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Living Cationic Polymerization of Isobutyl Vinyl Ether by Hydrogen Chloride/Lewis Acid Initiating Systems in the Presence of Salts: In-Situ Direct NMR Analysis of the Growing Species[1]

Masami Kamigaito, Yoshihiro Maeda, Mitsuo Sawamoto, and Toshinobu Higashimura*

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606-01, Japan

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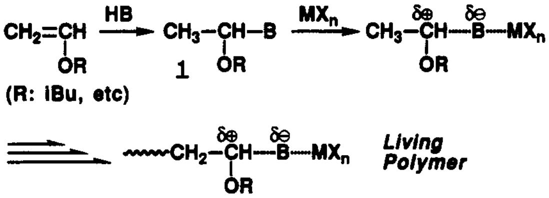
ABSTRACT: Cationic polymerization of isobutyl vinyl ether (IBVE) was carried out with use of the HCl–IBVE adduct [1: $CH_3CH(O\mathit{i}Bu)Cl$]/Lewis acid (MX_n) initiating systems in CH_2Cl_2 at −15 °C. Living polymers were obtained with 1 in conjunction with weak Lewis acids such as $ZnCl_2$ and $SnBr_4$; in contrast, the 1/MX_n initiating systems with strong Lewis acids ($SnCl_4$, $TiCl_4$, and $EtAlCl_2$) gave nonliving polymers. However, on addition of ammonium salts ($\mathit{n}Bu_4N^+Y^-$) and phosphonium salts ($\mathit{n}Bu_4P^+Y^-$) carrying nucleophilic anions ($Y^- = Cl^-, Br^-, I^-, CH_3CO_2^-$), well-defined living polymers were indeed obtained ($\bar{M}_w/\bar{M}_n \sim 1.1$) with the $SnCl_4$-based system. As model reactions of these living and nonliving polymerizations, a series of mixtures of 1 and MX_n in the presence and absence of the salts were analyzed in CH_2Cl_2 at −78 °C or above directly by ^1H NMR spectroscopy. Upon mixing $SnCl_4$ with 1, the α-methine and the pendant methylene absorptions of 1 shifted remarkably downfield (e.g., up to ca. 10 ppm for the former), and the extent of the downfield shifts increased with increasing $SnCl_4$ concentration. On further addition of the salts with nucleophilic anions, the downfield signals returned to the original upfield position for the covalent adduct 1 alone. Thus, 1/$SnCl_4$ generates an ionic growing species that is in a rapid equilibrium with the covalent precursor 1, and the salts suppress the ionic dissociation of the growing carbocation to induce living cationic polymerization.

Introduction

Binary initiating systems that consist of a protonic acid (HB) and a *weak* Lewis acid (MX_n) have been shown to induce living cationic polymerization of vinyl ethers.[2] The typical examples of these HB/MX_n systems are HI/I_2,[3] HI/ZnX_2 (X = I, Br, Cl),[4,5] $RCO_2H/ZnCl_2$,[6] etc. The polymerization proceeds as shown in eq 1: Adduct 1 is formed from a monomer and HB prior to polymerization, and then the C–B bond is activated by MX_n to initiate living propagation. To achieve such living polymerization, the HB/MX_n systems require judicious choice of HB, the anion (B^-) of which should have moderate nucleophilicity, and MX_n with moderate acidity. For example, polymerizations of vinyl ethers with a *strong* Lewis acid such as $EtAlCl_2$ (coupled with CF_3CO_2H, etc., as HB) result in polymers with uncontrolled molecular weights and molecular weight distributions (MWDs).[6,7] These observations indicate that, in addition to the nucleophilicity of B^-, the Lewis acidity of MX_n strongly affects the nature of the growing species.



$$\underset{OR}{CH_2{=}CH} \xrightarrow{HB} \underset{1}{CH_3{-}\underset{OR}{CH}{-}B} \xrightarrow{MX_n} CH_3{-}\underset{OR}{\overset{\delta\oplus}{CH}}\cdots\overset{\delta\ominus}{B}{-}MX_n \qquad (1)$$

(R: iBu, etc)

$$\rightleftharpoons \sim\sim CH_2{-}\underset{OR}{\overset{\delta\oplus}{CH}}\cdots\overset{\delta\ominus}{B}{-}MX_n \quad \text{Living Polymer}$$

Despite the findings of a variety of HB/MX_n initiating systems, it still remains unknown what the nature of the propagating species in living cationic polymerization is (ionic or covalent) and how different living and nonliving growing species are. Recently, several research groups independently studied, spectroscopically and kinetically, the nature of the growing species in the living cationic polymerization and related model reactions.[8–13] Although these studies in common suggested some ionic character of the propagating species, none of them have yet succeeded in detecting ionic and related intermediates by direct spectroscopic analysis.

