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Living Cationic Polymerization of Vinyl Ether with Methanol/Metal Chloride Initiating Systems: Relationship between Polymerization Behavior and the Nature of Lewis Acids

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ABSTRACT: Cationic polymerization of vinyl ether (VE) was examined with methanol/metal chloride initiating systems instead of those with the conventionally used VE−protonic acid adduct initiators. With $MoCl_5$, a highly oxophilic metal halide, the polymerization of isobutyl VE (IBVE) using methanol proceeded in a living fashion in the presence of ethyl acetate, although the reaction was not controlled in conjunction with IBVE−HCl adduct. Furthermore, in the methanol-initiated polymerization, the Lewis acids used could be classified mainly into three categories in terms of polymerization behavior: those producing long-lived species (e.g., $MoCl_5$, $NbCl_5$, and $ZrCl_4$), those inducing uncontrolled polymerization (e.g., $GaCl_3$ and $FeCl_3$), or those showing no activity at all (e.g., $ZnCl_2$ and $InCl_3$). The matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI−TOF−MS) spectra of the product polymers and the direct ^1H NMR analysis of the reaction mixtures revealed that the controlled polymerization starts with an exchange reaction between the methoxy group of methanol and the chloride anion of a metal chloride to generate HCl, the true initiator. With some Lewis acids such as $NbCl_5$, the polymerization proceeds only via thus produced C−Cl terminals as dormant species, whereas rapid equilibrium between the C−Cl ends and acetal structures is involved in the propagation reaction with other Lewis acids such as $ZrCl_4$. The trends in Lewis acids correlated with the nature of their central metals, i.e., their "oxophilicity" and "chlorophilicity".

Introduction

For decades, living cationic polymerization has been mainly achieved using a suitably nucleophilic counteranion from an initiator and/or a metal halide, an externally added weak Lewis base, or an added salt.[1] Initiators (cationogens) are also critical for achieving controlled polymerization. For instant and quantitative initiation, compounds similar in structure to the propagating chain ends are often used as cationogens, more specifically, compounds with a carbon−heteroatom bond including a carbon−halogen or carbon−oxygen bond. For example, in the polymerization of vinyl ether (VE), monomer and protonic acid adducts such as VE−HCl, VE−CH_3COOH, or VE−CF_3COOH have been used for living polymerization.[2−7] The carbocation was generated from these initiators by a Lewis acid extraction of the halogen atom or acetoxy group. However, the disadvantage of these compounds is that they must be synthesized. In addition, the α-haloether (VE−HCl adduct) is harmful, which is problematic for industrial use. Therefore, the use of more convenient and harmless compounds is desired to increase the versatility of living cationic polymerization.

Recently, we demonstrated that a variety of metal halides could induce living cationic polymerization of VE by combining a suitable added base (ester or ether) or salt ($n\mathrm{Bu_4NCl}$) in conjunction with isobutyl VE−HCl adduct (IBVE−HCl) as a cationogen.[8] For base-assisting systems,[3,9] a weak Lewis base stabilizes the carbocation and/or moderates the metal halide (Scheme 1). Hence, the polymerization activity of Lewis acids relates to the strength of the interaction with the propagating end chloride anion and carbonyl (or ether) oxygen of an added base.[8,10−12] Polymerization using group 6 elements, $MoCl_5$ and WCl_6, has never induced controlled reactions. These early transition metal halides have a strong affinity toward oxygen atoms, which is exemplified by their high activity in reactions accompanying the scission of carbon−oxygen bonds.[13] In addition, it was reported that the combination of these metal halides and ethanol allowed the control of metathesis polymerization of acetylene derivatives.[14,15] In this case, modification of the catalysts was a key to achieving living polymerization.

On the basis of these results, we focused our attention on cationic polymerization using an alcohol with various metal halides. Alcohol has rarely been used as a key ingredient for a living cationic polymerization of VE,[16,17] although it can be a cocatalyst for metal halides, acting as a proton source. In this study, we examined the possibility of living cationic polymerization of VE using methanol as a cationogen combined with a variety of metal halides in the presence of an added base. Furthermore, polymerization mechanisms are discussed based on matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI−TOF−MS) spectra of the product polymers and ^1H NMR analysis of the reaction solutions. Comparison between the methanol system and its IBVE−HCl counterpart was also made, focusing on the relationships between the differences in the behavior and the nature of the metal halides.

Experimental Section

Materials. IBVE (TCI; >99.0%), ethyl acetate (Wako; >99.5%), dichloromethane (Nacalai Tesque; 99%), and 1,2-dichloroethane (Wako; >99.5%) were distilled twice over calcium hydride before use. Toluene-d_8 (Cambridge Isotope

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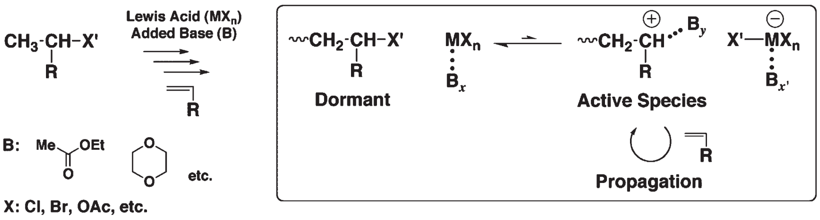
Scheme 1. Living Cationic Polymerization in the Presence of an Added Base



Laboratories, Inc.) was distilled over sodium 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. Anhydrous methanol (Nacalai Tesque; 99.8%; H_2O $<$50 ppm) was used without further purification. Toluene (Wako; 99.5%) was dried by passage through solvent purification columns (Glass Contour). IBVE−HCl adduct was prepared from the addition reaction of IBVE with HCl.[18] 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 $FeCl_3$, a stock solution in diethyl ether was prepared from commercial anhydrous $FeCl_3$ (Aldrich; 99.99%). For $GaCl_3$, a stock solution in hexane was prepared from commercial anhydrous $GaCl_3$ (Aldrich; 99.999+%). For $InCl_3$, $AlCl_3$, $HfCl_4$, $ZrCl_4$, and $BiCl_3$, stock solutions in ethyl acetate were prepared from commercial anhydrous $InCl_3$ (Strem; 99.999%), $AlCl_3$ (Aldrich; 99%), $HfCl_4$ (Strem; 99.9+%), $ZrCl_4$ (Aldrich; 99.99%), and $BiCl_3$ (Aldrich; 99.999%). For $GeCl_4$, a stock solution in dichloromethane was prepared from commercial anhydrous $GeCl_4$ (Wako; 99.99%). For $NbCl_5$, a stock solution in a mixture of dichloromethane and ethyl acetate was prepared from commercial anhydrous $NbCl_5$ (Strem; 99.99%). Because pure, solid $MoCl_5$ (Aldrich; 99.99%) and WCl_6 (Strem; 99.9%) did not dissolve completely in 1,2-dichloroethane, the heterogeneous solutions were used for polymerization. For polymerization with $MoCl_5$ using methanol as a cationogen, homogeneous stock solution in the mixture of 1,2-dichloroethane and methanol (equimolar amount toward $MoCl_5$) was prepared. All chemicals except for toluene were stored in brown ampules under dry nitrogen.

