride anion) than with a carbonyl (or ether) oxygen atom, while others, including $TiCl_4$ and $AlCl_3$, would interact more strongly with the oxygen atom. The activity of each metal halide for living cationic polymerization in the presence of an added base depends not on the "absolute" strength of Lewis acidity, but on the balance between the interaction with the propagating end chlorine atom and the carbonyl (or ether) oxygen atom of the added base, that is, the "relative" strength based on the degree of chlorophilicity and oxophilicity.

Metal halides with central metals of the same group tend to interact similarly with certain functional groups.[20] Some central metal elements of the halides examined in this study belong to the same groups, thus their polymerization behaviors were compared. The orders of the polymerization activity in the presence of ethyl acetate were as follows:

$$\text{group 4: } \mathrm{HfCl_4} \sim \mathrm{ZrCl_4} > \mathrm{TiCl_4}$$

$$\text{group 13: } \mathrm{GaCl_3} > \mathrm{InCl_3} > \mathrm{AlCl_3}$$

$$\text{group 14: } \mathrm{SnCl_4} \gg \mathrm{SiCl_4} \sim \mathrm{GeCl_4}$$

One of the important factors influencing their activity is the interaction of the Lewis acids with ethyl acetate or the chlorine atom of the propagating end. Therefore, IR analysis has been used as a measure of the interaction with ethyl acetate,[21] and of Friedel−Crafts benzylation using benzyl chloride,[10] which accompanies the extraction of chloride anions by the Lewis acid (only $SnCl_4$ was examined in the Friedel−Crafts benzylation as a group 14 metal). Interaction with ethyl acetate (ref 21):

$$\text{group 4: } \mathrm{TiCl_4} > \mathrm{ZrCl_4}$$

$$\text{group 13: } \mathrm{GaCl_3} > \mathrm{AlCl_3} > \mathrm{InCl_3}$$

$$\text{group 14: } \mathrm{SnCl_4} > \mathrm{GeCl_4} > \mathrm{SiCl_4}$$

Friedel−Crafts benzylation activity (ref 10):

$$\text{group 4: } \mathrm{HfCl_4} > \mathrm{ZrCl_4} > \mathrm{TiCl_4}$$

$$\text{group 13: } \mathrm{GaCl_3} > \mathrm{AlCl_3} > \mathrm{InCl_3}$$

In group 4, $TiCl_4$ interacts with ethyl acetate more strongly than $ZrCl_4$ does, but it is the poorest catalyst for the extraction of a chloride anion. This trend corresponds to the activity of the cationic polymerization in the presence of ethyl acetate. On the other hand, a different order was obtained for the group 13 metal chlorides. The interaction with ethyl acetate and the strength for extraction of a chloride anion show the same trend, whereas the reactivity is in a different order for cationic polymerization; the order of $AlCl_3$ and $InCl_3$ is reversed. This reflects the stronger acidity of $AlCl_3$ compared with $InCl_3$, whereas $AlCl_3$ interacts more strongly with carbonyl oxygen and $InCl_3$ interacts more strongly with chloride anions. According to the HSAB theory,[15] $TiCl_4$ and $AlCl_3$ are classified as hard acids, because they belong to the upper period in each group. In addition, carbonyl oxygen is classified as a hard base and the chloride anion as a borderline hard/soft base. This classification provides a good explanation for the polymerization behavior mentioned above, that is, hard $TiCl_4$ and $AlCl_3$ interact more strongly with the hard carbonyl oxygen, while soft $HfCl_4$ and $InCl_3$ interact more strongly with the "softer" chloride anion.