In this study, therefore, we set two primary objectives: (i) to develop new initiating systems based on strong Lewis acids for living cationic polymerization of vinyl ethers and (ii) to uncover the nature of the growing species therein by direct NMR analysis. In the first part, we investigated living cationic polymerization of isobutyl vinyl ether (IBVE) employing hydrogen chloride (HCl) in conjunction with not only weak ($ZnCl_2$ and $SnBr_4$) but also strong Lewis acids ($EtAlCl_2$, $TiCl_4$, and $SnCl_4$). The polymerizations with a strong Lewis acid turned out to be uncontrolled; however, we found a series of ammonium and phosphonium salts with various anions (e.g., $\mathit{n}Bu_4N^+Y^-$ and $\mathit{n}Bu_4P^+Y^-$; $Y^- = Cl^-, Br^-, I^-, CH_3CO_2^-$) employed along with these initiating systems to permit living cationic polymerization.[1a,14] Similar but limited uses of added salts (mostly $\mathit{n}Bu_4N^+Cl^-$) have been reported for living polymerizations of *p*-methoxystyrene,[14b,15] styrene,[16] isobutylene,[17] and isobutyl vinyl ether.[1a,18] The second part of this study concerned in-situ NMR analysis of model reactions for these living processes based on strong Lewis acids (HCl/$SnCl_4$ system, etc.) and the added onium salts. The use of the strong Lewis acid allowed us to directly observe the generation of carbocationic species and to understand the role of the added salts in attaining living polymerization.

Results and Discussion

1. Living Cationic Polymerization. (a) Polymerization with HCl–IBVE Adduct (1)/Lewis Acid (MX_n).

IBVE was polymerized with 1, which was synthesized by addition of dry HCl gas to IBVE, in conjunction with a variety of Lewis acids (MX_n) in CH_2Cl_2 at −15 °C. As shown in Figure 1, the initiating systems based on strong Lewis acids, ethyl aluminum dichloride ($EtAlCl_2$), titanium tetrachloride ($TiCl_4$), and tin tetrachloride ($SnCl_4$), induced almost instantaneous, extremely rapid polymer-

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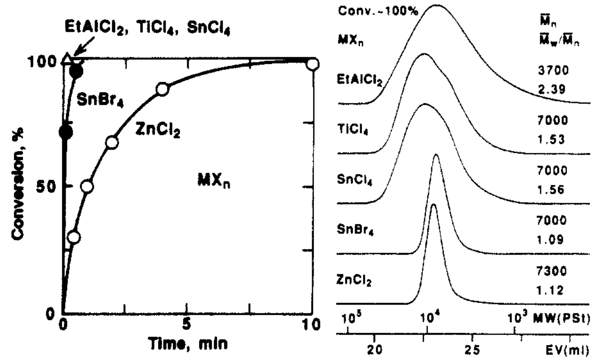


Figure 1. Time–conversion curves for the polymerization of IBVE with 1/MX$_n$ in CH_2Cl_2 at -15 °C and MWD curves of poly(IBVE): $[M]_0 = 0.38$ M; $[1]_0 = 5.0$ mM; $[MX_n]_0 = 2.0$ mM. MX$_n$: $EtAlCl_2$, $TiCl_4$, $SnCl_4$ (△); $SnBr_4$ (●); $ZnCl_2$ (○).

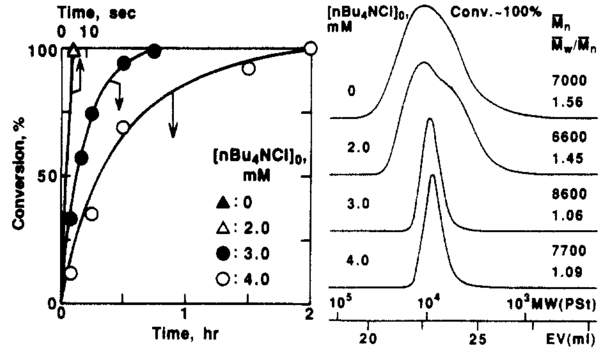


Figure 2. Effects of added nBu_4NCl on IBVE polymerization with 1/$SnCl_4$ in CH_2Cl_2 at -15 °C: $[M]_0 = 0.38$ M; $[1]_0 = 5.0$ mM; $[SnCl_4]_0 = 2.0$ mM: $[nBu_4NCl]_0 = 0$ (▲), 2.0 (△), 3.0 (●), 4.0 (○) mM.

izations. With weak Lewis acids, tin tetrabromide ($SnBr_4$) and zinc chloride ($ZnCl_2$), slower but efficient polymerizations occurred. The overall polymerization rate apparently followed the empirical order of the Lewis acidity of the five metal halides.