Polymerization Procedures. The following is a typical polymerization procedure (the $CH_3OH/ZrCl_4$ system as an example; a total volume of the polymerization solution: 5.0 mL). 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 for 10 min. Toluene (3.30 mL), heptane (0.25 mL), ethyl acetate (0.45 mL; 4.6 mmol), and IBVE (0.50 mL; 3.8 mmol) were added into the tube using dry syringes, successively. The polymerization was started by the addition of a equimolar mixture (0.50 mL; 50 mM; 2.5×10^{-2} mmol) of CH_3OH and $ZrCl_4$ in toluene/ethyl acetate (9/1, v/v) to the solution at 0 °C (for some cases, reactions were started by the addition of IBVE to a solution containing toluene, an added base, CH_3OH, and a metal chloride). A small amount of the reaction mixture (~1 mL) was extracted several times (1.5, 4.5, 8.5, and 21 h later) to be terminated with prechilled ethanol (~1 mL) containing a small amount of an aqueous ammonia solution (0.1%). The monomer conversion values were determined by gas chromatography using heptane (5 vol %) as an internal standard (23, 51, 73, and 95%, respectively; for some cases, monomer conversion values were determined by gravimetry). The quenched mixtures were washed with dilute hydrochloric acid, an aqueous sodium hydroxide solution, and then water to remove the initiator residues. The volatiles were then removed under reduced pressure, and the residues were vacuum-dried overnight at room temperature to yield colorless, gummy polymers. The gel permeation chromatography (GPC) analysis results were as follows: M_n = 3.6, 7.0, 9.6, and 11.5×10^3; M_w/M_n = 1.21, 1.14, 1.11, and 1.10, respectively).

Characterization. The molecular weight distribution (MWD) of the polymers was measured by 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 $= 4 \times 10^5$, 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, $M_w/M_n \leq 1.1$; see Supporting Information (Figure S1) for an example]. NMR spectra were recorded with a JEOL JNM-LA 500 spectrometer (500.00 MHz for ^{1}H). MALDI−TOF−MS spectra were recorded with a SHIMADZU/KRATOS AXIMA-CFR spectrometer (linear mode; voltage: 20 kV; pressure: $< 1.9 \times 10^{-3}$ Pa) using dithranol as the matrix and sodium trifluoroacetate as the ion source.[19] A solution (2−3 μL) containing a polymer, the matrix, and the ion source (polymer/matrix/ion source = 1 mg/8 mg/1 mg in 1 mL of THF) was casted on a stainless steel sample plate (Shimadzu Biotech, DE1580TA) and loaded to the spectrometer.

Results and Discussion

1. Cationic Polymerization of Vinyl Ether with $MoCl_5$ and WCl_6 Using Methanol. Cationic polymerization of IBVE was examined with $MoCl_5$ or WCl_6 using methanol in the presence of ethyl acetate in toluene at 0 °C. The reactions were initiated by adding a mixed solution of methanol and Lewis acid in 1,2-dichloroethane (for $MoCl_5$) or in toluene/1,2-dichloroethane (for WCl_6) to a mixture of monomer and an added base in toluene. The results are summarized in Table 1 along with those using IBVE−HCl. With $MoCl_5$ and IBVE−HCl, polymerization was complete in seconds, yielding a polymer with a broad MWD (entry 1). Reactions under various conditions such as with a stronger base (THF), at low temperature (−78 °C), or in the presence of an added salt (nBu$_4$NCl) were also not controlled (Supporting Information; Table S1). In contrast, the reaction was obviously moderated with the use of methanol (entry 2). The M_w/M_n of the resulting polymer was lower than 1.1, and the GPC curves of the product polymers shifted toward the higher molecular weight region with the increase of monomer conversion, which indicates the production of a long-lived species. An added base, ethyl acetate, was indispensable for controlling the reaction (Supporting Information; Table S1). With WCl_6, polymerization using methanol proceeded very fast to give polymers with broad MWDs similar to those using IBVE−HCl (entries 3 and 4).

The combination of $MoCl_5$ and methanol resulted in a controlled reaction as shown above, thus this system was

Table 1. Cationic Polymerization of Isobutyl Vinyl Ether (IBVE) with $MoCl_5$ and WCl_6 Using Methanol[a]

entry	metal halide	cationogen	time	convn (%)	$M_n \times 10^{-3}$ (calcd)	$M_n \times 10^{-3}$ [b]	M_w/M_n [b]
1	$MoCl_5$	IBVE−HCl	5 s	96	18.3	15.8	3.80
2		CH_3OH	25 min	94	14.2	16.2	1.05
3	WCl_6	IBVE−HCl	10 s	96	18.3	8.2	2.26
4		CH_3OH	10 s	45	6.8	10.0	2.47

[a] $[IBVE]_0$ = 0.76 M, $[IBVE{-}HCl]_0$ = 4.0 mM or $[CH_3OH]_0$ = 5.0 mM, [metal halide]$_0$ = 5 mM, [ethyl acetate] = 1.0 M, 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).

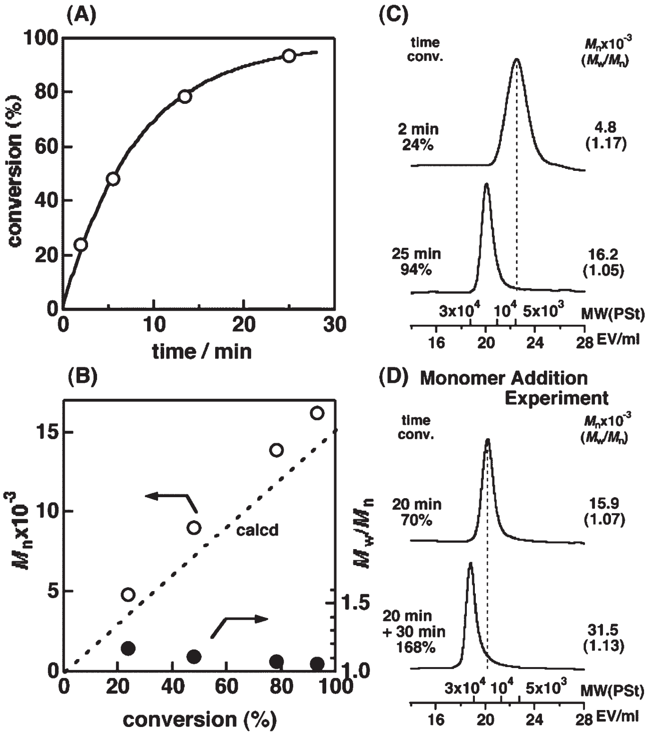


Figure 1. (A) Time−conversion curve, (B) M_n and M_w/M_n for the polymerization of isobutyl vinyl ether (IBVE) with $MoCl_5$ using methanol, (C) molecular weight distribution (MWD) curves for the poly(IBVE)s, and (D) MWD curves for the poly(IBVE)s in the monomer addition experiment {$[IBVE]_0$ = 0.76 M, $[IBVE]_{added}$ = 0.76 M [for (D)], $[CH_3OH]_0$ = 5.0 mM, $[MoCl_5]_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, 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)}.

examined in detail. The time−conversion curves and M_n, M_w/M_n−conversion plots are shown in Figure 1. With an equimolar amount of methanol and $MoCl_5$ (5.0 mM/5.0 mM), the polymerization proceeded without an induction period (Figure 1A) and the rate was first-order (Supporting Information; Figure S2), which suggests that the reaction proceeded with a relatively simple mechanism. The M_n values increased linearly along the calculated lines based on the amount of methanol (Figure 1B). Furthermore, in the monomer addition experiment (Figure 1D), the GPC peak shifted to the higher MW region after the addition of a fresh feed of IBVE, indicating the occurrence of living polymerization.

Reactions with various amounts of methanol are summarized in Table 2 [see Figure S2 (Supporting Information) for the graphs]. The calculated values in Table 2 are based on the total amounts of methanol contained in the solutions. With twice as much methanol as the catalyst (entry 2), polymerization proceeded at almost the same rate as with the previous case and the product polymers had M_n very similar to that of the product with 5.0 mM of methanol (entry 1).