2. Living Cationic Polymerization Using $NbCl_5$ and $TaCl_5$ in the Presence of an Added Salt. With $NbCl_5$, $TaCl_5$, and $MoCl_5$, polymers with unimodal but broad MWDs were obtained in the presence of an added base (Table 2, entries 32−40). In addition, the M_n values were very high compared to the calculated ones regardless of the monomer conversion in some reactions such as those using $TaCl_5$. As shown in Scheme 2, the exchange rate is considered to be small for polymerization in the presence of an added base. Thus, the propagating species generated reacts with a larger number of monomers before it reverts to the dormant species. Incidentally, computer simulations have predicted that such polymers will be obtained when the exchange rate is sufficiently slow.[22] From this perspective, it is suggested that the abnormal stability of the hexachloride anion, which is produced by the extraction of chloride anion from the propagating chain end, results in uncontrolled reactions using pentachlorides of $NbCl_5$, $TaCl_5$, and $MoCl_5$, in conjunction with an added base. Thus, as shown in Scheme 2B, polymerization using an added salt, $n\mathrm{Bu_4NCl}$, was investigated, which is considered to contribute to the production of hexachloride anions by easily providing chloride anion to pentachloride Lewis acids. Tetrabutylammonium salts ($n\mathrm{Bu_4NX}$; X: Cl, Br, I, etc.) are known to be effective for living polymerization using

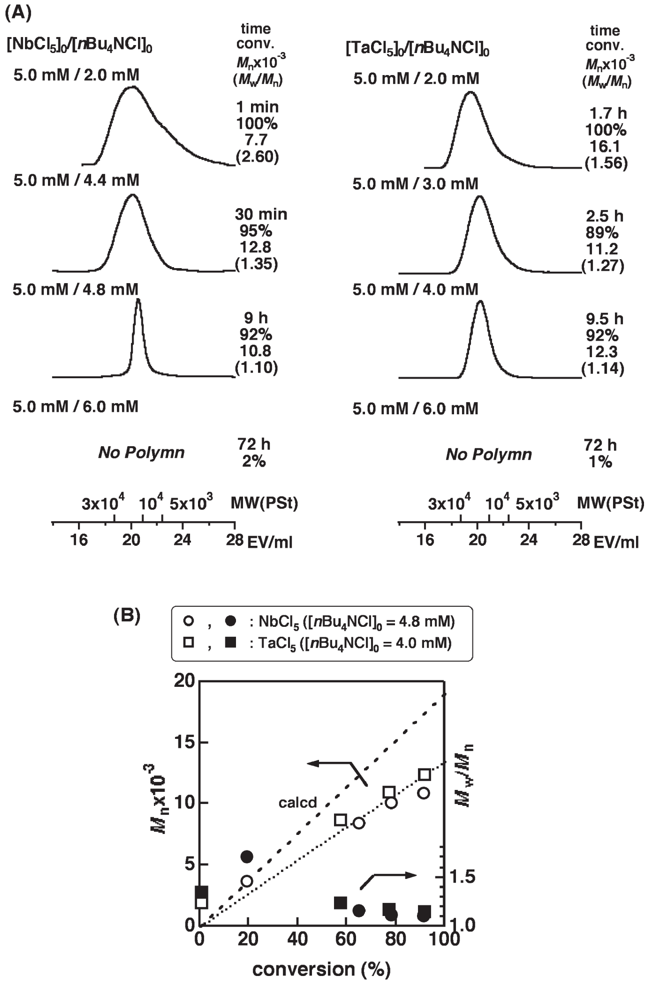
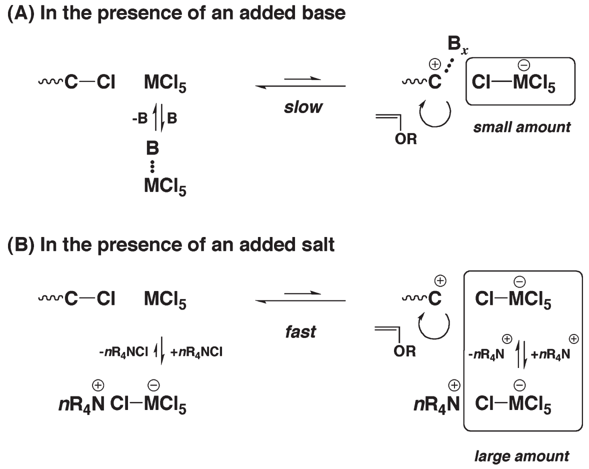