The polymers obtained with the three strong Lewis acids had broad MWDs, and these polymerizations were not living. In contrast, the 1/$ZnCl_2$ system gave living polymers with narrow MWDs ($\bar{M}_w/\bar{M}_n \sim 1.1$) in CH_2Cl_2 like the reported living systems with IBVE/1/$ZnCl_2$ in toluene[13] and 2-chloroethyl vinyl ether (CEVE)/HCl–CEVE adduct/$ZnCl_2$ in CH_2Cl_2.[9] As indicated by the narrow MWD shown in Figure 1, the 1/$SnBr_4$ system also led to living cationic polymerization of IBVE where the number-average molecular weight ($\bar{M}_n$) of the polymers were in direct proportion to IBVE conversion. This is the first example of living cationic polymerization of vinyl ethers with an $SnBr_4$-based system.

(b) Polymerization with Strong Lewis Acids in the Presence of nBu_4NCl. The IBVE polymerizations with strong Lewis acids proved to be nonliving, and thus we herein examined polymerizations in the presence of nBu_4NCl at varying concentrations.

First, the $SnCl_4$-based systems were investigated (Figure 2). With use of nBu_4NCl equimolar to $SnCl_4$ or below, an almost instantaneous polymerization proceeded as in the absence of the salt, and the MWDs of the polymers still remained broad. However, addition of increasing amounts of nBu_4NCl drastically retarded the polymerization, and in parallel with this, the MWDs of the polymers became progressively narrower ($\bar{M}_w/\bar{M}_n < 1.1$). This suggests that living cationic polymerization of vinyl ethers is indeed feasible even with use of a strong Lewis acid ($SnCl_4$) in the presence of an added salt (nBu_4NCl).

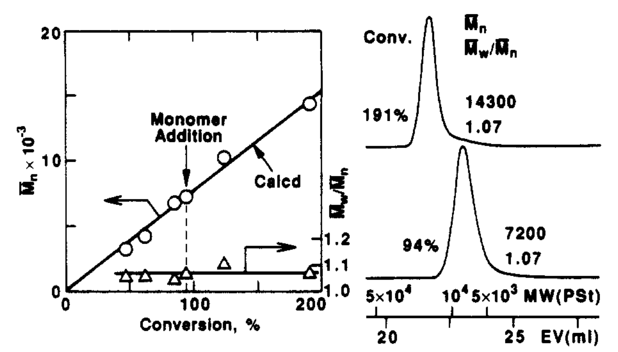


Figure 3. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(IBVE) obtained in a monomer-addition experiment in the polymerization with 1/$SnCl_4$/nBu_4NCl in CH_2Cl_2 at -15 °C: $[M]_0 = [M]_{add} = 0.38$ M; $[1]_0 = 5.0$ mM; $[SnCl_4]_0 = 2.0$ mM; $[nBu_4NCl]_0 = 4.0$ mM. The "Calcd" solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per 1 molecule.

Table I
Polymerization of IBVE 1/MX$_n$/nBu_4NCl[a]

MX$_n$	$[nBu_4NCl]_0$, mM	time	conv, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
$TiCl_4$	0	10 s	100	7000	1.53
	1.0	1 min	100	7300	1.24
	1.5	5 min	45	4800	1.07
		30 min	75	5900	1.07
		2 h	89	7100	1.06
	2.0	28 days	89	6600	1.06
	4.0	1 day	0		
$EtAlCl_2$	0	10 s	100	3700	2.39
	1.5	5 min	23	28300	1.72
		30 min	90	27100	1.82
		1 h	97	24600	1.84
	4.0	2 days	0		

[a] $[M]_0 = 0.38$ M; $[1]_0 = 5.0$ mM; $[MX_n]_0 = 2.0$ mM; in CH_2Cl_2, at -15 °C.