Table 2. Cationic Polymerization of Isobutyl Vinyl Ether (IBVE) Using $MoCl_5$ with Various Amounts of Methanol[a]

entry	$[CH_3OH]_0$ (mM)	time (min)	convn (%)	$M_n \times 10^{-3}$ (calcd)[b]	$M_n \times 10^{-3}$[c]	M_w/M_n[c]
1	5.0	25	94	14.2	16.2	1.05
2	10	25	93	7.0	14.3	1.12
3	15	25	92	4.7	9.8	1.26
4	25	15	96	2.9	6.2	1.53

[a] $[IBVE]_0$ = 0.76 M, $[CH_3OH]_0$ = 5.0, 10, 15, or 25 mM, $[MoCl_5]_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, in toluene at 0 °C. [b] On the basis of the total amount of methanol. [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).

This indicates that only an equimolar amount of methanol reacted with $MoCl_5$, releasing protons to initiate the polymerization even when excess methanol was used. Interestingly, the rest of methanol did almost no harm to the livingness. With more amounts of methanol (15 and 25 mM; entries 3 and 4) than $MoCl_5$ (5.0 mM), on the other hand, there appeared obvious tailings in the GPC curves of the polymers, especially in those obtained at the later stage of the polymerization, although the rates were nearly similar. These results suggest that the excess methanol induced some undesired reactions such as chain transfer and/or termination.[20]

MALDI−TOF−MS analyses of the product polymers were conducted to study the terminal structures of the product polymers (Figure 2). The analyzed polymers were prepared by quenching with ammonious ethanol. Only one series of peaks was observed in the spectrum of the polymer obtained from the reaction with equimolar amounts of methanol and $MoCl_5$, where the peak values agreed with those expected from the polymer structure with ethoxy ω-ends derived from the quenching agent. The absence of methoxy ω-ends indicates no reaction between methanol and the propagating chain end. This suggests that the dormant species is not acetal, although the protons of methanol are included in the polymer chains as an initiator fragment. In contrast, with five times as much methanol as $MoCl_5$, there are two kinds of peaks whose masses agree with those expected from the structures with both ethoxy (main peaks) and methoxy (−14 from main peaks) ω-ends in the spectrum of the polymer produced. The existence of the methoxy ω-ends in addition to the tailing in GPC curves (Supporting Information; Figure S2) supports the view that excess methanol reacted with the propagating ends during the polymerization, forming acetal groups and releasing protons that induced chain transfer.

The postulated mechanism of the methanol/$MoCl_5$ initiating system is shown in Scheme 2. The reaction between equimolar amounts of methanol and $MoCl_5$ leads to ligand exchange and produces some kind of Mo catalyst species such as $MoCl_4(OMe)$ and/or $MoOCl_3$[21−24] to liberate HCl equimolar to methanol ($[CH_3OH] \le [MoCl_5]$) or to $MoCl_5$ ($[CH_3OH] > [MoCl_5]$). The generated HCl smoothly initiates polymerization to produce the propagating chain end

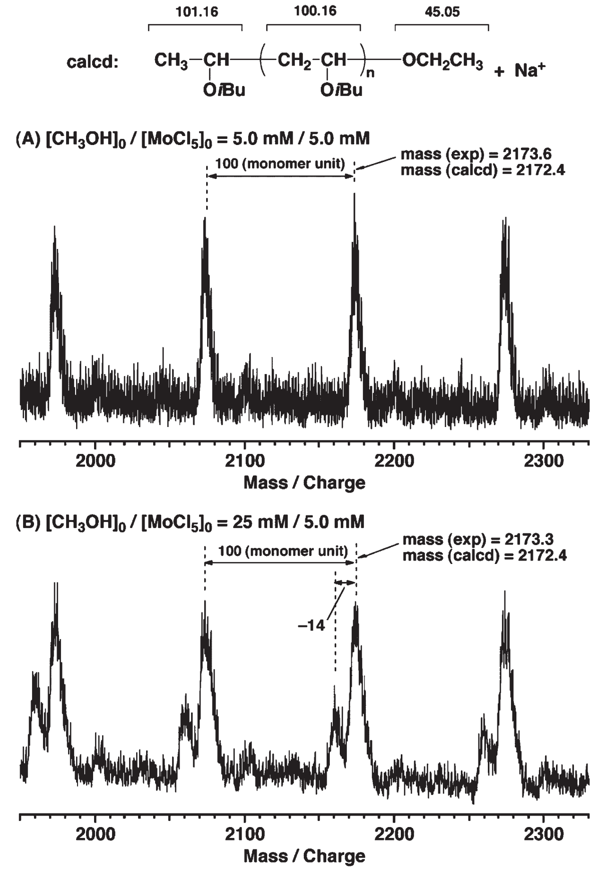
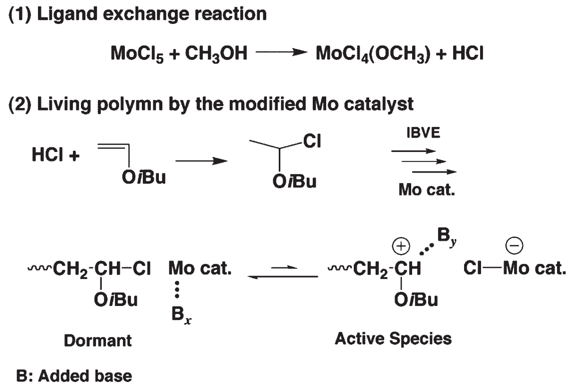


Figure 2. MALDI−TOF−MS spectra of poly(isobutyl vinyl ether)s [poly(IBVE)s] obtained with $CH_3OH/MoCl_5$: (A) 5.0 mM/5.0 mM, M_n (GPC) = 4.0×10^3, M_w/M_n (GPC) = 1.24; (B) 25 mM/5.0 mM, M_n (GPC) = 3.7×10^3, M_w/M_n (GPC) = 1.31. Polymerization conditions: $[IBVE]_0$ = 0.76 M, $[CH_3OH]_0$ = 5.0 or 25 mM, $[MoCl_5]_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, in toluene at 0 °C.

with the $\sim CH_2CH(OiBu)Cl$ structure. If the oxygen atom in methanol coordinates with the Mo atom to form $-OCH_3$ or =O, it does not react with the propagating end. Furthermore, such coordination moderates the Lewis acidity, which is often critical to control the reaction in cationic polymerization.[25] In addition, the reaction between methanol and $MoCl_5$ is one-to-one at any ratio. As shown here, living polymerization of VE using Mo catalyst was achieved for the first time by using methanol as an initiator.

2. Cationic Polymerization of Vinyl Ether with Various Methanol/Metal Chloride Initiating Systems. (*a*). *Polymerization Results.* The remarkable results of the Mo case motivated us to investigate cationic polymerization with other methanol/metal chloride initiating systems. The reactions were examined using equimolar or more than equimolar amounts of methanol to metal halides in the presence of an added base in toluene at 0 °C. The added base for each metal halide was chosen based on its polymerization behavior using IBVE−HCl.[8] The results are summarized in Table 3, and time−conversion, M_n, M_w/M_n−conversion plots, and MWD curves of the product polymers are shown in Figures 3 and 4 for $NbCl_5$, $ZrCl_4$, and $GaCl_3$ (see Supporting Information for other metal halides; Figure S4). Almost all metal halides used here induced living cationic polymerization in conjunction with IBVE−HCl in the presence of an added base.[1,8] In contrast, these catalysts are categorized mainly into three groups in the methanol-assisted polymerization in terms of their polymerization behavior. First, with $NbCl_5$, $SiCl_4$, $GeCl_4$, $ZrCl_4$, $HfCl_4$, $TiCl_4$, $AlCl_3$, and $SnCl_4$, the GPC curves of the product polymers shifted toward the higher molecular weight region with the progression of polymerization, which suggested the production of a long-lived species.[26] Second, with $GaCl_3$ and $FeCl_3$, the reactions proceeded in an uncontrolled fashion to produce polymers with monodisperse but broad MWDs and high molecular weights even in the early stage of the polymerization. Lastly, no polymerization occurred with $ZnCl_2$, $InCl_3$, and $BiCl_3$.