Figure 2. (A) Molecular weight distribution curves for poly(isobutyl vinyl ether)s [poly(IBVE)]s and (B) M_n and M_w/M_n for the polymerization of IBVE {Polymerization conditions: $[\text{IBVE}]_0$ = 0.76 M, $[\text{IBVE-HCl}]_0$ = 4.0 mM, $[\text{metal halide}]_0$ = 5.0 mM, $[n\text{Bu}_4\text{NCl}]_0$ = 2.0−6.0 mM, [ethyl acetate] = 10 mM for $NbCl_5$ and 200 mM for $TaCl_5$, in dichloromethane at 0 °C; M_n: number-average molecular weight, M_w/M_n: polydispersity ratio (weight-average molecular weight/number-average molecular weight), by GPC (polystyrene calibration)}.

Scheme 2. Postulated Equilibriums between the Dormant and Active Species in the Cationic Polymerization Using Metal Pentachlorides ($NbCl_5$ and $TaCl_5$) (A) in the Presence of an Added Base and (B) in the Presence of an Added Salt (M: Nb or Ta; B: Added Base)



Lewis acids such as $SnCl_4$.[23] Polymerization was performed in CH_2Cl_2, because an appreciable amount of precipitation was produced in toluene when metal halides and $n\text{Bu}_4\text{NCl}$ were mixed.

Cationic polymerization of IBVE was examined in the presence of $n\text{Bu}_4\text{NCl}$ with various concentrations, in conjunction with IBVE−HCl in CH_2Cl_2 at 0 °C ($[\text{IBVE}]_0$ = 0.76 M, $[\text{IBVE-HCl}]_0$ = 4.0 mM, $[\text{metal halide}]_0$ = 5.0 mM, $[n\text{Bu}_4\text{NCl}]_0$ = 2.0−6.0 mM, [ethyl acetate] = 10 mM for $NbCl_5$ and 200 mM for $TaCl_5$). With 2.0 mM of $n\text{Bu}_4\text{NCl}$, polymerization using $NbCl_5$ proceeded very rapidly to produce polymers with broad MWDs (Figure 2A). With 4.4 mM of $n\text{Bu}_4\text{NCl}$, the reaction was retarded compared to that with 2.0 mM, and the MWDs of the product polymers were narrower. With 4.8 mM of $n\text{Bu}_4\text{NCl}$, the rate was much lower, and polymers with very narrow MWDs were obtained. The M_n values increased linearly toward the monomer conversion, which supports the occurrence of living polymerization. On the other hand, polymerization did not proceed at all in the presence of $n\text{Bu}_4\text{NCl}$ with more than an equivalent amount to the catalyst. This is because the pentachloride $NbCl_5$ can coordinate only one basic molecule (chloride anion in this case) to be stabilized as a hexacoordinated species. Similar behavior was observed with $TaCl_5$. Although the reaction was not controlled with 2.0 mM of $n\text{Bu}_4\text{NCl}$, polymers with narrow MWDs were obtained for salt concentrations higher than 4.0 mM and the M_n values increased in direct proportion to the monomer conversion (Figure 2). More than an equivalent amount of $n\text{Bu}_4\text{NCl}$ to that of $TaCl_5$ suppressed the polymerization, as observed with $NbCl_5$. Increasing the amount of MCl_6^- (M = Nb, Ta) and maintaining a low MCl_5 concentration by the use of $n\text{Bu}_4\text{NCl}$ could adjust the rate and the balance of the equilibrium between the propagating and dormant species, and bring about the even propagation of each chain without undesired reactions.