The living nature was further demonstrated by "monomer-addition" experiments where a fresh feed of monomer was added to the reaction mixture just before the initial charge of the monomer had been consumed. The added monomer feed was smoothly polymerized at nearly the same rate as in the first stage. As shown in Figure 3, before and after the monomer addition, the $\bar{M}_n$ of the polymers increased in direct proportion to monomer conversion and agreed with the calculated values assuming that one polymer chain forms per 1 molecule. The $\bar{M}_n$ depended on the concentration of neither $SnCl_4$ nor nBu_4NCl. The MWDs stayed very narrow throughout the reactions ($\bar{M}_w/\bar{M}_n < 1.1$).

The polymerization with use of the salt also led to living polymers with high molecular weights. For example, at $[M]_0/[1]_0/[SnCl_4]_0/[nBu_4NCl]_0 = 2500/2.5/2.0/3.0$ mM, the polymerization in CH_2Cl_2 at -15 °C occurred smoothly and completely in 2 h to give polymers with $\bar{M}_n$ of 94 800 and a narrow MWD ($\bar{M}_w/\bar{M}_n = 1.10$). The $\bar{M}_n$ value was in good agreement with the calculated value (100 000) by the $[M]_0/[1]_0$ ratio (or $\overline{DP}_n = 1000$).

Polymerizations with the other strong Lewis acids were also carried out in the presence of nBu_4NCl. As summarized in Table I, the 1/$TiCl_4$ system (5.0/2.0 mM) gave living polymers with narrow MWDs ($\bar{M}_w/\bar{M}_n < 1.1$) in the presence of nBu_4NCl (1.5 mM), where a quantity of the salt required to generate living polymers is smaller than that in the polymerization by 1/$SnCl_4$. At higher concentrations of nBu_4NCl, polymerizations were extremely retarded. The polymerization with the $EtAlCl_2$-based system was also retarded on addition of nBu_4NCl (1.5 mM); however, the $\bar{M}_n$ values were larger than the calculated values, and the MWDs were broad. Further addition of

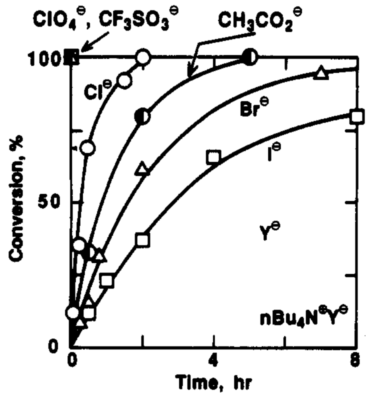


Figure 4. Time–conversion curves for the polymerization of IBVE with 1/SnCl$_4$/nBu$_4$NY in CH$_2$Cl$_2$ at −15 °C: $[M]_0 = 0.38$ M; $[1]_0 = 5.0$ mM; $[SnCl_4]_0 = 2.0$ mM; $[nBu_4NY]_0 = 4.0$ mM. Y$^-$ = ClO$_4^-$ (▲); CF$_3$SO$_3^-$ (◧); I$^-$ (□); Br$^-$ (△); Cl$^-$ (○); CH$_3$CO$_2^-$ (◐).

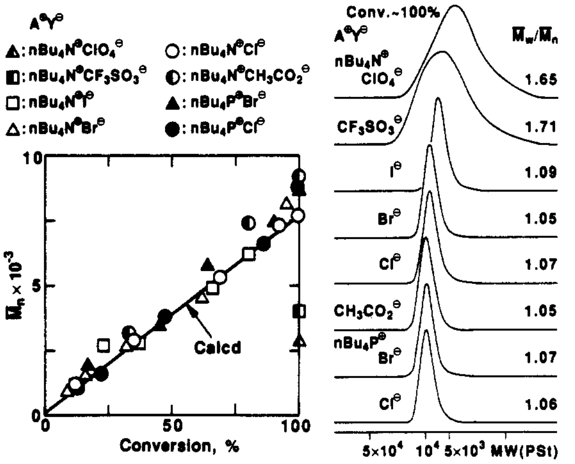


Figure 5. $\bar{M}_n$ and MWD curves of poly(IBVE) obtained with 1/SnCl$_4$/A$^+$Y$^-$ in CH$_2$Cl$_2$ at −15 °C: $[M]_0 = 0.38$ M; $[1]_0 = 5.0$ mM; $[SnCl_4]_0 = 2.0$ mM; $[A^+Y^-]_0 = 4.0$ mM. A$^+$Y$^-$: for A$^+$ = nBu$_4$N$^+$, ClO$_4^-$ (▲), CF$_3$SO$_3^-$ (◧), I$^-$ (□), Br$^-$ (△), Cl$^-$ (○), CH$_3$CO$_2^-$ (◐); for A$^+$ = nBu$_4$P$^+$, Br$^-$ (▲), Cl$^-$ (●). The "Calcd" solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per 1 molecule.