Scheme 2. Possible Mechanism of the Polymerization with the $CH_3OH/MoCl_5$ Initiating System



Monomer addition experiments were conducted to confirm the living nature of the polymerization using Lewis acids that produced long-lived species with the methanol-initiating system. As shown in Figure 5, peaks of the GPC curves shifted toward the higher molecular weight region without remaining original polymers after the addition of a fresh feed of the monomer. A linear increase of the M_n values toward the monomer conversion was also confirmed. These results indicate the progression of living polymerization by using methanol as a cationogen in conjunction with suitable metal chlorides.

There are also noticeable differences among the metal halides that produced long-lived species. The initiation efficiencies of methanol estimated from M_n of the product polymers varied by Lewis acid.[27] Nearly quantitative initiation was achieved with many Lewis acids such as $NbCl_5$ and $ZrCl_4$ using an equimolar amount of methanol to the catalyst, but initiation did not reach the 100% level with $AlCl_3$ and was less than 50% with $SnCl_4$. The lower efficiency appears to stem from the difficulty in ligand exchange. In addition, the numbers of methanol molecules that react with a metal halide and work as a proton source differed according to the metal halides. Only amounts equal to the catalyst worked with some acids like $SiCl_4$ and $MoCl_5$, while twice the amount could induce initiation with others, as shown in Table 3. Furthermore, with $ZrCl_4$, the M_n values of the product polymers increased along with the calculated line determined assuming that four molecules of methanol were involved in the initiation step (Figure 3B).

The characteristics of the metal halides also affected the polymerization rate. Although the reactions using methanol with almost all Lewis acids proceeded slower than those using IBVE−HCl (4.0 mM) under similar conditions, faster reactions were observed with two acids, $SiCl_4$ and $GeCl_4$. In particular, with $SiCl_4$, the rate was about ten times larger than that with IBVE−HCl.[28] In addition, with some metal halides like $ZrCl_4$, the rates were almost independent of the amounts of methanol, although up to four molecules of methanol per metal halide were used for the ligand exchange. There are some other unclear points about the polymerization rates, which are currently being investigated in detail.

Table 3. Cationic Polymerization of Isobutyl Vinyl Ether (IBVE) with Various Metal Halides Using Methanol[a]

entry	metal halide	$[CH_3OH]_0$ (mM)	time	convn (%)	$M_n \times 10^{-3}$ (calcd)[b]	$M_n \times 10^{-3}$[c]	M_w/M_n[c]
1	$NbCl_5$	5.0	2.5 h	91	13.9	10.9 (10.4)[d]	1.26 (1.04)[d]
2		10	2.5 h	94	7.1	7.4	1.08
3	$SiCl_4$	5.0	46.5 h	71	10.9	10.5	1.03
4		10	31 h	93	7.1	12.3	1.05
5	$GeCl_4$	5.0	191.5 h	93	14.1	15.0	1.17
6		10	192 h	93	7.1	12.5	1.10
7	$ZrCl_4$	5.0	21 h	95	14.5	11.5	1.10
8		10	21.5 h	92	7.0	7.0	1.13
9	$HfCl_4$	5.0	22 h	95	14.4	11.8	1.23
10		10	10 h	79	6.0	7.5	1.23
11	$TiCl_4$	5.0	387 h	19	2.9	2.9 (2.7)[d]	1.62 (1.25)[d]
12		10	387 h	41	3.1	2.5 (2.4)[d]	1.48 (1.25)[d]
13	$SnCl_4$	5.0	7 min	87	13.2	32.0	1.27
14		10	7 min	96	7.3	12.4	1.49
15	$AlCl_3$	5.0	10 h	84	12.8	17.7	1.19
16		10	9.5 h	81	6.2	10.7	1.27
17	$GaCl_3$	5.0	248 h	56	8.5	14.4	2.11
18		10	28 h	25	3.8	11.1	2.14
19	$FeCl_3$	5.0	5.4 h	89	13.5	15.9	3.73
20		10	4 h	92	7.0	14.5	2.40
21	$ZnCl_2$	5.0	23 h	0	-	-	-
22		10	23.5 h	0	-	-	-
23	$InCl_3$	5.0	23.5 h	0	-	-	-
24		10	22.5 h	1	-	-	-
25	$BiCl_3$	5.0	23 h	3	-	-	-
26		10	23 h	2	-	-	-

[a] $[IBVE]_0$ = 0.76 M, $[CH_3OH]_0$ = 5.0 or 10 mM, [metal halide]$_0$ = 5.0 mM, [added base] = 1.0 M, in toluene at 0 °C (added base: ethyl acetate for Nb, Zr, Hf, Ti, Sn, Al, Zn, In, Bi; 1,4-dioxane for Si, Ge, Fe, THF for Ga). [b] On the basis of the amount of methanol. [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] For a main peak.

(*b*). *MALDI−TOF−MS Analyses of the Product Polymers*. The product polymers obtained using metal halides that produced long-lived species were analyzed by MALDI−TOF−MS to elucidate the polymerization mechanisms. All the polymers were produced with equimolar amounts of methanol and the catalyst and by quenching with ammonious ethanol. MALDI analysis revealed that two types of spectra were observed depending on the metal halide used. The spectra of the polymers from $NbCl_5$ and $ZrCl_4$, the representative catalysts for each case, are shown in Figure 6 (those from other metal halides are included in the Supporting Information; Figure S5).

With $NbCl_5$, $SiCl_4$, $GeCl_4$, and $AlCl_3$, the observed peaks were only in a single set whose mass numbers agreed with those expected from the structure with an ethoxy group at the ω-ends (Figure 6A). Similar to the case with $MoCl_5$, these peaks indicate that the methoxy group from methanol is bonded to the metal atom and that the once attached methoxy group does not react with the propagating polymer chains.

In sharp contrast, several sets of peaks were observed with $ZrCl_4$, $HfCl_4$, $TiCl_4$, and $SnCl_4$ (Figure 6B). One set of major peaks corresponds to the polymer structure with an ethoxy group at the ω-ends. The m/z values of the other peaks were −56, −42, −14, and +28. These values clearly agreed with the structures whose ω-ends contained various acetals such as those with a methoxy group and an isobutoxy group, two isobutoxy groups, and two methoxy groups, or the structures whose side chains are not isobutoxy but methoxy groups. The generation of acetal chain ends via the reaction with alkoxy groups on the metal atoms of the modified catalyst or methanol, and the reactivation of such acetal ends, as shown in Scheme 3, were likely responsible for the resulting structures.

(*c*). *In Situ ^1H NMR Analysis of the Polymerization Solutions*. Since various acetal structures were obtained, the identification of the dormant species during the reactions is important in discussing the polymerization mechanisms. Thus, ^1H NMR analysis of the polymerization solutions was performed. In a sealed NMR tube under N_2 atmosphere, IBVE was polymerized using $NbCl_5$, $ZrCl_4$, or $GaCl_3$ in conjunction with methanol, of which concentrations are higher than in the usual polymerization (to obtain clear spectra) in toluene-d_8 at 0 °C. The spectra were recorded as soon as possible after the initiation. The results are summarized in Figure 7. The peaks shown correspond to the methine protons of the monomeric species (quartet) and the polymer chain ends (broad and complex). Spectrum A was obtained from the solution containing IBVE−HCl, IBVE, and ethyl acetate, and spectrum B from that containing methanol in addition to the three components for A.