The ^{1}H NMR spectra of the polymers produced by $NbCl_5$ or $TaCl_5$ with $n\text{Bu}_4\text{NCl}$ revealed no peaks derived from undesired reactions, such as those of olefin protons that were observed in polymers obtained using ethyl acetate at 60 °C (Supporting Information). In addition, a single series of peaks that corresponded with the calculated values (based on IBVE α-end and methoxy ω-end) was obtained from the MALDI−TOF−MS spectra (Supporting Information). These results support the occurrence of living polymerization with $NbCl_5$ and $TaCl_5$ in the presence of $n\text{Bu}_4\text{NCl}$. Lower values of M_n than those calculated were probably due to a small amount of residual water that was not completely removed and which acted as a cationogen.

On the other hand, polymerization using $MoCl_5$ and WCl_6 in the presence of $n\text{Bu}_4\text{NCl}$ was not controlled at all and resulted in polymers with broad MWDs. Suitable conditions for control of the reactions using these Lewis acids are currently under investigation.[24]

3. Overview of Living Cationic Polymerization of Vinyl Ether.

Living cationic polymerization of vinyl ether has been developed with various initiating systems since its first achievement using the HI/I_2 system reported in 1984.[1] In each system, the key to attaining livingness is how to suppress the surplus production of the active species, the unstable propagating carbocation frequently causing undesired reactions such as chain-transfer. To this end, a nice balance of the dormant-active equilibrium should be established. The methods for living polymerization are mainly classified into certain categories, as shown in Chart 2. One method is, as with the HI/I_2 system, the adjustment of the equilibrium by nucleophilic counteranions produced by extracting the atom

Table 3. Cationic Polymerization of Isobutyl Vinyl Ether (IBVE) with Various Metal Halides in the Presence of $n\mathrm{Bu_4NCl}$[a]

entry	metal halide	$[n\mathrm{Bu_4NCl}]_0$ (mM)	time	convn (%)	$M_n \times 10^{-3}$ (calcd)	$M_n \times 10^{-3}$[b]	M_w/M_n[b]
1	$SnCl_4$	8.0	0.5 h	73	13.9	14.9	1.03
2		10	1 h	1	–	–	–
3	$TiCl_4$	2.0	30 s	100	19.0	11.0	1.13
4		6.0	144 h	54	10.3	7.0	1.03
5[c]	$FeCl_3$	4.0	3 s	95	18.1	4.8	2.06
6[c]		6.0	5 min	58	11.0	6.2	1.84
7[c]		10	8 h	17	3.3	7.5	1.67
8	$EtAlCl_2$	3.0	10 s	100	19.0	36.1	2.13
9		4.0	31 h	14	2.6	21.0	1.90
10	$GaCl_3$	4.0	4 s	100	19.0	9.2	2.98
11		5.0	4 s	100	19.0	8.6	2.52
12	$SiCl_4$	0.1	672 h	27	5.0	10.5	1.86
13		0.5	673 h	9	1.8	7.4	2.56
14	$GeCl_4$	0.1	672 h	37	7.1	8.6	1.80
15		0.5	673 h	16	3.0	10.5	2.15

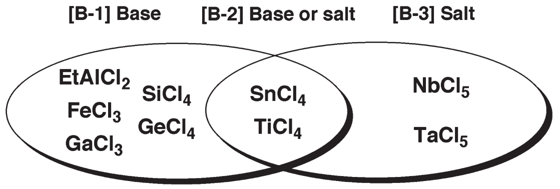
[a] $[\mathrm{IBVE}]_0$ = 0.76 M, $[\mathrm{IBVE{-}HCl}]_0$ = 4.0 mM, $[\text{metal halide}]_0$ = 5.0 mM, $[n\mathrm{Bu_4NCl}]_0$ = 0.1–10 mM, in CH_2Cl_2 at 0 °C. [b] M_n: number-average molecular weight, M_w/M_n: polydispersity ratio (weight-average molecular weight/number-average molecular weight), by GPC (polystyrene calibration). [c] Containing diethyl ether (250 mM).