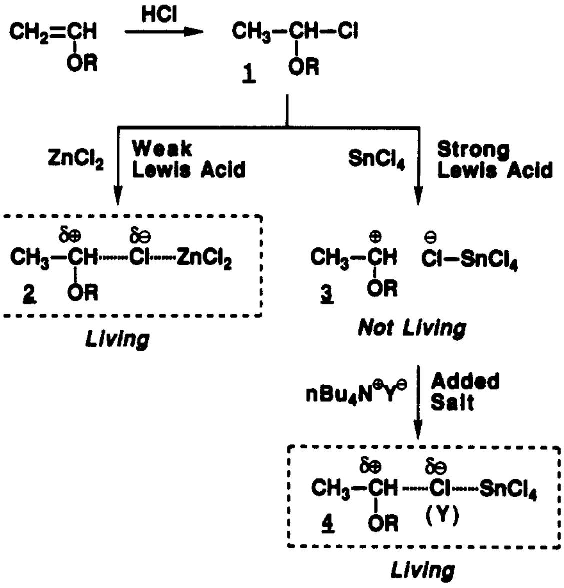
nBu$_4$NCl extremely retarded the reaction. Thus, 1/EtAlCl$_2$ failed to give living polymers even in the presence of nBu$_4$NCl. This point should be investigated further.[19]

(c) Polymerization with SnCl$_4$ in the Presence of Various Salts. In order to clarify what types of salts are suited for living cationic polymerization, the IBVE polymerization with 1/SnCl$_4$ was investigated in the presence of various salts (A$^+$Y$^-$) that carry anions with varying nucleophilicity.

As shown in Figure 4, added ammonium salts with nucleophilic anions (Cl$^-$, Br$^-$, I$^-$, and CH$_3$CO$_2^-$) drastically retarded the polymerization. In contrast, such an effect was not observed for salts with less nucleophilic anions (ClO$_4^-$ and CF$_3$SO$_3^-$).[20]

In parallel with these observations, polymers obtained in the presence of nBu$_4$NClO$_4$ and nBu$_4$NOSO$_2$CF$_3$ had broad MWDs (Figure 5) analogous to those obtained in the absence of salts (cf. Figure 1). In sharp contrast, the systems with nucleophilic anions invariably gave polymers with narrow MWDs ($\bar{M}_w/\bar{M}_n < 1.1$) (Figure 5). Furthermore, phosphonium chloride and bromide (nBu$_4$PCl and nBu$_4$PBr) gave polymers with narrow MWDs as did the corresponding ammonium salts. The $\bar{M}_n$ values of the polymers obtained in the presence of these nucleophilic anions were directly proportional to monomer conversion and in good agreement with the calculated values assuming that one molecule of 1 generates one living polymer chain.

Scheme I



These results indicate that not only the chloride anion (Cl$^-$), which is the so-called "common ion" for the HCl-based initiating systems like 1/SnCl$_4$, but also other nucleophilic anions (Br$^-$, I$^-$, and CH$_3$CO$_2^-$) are effective in converting the originally uncontrolled polymerization with 1/SnCl$_4$ into living. Scheme I illustrates such an effect of the added salt in comparison with the 1/ZnCl$_2$ system. It is proposed that, because of its strong Lewis acidity, SnCl$_4$ generates a binary counteranion $^-$Cl···SnCl$_4$, which is too weakly nucleophilic to stabilize the growing carbocation but instead leads to highly dissociated and nonliving species like 3. The added salt may convert 3 into a nondissociated and living species 4. In this regard, the species 4 may be similar in nature to the living species 2 derived from 1/ZnCl$_2$.

The conversion of 3 into 4 is due to the suppression of the dissociation through supplying the nucleophilic anions and/or due to a decrease of the Lewis acidity (or concentration) of SnCl$_4$ by complexation of the nucleophilic anions. It has quite recently been reported that, in the living polymerization of styrene with CH$_3$CH(Ph)Cl/SnCl$_4$/nBu$_4$NCl, nBu$_4$N$^+$Cl$^-$ reacts with SnCl$_4$ to give nBu$_4$N$^+$SnCl$_5^-$, and the generated tin pentachloride anion (SnCl$_5^-$) acts as a weak Lewis acid activator.[21] Another research group has also quite recently shown that 1/nBu$_4$N$^+$TiCl$_5^-$ induces living cationic polymerization of IBVE,[18] though it is not clarified yet whether nBu$_4$N$^+$TiCl$_5^-$ acts as a weak Lewis acid activator or as a strong dipole like nBu$_4$N$^+$ClO$_4^-$, which leads to living polymerization of IBVE in the presence of hydrogen iodide (HI) but without any Lewis acid.[22] Obviously, it awaits for further clarification how the added salts act in achieving living cationic polymerization.