With $NbCl_5$, which produced polymers with a single terminal structure, the generation of C−Cl ends was confirmed by the emerging peaks around 5.8 ppm (Figure 7C). This supports the mechanism involving HCl formation by exchange of a chloride anion and the methoxy group between the metal chloride and methanol, and initiation by the generated HCl, as described in the previous sections.

In contrast, both C−Cl ends and acetal bonds were present in the case of $ZrCl_4$ (Figure 7D), which gave polymers with several types of terminal structures. Furthermore, the presence of VE−HCl adducts and acetals with various combinations of alkoxy groups was identified from the spectrum of the reaction mixture at the early stage (Figure 7E). These two spectra support the polymerization mechanism shown in Scheme 3, namely, the production of acetal species by the reaction between the propagating carbocation and alkoxy groups derived from methanol or an alkoxy coordinated catalyst, as well as simple ligand exchange leading to the HCl adduct as in the case with $NbCl_5$ or $MoCl_5$. In addition, the generated acetal species can be reactivated to produce the propagating carbocation, which is obvious from the presence of various monomeric acetal species such as 1,1-dimethoxyethane or 1,1-diisobutoxyethane (Figure 7E) and their

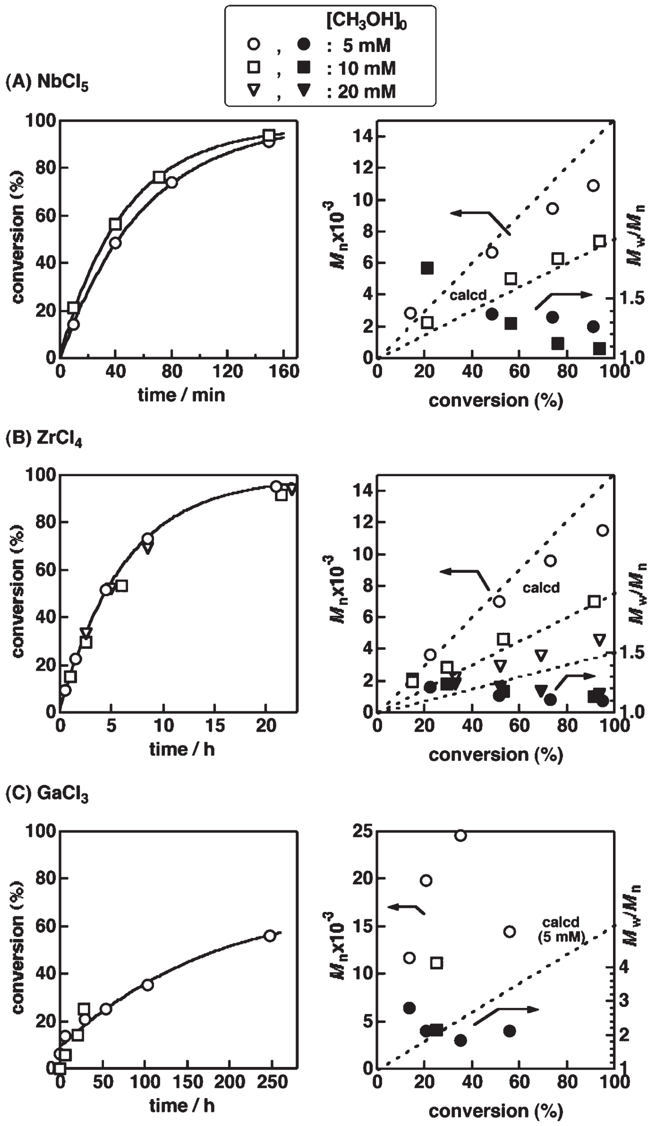


Figure 3. Time−conversion curves and M_n and M_w/M_n for the polymerization of IBVE with (A) NbCl$_5$, (B) ZrCl$_4$, and (C) GaCl$_3$ using methanol {[IBVE]$_0$ = 0.76 M, [CH$_3$OH]$_0$ = 5.0, 10, or 20 mM, [metal halide]$_0$ = 5.0 mM, [added base] = 1.0 M (ethyl acetate for NbCl$_5$ and ZrCl$_4$, THF for GaCl$_3$), 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)}.

consumption (all of the monomeric acetals and VE−HCl adducts were consumed after some period of time under the examined conditions). The ZrCl$_4$ case is novel and very interesting because living polymerization proceeds despite the coexistence of two different types of propagating species (dormant species), those with C−Cl bonds and acetals. These results suggest that there is little difference in the rate or energy of activation to generate a carbocation between the two types of dormant species, another intriguing observation.

Contrary to these two Lewis acids producing C−Cl bonds, only acetal chain ends were observed in the spectrum with GaCl$_3$ (Figure 7F), which induced uncontrolled polymerization, to give polymers with high molecular weights regardless of monomer conversion. This shows no ligand exchange reaction is involved in the reaction using GaCl$_3$, thus the polymerization proceeds by abstracting a methoxy group at a polymer terminal to generate the propagating carbocation and by returning it to the terminal, forming the dormant acetal species.[29] Although the reaction using ZrCl$_4$ also involved the acetal species, the coexistence of C−Cl ends should contribute to the control of the polymerization because the generated carbocation can return to the dormant species by both alkoxy groups and chloride anions.

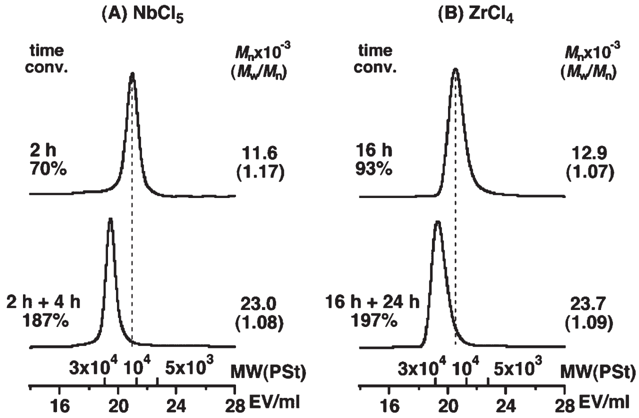


Figure 5. Molecular weight distribution curves for poly(isobutyl vinyl ether)s [poly(IBVE)s] in the monomer addition experiments using (A) NbCl$_5$ and (B) ZrCl$_4$ {[IBVE]$_0$ = [IBVE]$_{added}$ = 0.76 M, [CH$_3$OH]$_0$ = 5.0 mM, [metal halide]$_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, in toluene at 0 °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)}.