Chart 2. Classification of Various Metal Halides for the Cationic Polymerization of Isobutyl Vinyl Ether Based on the Method to Achieve Living Polymerization

(A) Counteranion (ref. 1, 18, 23, 25)

I_2, ZnX_2 (X: Cl, Br, I), $SnBr_4$, SnX'_2 (X': Cl, I)

(B) Additive



*** Examined only with added base**

$ZrCl_4$, $HfCl_4$, $AlCl_3$, $InCl_3$, $SbCl_3$, $BiCl_3$

(C) Not controlled

$MoCl_5$, WCl_6

attached to the initiating and propagating ends (halogen atoms, acetoxy groups, etc.) using a weak Lewis acid [I_2, ZnX_2 (X: Cl, Br, I), $SnBr_4$, SnX'_2 (X′: Cl, I), etc.; Chart 2A].[1,18,23,25] Another method is the use of additives, weak Lewis bases or ammonium salts. Most of the Lewis acids belong to this category. In this study, polymerization combined with $n\mathrm{Bu_4NCl}$ was also examined using some Lewis acids with which the reaction was controlled in the presence of an added base (Table 3). The results clearly show that metal halides for the system using additives are classified into three groups: the controlled reaction is induced in conjunction with an added base [B-1], an added salt [B-3], or both of these [B-2]. The additives also have other roles, such as the stabilization of the propagating carbocation and the moderation of Lewis acidity, in addition to the adjustment of the equilibrium balance and rate between the active and dormant species. The key to living polymerization is the selection of a suitable method based on the nature of each metal halide.

Conclusion

A variety of metal halides were shown to catalyze living polymerization of IBVE in conjunction with suitable additives. The use of an additive, a weak Lewis base or an ammonium salt, brought considerable retardation of the reactions compared to those without an additive, by interacting with the metal halides. One feature of the behavior of these metal halides is the significant difference in activity: some acids require only a few seconds for completion, whereas for others it can take more than a few weeks to complete reactions in the presence of an added base. The difference results from the balance between the chlorophilic and the oxophilic nature of each metal halide. In addition, although esters or ethers as the added base are key ingredients for living polymerization with most metal halides, reactions using the metal pentachlorides $NbCl_5$ and $TaCl_5$ were not controlled with an added base. Pentachloride-mediated reactions were transformed into living polymerization by the use of an added salt, $n\mathrm{Bu_4NCl}$. Diversification of the initiating systems used for living cationic polymerization is expected to contribute not only to the development of initiating systems for monomers whose reactions are difficult to control or propagate, but also for the establishment of a novel index of Lewis acidity for metal halides based on their living polymerization activity, which would be applicable to various reactions.

Acknowledgment. A.K. expresses his special thanks to The JSPS Research Fellowships for Young Scientists and The Global COE Program "Global Education and Research Center for Bio-Environmental Chemistry" of Osaka University.

Supporting Information Available: Figures showing time–conversion curves and M_n–conversion curves of polymerization, NMR spectra, and MALDI spectra, and tables giving some polymerization data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For the pioneering study on living cationic polymerization of vinyl ether: Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265–268.
(2) For the pioneering studies on living cationic polymerization of isobutene: (a) Faust, R.; Kennedy, J. P. *Polym. Bull.* **1986**, *15*, 317–323. (b) Faust, R.; Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1847–1869.
(3) For reviews: (a) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111–172. (b) Kennedy, J. P.; Ivan, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*; Hanser: New York, **1992**. (c) Matyjaszewski, K.; Sawamoto, M. In *Cationic Polymerizations*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, **1996**; Chapter 4. (d) Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2285–2293. (e) Puskas, J. E.; Kaszas, G.

Prog. Polym. Sci. **2000**, *25*, 403–452.(f) De, P.; Faust, R. In *Macromolecular Engineering. Precise Synthesis, Materials Properties, Applications*.; Matyjaszewski, K.; Gnanou, Y.; Leibler, L., Ed.; WILEY-VCH GmbH & Co. KGaA: Weinheim, Germany, **2007**; Chapter 3. (g) Goethals, E. J.; Prez, F. D. *Prog. Polym. Sci.* **2007**, *32*, 220–246.