2. ^{1}H NMR Analysis. To clarify the nature of the growing species in the 1/MX$_n$-initiated polymerization in the absence and presence of added salts, the interaction of 1 with MX$_n$ and the salts was directly monitored by ^{1}H NMR spectroscopy. To this end, we carried out model reactions in which adduct 1 was employed as the simplest model of the polymer terminal that would be generated from the 1/MX$_n$ initiating systems.

(a) Salt-Free System: Generation of Carbocations from Covalent Precursor 1. Figure 6 shows the ^{1}H NMR spectra of mixtures of 1 and SnCl$_4$ in CD$_2$Cl$_2$ at −78 °C, where the concentration of 1 was constant but that of SnCl$_4$ was varied. As shown in Figure 6A, the methine

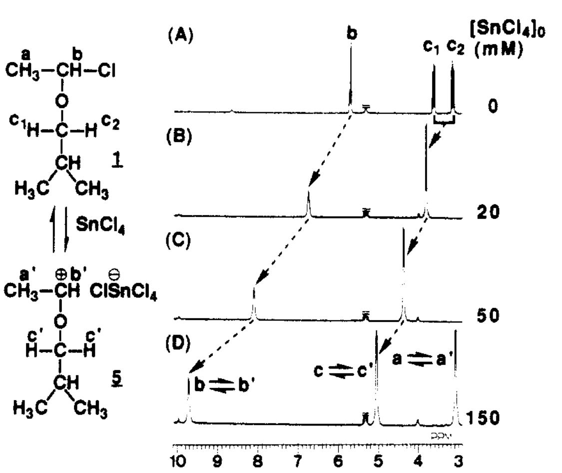


Figure 6. ^{1}H NMR spectra of the mixture of $1/SnCl_4$ in CD_2Cl_2/*n*-hexane (9/1) at −78 °C with varying $SnCl_4$ concentration: $[1]_0$ = 100 mM. $[SnCl_4]_0$ = 0 (A), 20 (B), 50 (C), 150 (D) mM.

proton b of 1, which is adjacent to the chlorine, absorbs at 5.7 ppm as a sharp quartet. The two methylene protons c_1 and c_2 ($-OCH_2-$) of the isobutyl group are diastereotopic due to the chiral α-carbon and give a pair of resonances.[11,13,23] On addition of $SnCl_4$, the α-methine proton b clearly shifted downfield and broadened (Figure 6B). Along with this change, the two methylene resonances coalesced into a single sharp doublet that is also downfield-shifted. Equally important, with increasing concentration of $SnCl_4$ (Figures 6C and 6D), the signals remarkably shifted downfield further; in particular, the methine proton b absorbs downfield at 9.7 ppm with an excess amount of $SnCl_4$ present. The downfield shifts of these absorptions evidently indicate the generation of an ionic species 5 that is in a fast equilibrium with the covalent species 1. The progressive downfield shift of the methine peak further indicates an increase in the concentration of the ionic species along with an increase of the $SnCl_4$ concentration. The coalescence of the diastereotopic methylene protons shows the loss of the diastereotopicity through racemization of 1, which also suggests the generation of an ionic species that mediates the interconversion of the two diastereomers.[23]

Thus, the use of $SnCl_4$ as an activator provided perhaps the first spectroscopic direct evidence for the generation of a carbocationic intermediate from a covalent precursor 1 through interaction with a strong Lewis acid, $SnCl_4$, under the conditions mimicking cationic polymerization.[24,25] Importantly, under these conditions, the IBVE polymerization with $1/SnCl_4$ is not living.

The other $1/MX_n$ systems (without added salts) were also analyzed by ^{1}H NMR (Figure 7). On mixing 1 with strong Lewis acids [$EtAlCl_2$ and $TiCl_4$ (parts B and C of Figure 7, respectively)] other than $SnCl_4$, the methine proton b shifted downfield and broadened analogously to the $SnCl_4$-based system, though the extent of the downfield shift depended on the type of the Lewis acids. This fact indicates that 1 interacts with strong Lewis acids to give the ionic species 5. The extent of the downfield shift may be related to not only the Lewis acidity but also the radius of the central atoms of the metal halides (Al < Ti < Sn). Interestingly, these three systems all failed to give living polymers (cf. Figure 1).