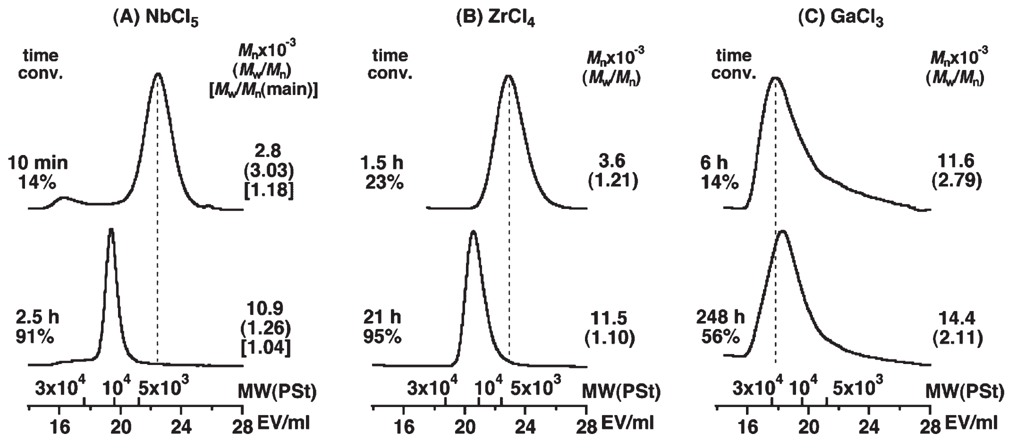


Figure 4. Molecular weight distribution curves for the poly(isobutyl vinyl ether)s [poly(IBVE)s] obtained in the polymerization with (A) NbCl$_5$, (B) ZrCl$_4$, and (C) GaCl$_3$ using methanol {[IBVE]$_0$ = 0.76 M, [CH$_3$OH]$_0$ = 5.0 mM, [metal halide]$_0$ = 5.0 mM, [added base] = 1.0 M (ethyl acetate for NbCl$_5$ and ZrCl$_4$, THF for GaCl$_3$), 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)}.

The clear relationships among the polymerization behavior, the MALDI−TOF−MS spectra of the product polymers, and the ^{1}H NMR spectra of the reaction solution led to the following conclusions. With some metal chlorides such as $NbCl_5$ or $ZrCl_4$, the long-lived species mediated polymerization using methanol proceeded only by the C−Cl propagating species produced from HCl, the true initiator, which was generated by the exchange reaction between methanol and metal chlorides ($NbCl_5$), or by both the C−Cl and the acetal ends ($ZrCl_4$). In contrast, uncontrolled polymerization with other metal chlorides such as $GaCl_3$ involved no such exchange reaction and proceeded only via the acetal bonds.

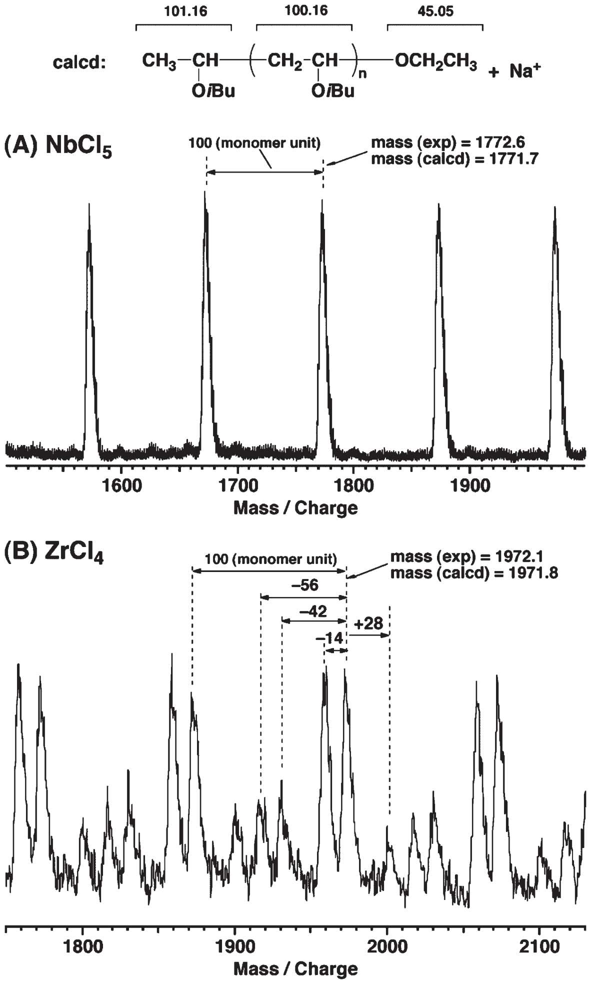


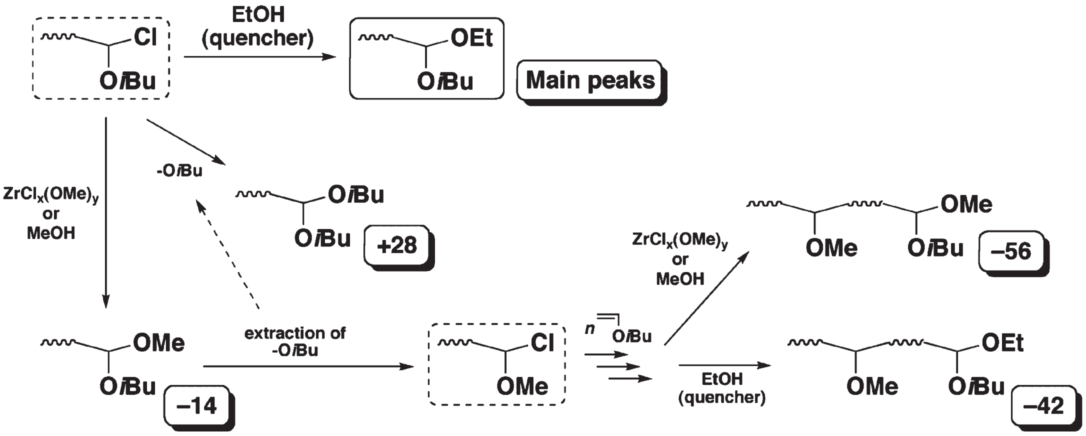
Figure 6. MALDI−TOF−MS spectra of poly(isobutyl vinyl ether)s [poly(IBVE)s] obtained with (A) $NbCl_5$ and (B) $ZrCl_4$ using methanol (5.0 mM): (A) M_n (GPC) = 2.6 × 10^3, M_w/M_n (GPC) = 1.18 (for a main peak); (B) M_n (GPC) = 3.6 × 10^3, M_w/M_n (GPC) = 1.21. Polymerization conditions: $[IBVE]_0$ = 0.76 M, $[CH_3OH]_0$ = 5.0 mM, [metal halide]$_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, in toluene at 0 °C.

(*d*). *Differences in Polymerization Behavior Using Methanol among Lewis Acids and Relationships with the Nature of Lewis Acids.* The Lewis acids used for cationic polymerization using methanol were classified mainly into three groups based on their behavior. For achieving controlled polymerization, it was important whether the exchange reaction between chloride anion and the methoxy group[21−24,30−33] occurred (Scheme 4). Here, comparison between polymerization behaviors with methanol and IBVE−HCl as initiators highlights a correlation between the catalyst classification in this study and the activity of Lewis acids in polymerization using IBVE−HCl in the presence of an added base. The order of polymerization rates of IBVE in the presence of ethyl acetate in toluene at 0 °C is as follows (for metal chlorides that induce controlled polymerization with the IBVE−HCl/added base initiating system):[8]

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

Almost all the Lewis acids that produced long-lived species in polymerization using methanol induced slower polymerization ($AlCl_3$, $HfCl_4$, $ZrCl_4$, $TiCl_4$, $SiCl_4$, $GeCl_4$; except for $SnCl_4$), whereas those which induced uncontrolled reaction or no polymerization belong to the active catalyst group ($GaCl_3$, $FeCl_3$, $InCl_3$, $ZnCl_2$; except for $BiCl_3$). These correlations can be explained by the differences in the nature of the Lewis acids, e.g., their oxophilicity and chlorophilicity. Lewis acids with an oxophilic central metal liberate one or more chloride anions by coordinating the methoxy group from methanol, leading to controlled polymerization. Those same Lewis acids induce slow reaction in the IBVE−HCl-initiated polymerization with ethyl acetate. This is because the metal center interacts more strongly with the carbonyl

Scheme 3. Polymerization Mechanism with the $CH_3OH/ZrCl_4$ Initiating System: The Formation of Acetal Bonds and Their Reactivation[a]



[a] Numbers in the scheme show the differences in molar mass of the peaks in the MALDI−TOF−MS spectra from its main peaks agreeing with the $\sim CH_2CH(OiBu)OEt$ structures.