(4) For a review by our group: Aoshima, S.; Yoshida, T.; Kanazawa, A.; Kanaoka, S. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1801–1813.

(5) Aoshima, S.; Higashimura, T. *Macromolecules* **1989**, *22*, 1009–1013.

(6) Yoshida, T.; Tsujino, T.; Kanaoka, S.; Aoshima, S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 468–472.

(7) Yoshida, T.; Kanazawa, A.; Kanaoka, S.; Aoshima, S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4288–4291.

(8) Kanazawa, A.; Hirabaru, Y.; Kanaoka, S.; Aoshima, S. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5795–5800.

(9) Baaz, M.; Gutmann, V. In *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Interscience: New York, **1963**; Vol. *1*, Chapter 5.

(10) Olah, G. A.; Kobayashi, S.; Tashiro, M. *J. Am. Chem. Soc.* **1972**, *94*, 7448–7461.

(11) Kobayashi, S.; Busujima, T.; Nagayama, S. *Chem.—Eur. J.* **2000**, *6*, 3491–3494.

(12) Deters, J. F.; McCusker, P. A.; Pilger, R. C. *J. Am. Chem. Soc.* **1968**, *90*, 4583–4585.

(13) Laszlo, P.; Teston, M. *J. Am. Chem. Soc.* **1990**, *112*, 8750–8754.

(14) Hanke, D. L.; Steigmann, J. *Anal. Chem.* **1954**, *26*, 1989–1992.

(15) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.

(16) Higashimura, T.; Kamigaito, M.; Kato, M.; Hasebe, T.; Sawamoto, M. *Macromolecules* **1993**, *26*, 2670–2673.

(17) Katayama, H.; Kitaguchi, H.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4023–4031.

(18) (a) Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 3988–3992. (b) Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1992**, *25*, 2587–2591.

(19) There are some incomplete chain extensions, especially in Figure 1B. However, quite a nice reaction before the second addition of the monomer and almost clean chain extensions after the addition suggest that the essential nature of the propagating species was good and some experimental limitations caused side reactions, such as termination reaction by adventitious water in the freshly added monomer, partial and vigorous increase in temperature by the abrupt propagation derived from incomplete mixing of the added monomer in the early stage after the addition, or the rapid change in polarity of the reaction solutions. In addition, the lower M_n values of polymers obtained with the $ZrCl_4$ systems than the calculated ones possibly resulted from the initiation by adventitious water. As shown in Figure S1, the M_n values increased linearly from the early stage of the reaction although they are lower than the calculated values.

(20) Satchell, D. P. N.; Satchell, R. S. *Chem. Rev.* **1969**, *69*, 251–278.

(21) Lappert, M. F. *J. Chem. Soc.* **1962**, 542–548.

(22) Matyjaszewski, K.; Szymanski, R.; Teodorescu, M. *Macromolecules* **1994**, *27*, 7565–7574.

(23) Kamigaito, M.; Maeda, Y.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1993**, *26*, 1643–1649.

(24) Polymerization using WCl_6 produced a polymer with narrow MWD (reaction time = 2 h, conv. = 84%, $M_n = 10400$, $M_w/M_n = 1.03$) in the presence of a stronger base, dimethyl sulfide (Me_2S)[26] (reaction conditions: $[\mathrm{IBVE}]_0 = 0.76$ M, $[\mathrm{IBVE{-}HCl}]_0 = 4.0$ mM, $[\mathrm{WCl_6}]_0 = 5.0$ mM, $[\mathrm{Me_2S}]_0 = 0.5$ M, in toluene at 0 °C).

(25) Kojima, K.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1989**, *22*, 1552–1557.

(26) Cho, C. G.; Feit, B. A.; Webster, O. W. *Macromolecules* **1990**, *23*, 1918–1923.