In contrast, upon mixing 1 with $SnBr_4$ and $ZnCl_2$ (parts E and F of Figure 7, respectively), none of such downfield shifts were observed.[26] However, the split signals of the methylene protons c_1 and c_2 coalesced into a single and slightly broadened peak with use of $SnBr_4$, and with $ZnCl_2$ the two signals did not coalesce but indeed broadened.[27]

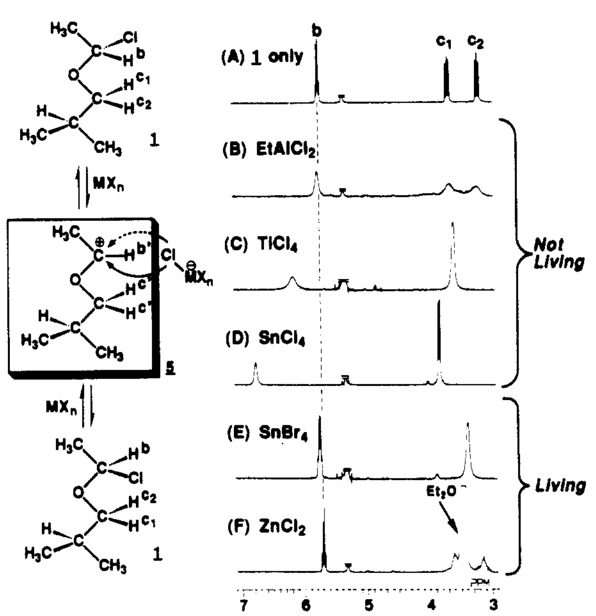


Figure 7. ^{1}H NMR spectra of 1 (A), the mixture of $1/MX_n$ in CD_2Cl_2/*n*-hexane (9/1) at −78 °C: $[1]_0$ = 100 mM; $[MX_n]_0$ = 20 mM. MX_n: $EtAlCl_2$ (B), $TiCl_4$ (C), $SnCl_4$ (D), $SnBr_4$ (E), $ZnCl_2$ (F). Only for $ZnCl_2$: in CD_2Cl_2/*n*-hexane/Et_2O (8/1/1).

In both cases, they did not shift downfield at all. These observations show that the diastereotopicity is lost via an ionic intermediate that enables inversion of configuration,[28] but the concentration of the ionic species is so low that the chemical shifts do not change. The observed difference in the instantaneous concentration of ionic species as a function of Lewis acids should be related to the living nature of the corresponding polymerizations, as will be discussed later.

At present, it cannot be concluded whether or not the ionic intermediate derived from a weak Lewis acid is different from that derived from a strong Lewis acid. However, it was at least demonstrated that the time-averaged concentration of activated ionic species is very low where living cationic polymerization occurs. Namely, the period where the dormant species 1 is activated by a weak Lewis acid, which induces living cationic polymerization of IBVE without additives, is much shorter than that by a strong Lewis acid which gives nonliving polymers.

(b) Effects of Added *n*Bu_4NCl: Suppression of the Ionic Species. Mixtures of 1 with $SnCl_4$ at varying concentrations of *n*Bu_4NCl were then analyzed in a similar way (Figure 8). On addition of a small amount of *n*Bu_4NCl (10 mM) to a mixture of $1/SnCl_4$ (100/20 mM), the downfield-shifted methine proton at 6.8 ppm (Figure 8B) moved upfield to 6.3 ppm (Figure 8C), which, however, was still downfield-shifted in comparison to that for the adduct 1 alone (Figure 8A). This shows that *n*Bu_4NCl suppresses the ionic dissociation of the growing species and thereby decreases the concentration of ionic species, which is, however, still high enough to be observable by ^{1}H NMR spectroscopy. Under these particular conditions ($[SnCl_4] \geq [n\text{Bu}_4\text{NCl}]$), the polymerization was not living yet (cf. Figure 2).