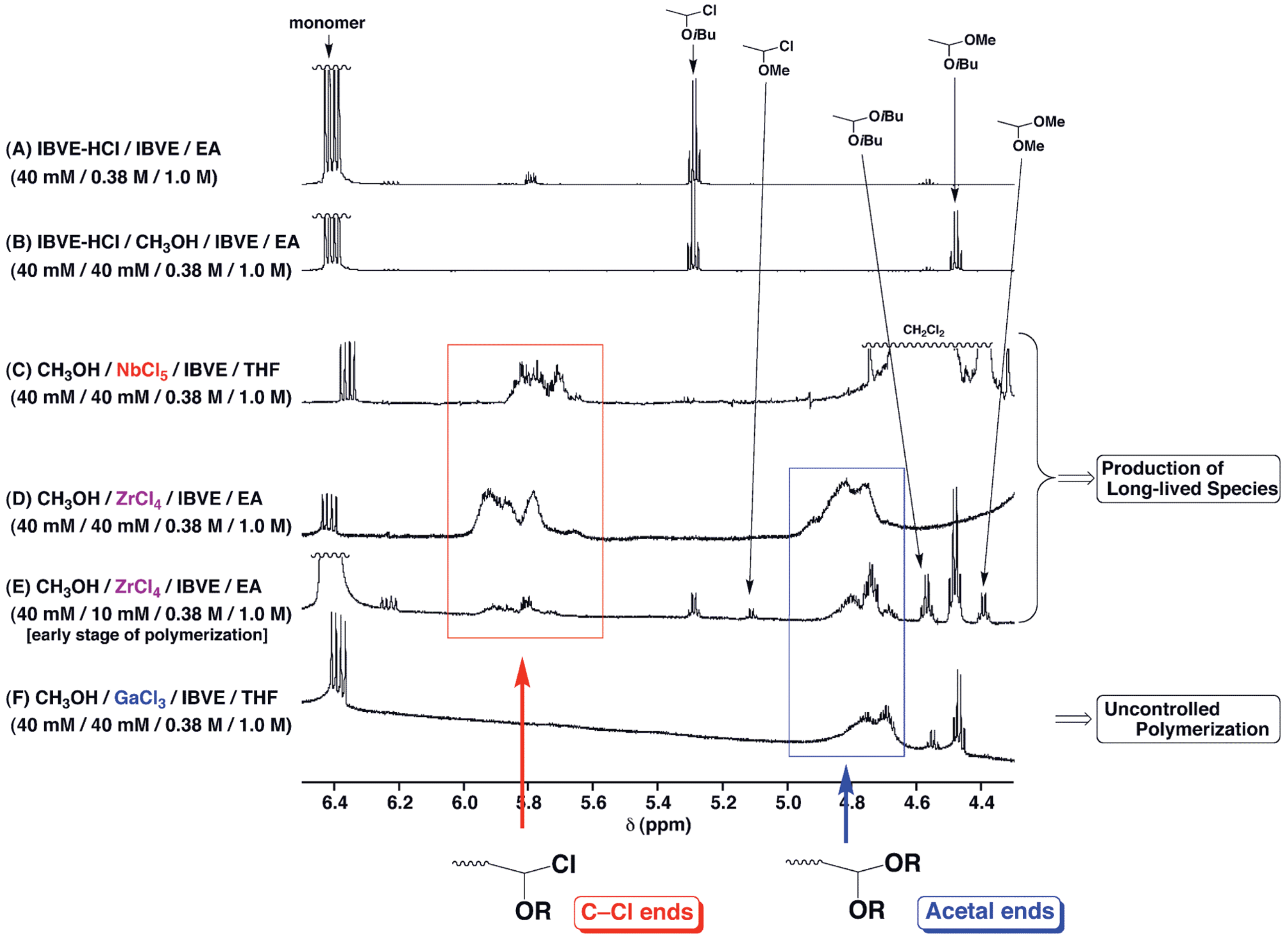
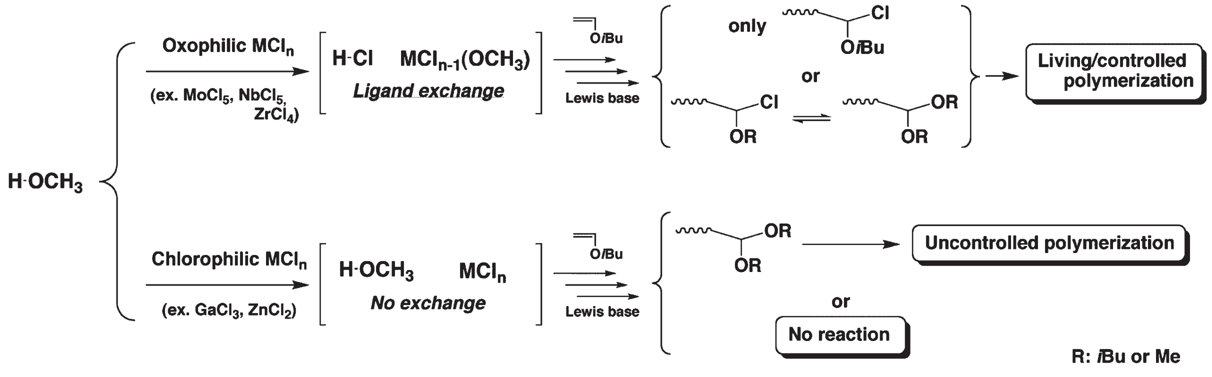


Figure 7. ^{1}H NMR spectra (the methine protons of the initiator molecules or the propagating ends) of (A) IBVE−HCl, (B) IBVE−HCl/CH$_3$OH, and (C)−(F) polymerization solutions with CH$_3$OH/metal chloride initiating systems (in toluene-d_8 at 0 °C, 500 MHz; EA: ethyl acetate).

Scheme 4. Polymerization Mechanisms of Cationic Polymerization of Isobutyl Vinyl Ether (IBVE) with CH$_3$OH/Metal Chloride Initiating Systems



group of ethyl acetate than with the propagating end chloride anion. In contrast, Lewis acids with a chlorophilic central metal prefer bonding with chloride anion and induce no exchange reaction with methanol, resulting in an uncontrolled reaction. Faster reaction, in turn, proceeds with the IBVE−HCl/ethyl acetate system due to a stronger interaction with the chloride anions than with the carbonyl group. The difference between the Lewis acids that catalyze uncontrolled reactions and those inducing no reaction lies in the absolute strength of the Lewis acidity. Chlorophilic and strong acids like GaCl$_3$ and FeCl$_3$ generate carbocations by forcibly abstracting the methoxy group, while chlorophilic but weak acids like ZnCl$_2$ and InCl$_3$ are not able to cleave the C−O bond.

Conclusions

This study demonstrated that cationic polymerization behavior with methanol/metal chloride initiating systems can be categorized into three main groups depending on the type of metal chloride used: long-lived species mediated, uncontrolled reaction, and no polymerization. The systems mediated by long-lived species involved an exchange reaction between the methoxy group of methanol and the chloride anion of the metal chloride to generate HCl, the true initiator for the controlled reaction. The propagating reaction was confirmed to proceed only via thus produced C−Cl ends or both acetal bonds and them by MALDI−TOF−MS and ^{1}H NMR studies. With this methanol initiating system, living polymerization using a molybdenum catalyst was achieved for the first time, as a result of moderation of $MoCl_5$ by the exchanged methoxy group. The difference in the polymerization behavior among Lewis acids correlates with the nature of the central metal, especially its oxophilicity and chlorophilicity. This classification is also a novel and useful index for various Lewis acids. Furthermore, since there is no need for troublesome preparation of the conventionally used harmful initiators, the alcohol initiating system will open up an avenue to the industrial use of living cationic polymerization.

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Supporting Information Available: Figures showing time−conversion curves and M_n−conversion plots of polymerization and MALDI−TOF−MS spectra and a table giving some polymerization data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For reviews on living cationic polymerization, see: (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., Eds.; Wiley-VCH GmbH & Co. KGaA: Weinheim, Germany, 2007; Chapter 3. (g) Aoshima, S.; Yoshida, T.; Kanazawa, A.; Kanaoka, S. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1801–1813.

(2) Higashimura, T.; Miyamoto, M.; Sawamoto, M. *Macromolecules* **1985**, *18*, 611–616.

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

(4) Kim, Y. H.; Heitz, T. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 525–533.

(5) Schappacher, M.; Deffieux, A. *Macromolecules* **1991**, *24*, 2140–2142.

(6) Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 3988–3992.

(7) Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1992**, *25*, 2587–2591.

(8) Kanazawa, A.; Kanaoka, S.; Aoshima, S. *Macromolecules* **2009**, *42*, 3965–3972.

(9) Kishimoto, Y.; Aoshima, S.; Higashimura, T. *Macromolecules* **1989**, *22*, 3877–3882.

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

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

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

(13) Guo, Q.; Miyaji, T.; Hara, R.; Shen, B.; Takahashi, T. *Tetrahedron* **2002**, *58*, 7327–7334.

(14) Masuda, T.; Yoshimura, T.; Fujimori, J.; Higashimura, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1805–1806.

(15) Masuda, T.; Mishima, K.; Fujimori, J.; Nishida, M.; Muramatsu, H.; Higashimura, T. *Macromolecules* **1992**, *25*, 1401–1404.

(16) In the following studies, *sec*- or *tert*-alcohols are used as initiators which generate *sec*- or *tert*-carbocation via the abstraction of the OH group for conventional or living cationic polymerization of isobutene or styrenes: (a) Nguyen, H. A.; Kennedy, J. P. *Polym. Bull.* **1981**, *6*, 47–54. (b) Mishra, M. K.; Chen, C. C.; Kennedy, J. P. *Polym. Bull.* **1989**, *22*, 455–462. (c) Chen, C. C.; Kaszas, G.; Puskas, J. E.; Kennedy, J. P. *Polym. Bull.* **1989**, *22*, 463–470. (d) Kaszas, G.; Puskas, J. E.; Chen, C. C.; Kennedy, J. P. *Polym. Bull.* **1988**, *20*, 413–419. (e) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 5405–5410. (f) Satoh, K.; Nakashima, J.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 396–401.

(17) For living cationic polymerization of VE with alcohol/BF_3OEt_2/dimethyl sulfide initiating system, see: Nakatani, K.; Ouchi, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 4194–4201.

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

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

(20) The M_n values of the obtained polymers should agree with those calculated based on the total amount of methanol when all of excess methanol is involved in highly efficient transfer reactions, although the MWDs become broader. The higher M_n values (Table 2, entries 2−4) indicate the low efficiency of transfer reactions. This may stem from the moderate basicity (nucleophilicity) of methanol and/or its much lower concentration than that of IBVE.

(21) Denisov, N. T.; Shuvalova, N. I.; Shuvalov, V. F. *Zh. Fiz. Khim.* **1971**, *45*, 2796–2799.

(22) Funk, H.; Schmeil, F.; Scholz, H. *Z. Anorg. Allg. Chem.* **1961**, *310*, 86–89.

(23) Modec, B.; Brencic, J. *Eur. J. Inorg. Chem.* **2005**, 1698–1709.

(24) Limberg, C.; Parsons, S.; Downs, A. J.; Watkin, D. J. *J. Chem. Soc., Dalton Trans.* **1994**, 1169–1174.

(25) The best way to examine the effect of this methanol modification is to conduct polymerization using isolated complexes such as $MoCl_4(OMe)$ and $MoOCl_3$ in conjunction with HCl as a cationogen. However, the preparation of these Mo species involves tough procedures.[24] Thus, polymerization was examined using IBVE−HCl as a cationogen with a premix of $MoCl_5$ and CH_3OH as a catalyst. With 4.0 or 8.0 mM of IBVE−HCl ($[CH_3OH]_0$ = $[MoCl_5]_0$ = 5.0 mM), the reaction proceeded smoothly to produce polymers with narrow MWDs and M_n values agreeing with those calculated based on the total amount of IBVE−HCl and CH_3OH (Supporting Information; Figure S3). These results support that the roles of CH_3OH are not only to generate protic species but to modify $MoCl_5$ into different forms moderated enough to induce living polymerization.

(26) Other alcohols (e.g., isopropyl alcohol, *tert*-butyl alcohol, ethylene glycol, etc.) also functioned as good cationogens for living polymerization in combination with suitable types of Lewis acids. Typical polymerization results using other alcohols with $ZrCl_4$ ($[IBVE]_0$ = 0.76 M, $[alcohol]_0$ = 5.0 mM, $[ZrCl_4]_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, in toluene at 0 °C) were as follows: with isopropyl alcohol, reaction time = 29 h, conversion = 96%, $M_n = 13.0 \times 10^3$ (calcd: 14.5×10^3), $M_w/M_n = 1.08$; with *tert*-butyl alcohol, reaction time = 53 h, conversion = 88%, $M_n = 13.4 \times 10^3$ (calcd: 13.3×10^3), $M_w/M_n = 1.09$; with ethylene glycol, reaction time = 25 h, conversion = 95%, $M_n = 8.6 \times 10^3$ (calcd: 7.3×10^3; based on the total amount of the hydroxy group), $M_w/M_n = 1.13$. The detailed results will be published in a near future.

(27) Protic impurities such as adventitious water possibly induce initiation reactions, especially in the case using oxophilic Lewis acids like $ZrCl_4$. Such unintended initiation reactions are responsible for slightly lower M_n values compared to the calculated ones (e.g., Figure 3B, circle symbols). The ability of protic impurities as initiating species for controlled polymerization was confirmed by the polymerization using $ZrCl_4$ without any cationogen, which produced polymers with very high M_n values and narrow MWDs.

(28) These cases, which are limited to these two Lewis acids, suggest the effect of the sizes of the metals. Silicon and germanium are small atoms that can coordinate four relatively large chloride anions to form the bulky metal tetrachlorides. Thus, the ligand exchange reaction, which liberates one chloride anion to accept the smaller methoxy group, contributes to diminishing the bulkiness around the central metal. This results in an increase in Lewis acidity, which causes larger polymerization rates.

(29) Since the product polymers have high molecular weights regardless of monomer conversion, it is believed that the activation energy of the production of the carbocation from the acetal by the catalyst is high and that the equilibrium between the dormant and active species is slow. Under such conditions, the carbocation is hard to produce but, once it is produced, reacts with a lot of monomer molecules to give high molecular weight polymers.

(30) Bradley, D. C.; Halim, F. M. Abd-El; Wardlaw, W. *J. Chem. Soc.* **1950**, 3450–3454.

(31) Bradley, D. C.; Halim, F. M. Abd-El; Mehrotra, R. C.; Wardlaw, W. *J. Chem. Soc.* **1952**, 4960–4963.

(32) Perkins, P. G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2599–2602.

(33) Ault, B. S.; Everhart, J. B. *J. Phys. Chem.* **1996**, *100*, 15726–15730.