Upon further addition of *n*Bu_4NCl (Figures 8D), under which conditions living cationic polymerization occurred (Figure 2–5), the methine signal b returned to the original upfield position for the covalent adduct 1 alone. Namely, the equilibrium was far shifted to the covalent species.[29] The methylene peak also shifted upfield and now split into the original two signals; however, they were clearly broader than the corresponding peak of 1. The broadening shows the occurrence of racemization of diastereomeric 1

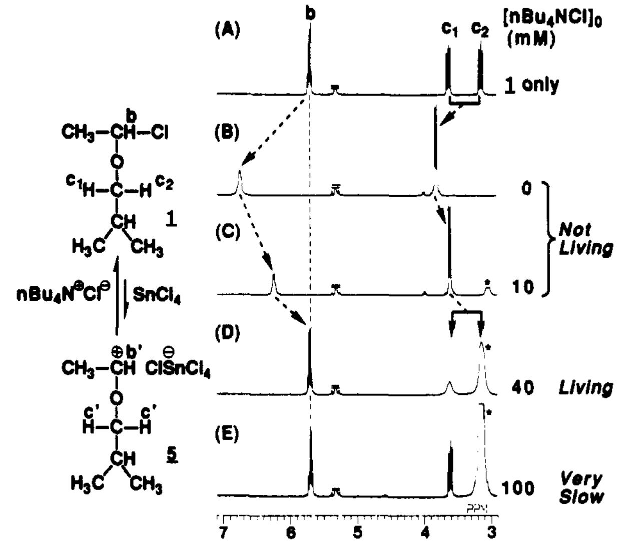


Figure 8. ^{1}H NMR spectra of 1 (A), the mixture of 1/MX_n/nBu$_4$NCl in CD_2Cl_2/n-hexane (9/1) at −78 °C with varying nBu$_4$NCl concentration: $[1]_0$ = 100 mM; $[SnCl_4]_0$ = 20 mM. $[n\mathrm{Bu_4NCl}]_0$ = 0 (B), 10 (C), 40 (D), 100 (E) mM. The signals marked with an asterisk: $(CH_3CH_2CH_2CH^*_2)_4NCl$.

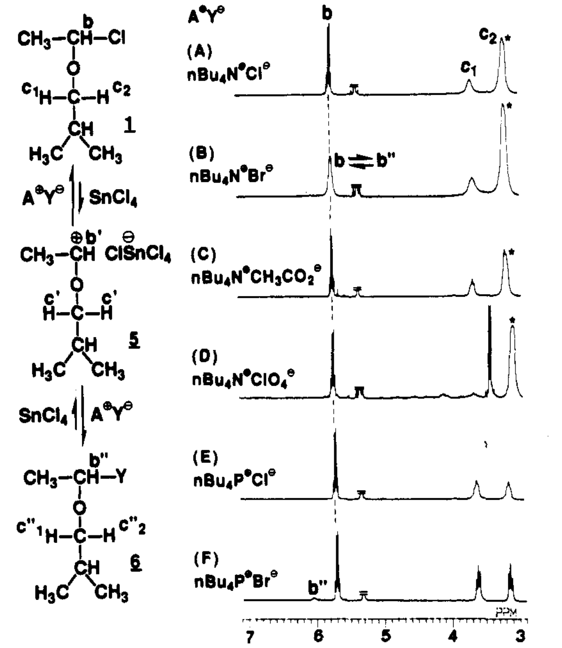


Figure 9. ^{1}H NMR spectra of the mixture of 1/MX_n/A^+Y^- in CD_2Cl_2/n-hexane (9/1) at −78 °C: $[1]_0$ = 100 mM; $[SnCl_4]_0$ = 20 mM; $[A^+Y^-]_0$ = 40 mM. A^+Y^- = $n\mathrm{Bu_4N^+Cl^-}$ (A), $n\mathrm{Bu_4N^+Br^-}$ (B), $n\mathrm{Bu_4N^+CH_3CO_2^-}$ (C), $n\mathrm{Bu_4N^+ClO_4^-}$ (D), $n\mathrm{Bu_4P^+Cl^-}$ (E), $n\mathrm{Bu_4P^+Br^-}$ (F). The signals marked with an asterisk: $(CH_3CH_2CH_2CH^*_2)_4NY$.

via the ionic species 5. These observations in the presence of excess nBu$_4$NCl are strikingly similar to those in another living system with 1 and a weak Lewis acid, $ZnCl_2$ (cf. Figure 7F), and all these systems can be characterized by a very low concentration of ionic growing species.

With use of higher concentration of nBu$_4$NCl (Figure 8E), the methylene peaks are almost the same as those for adduct 1 alone. This indicates the very slow racemization of 1. Along with this, the polymerization rate is very small at this nBu$_4$NCl/$SnCl_4$ ratio.

(c) Effects of Other Added Salts. Figure 9 shows spectra of mixtures of 1, $SnCl_4$, and various salts. In all cases, the methine proton b absorbed at 5.7 ppm, the same chemical shift for the adduct 1 alone; thus all these ammonium and phosphonium salts suppressed the ionic dissociation as did nBu$_4$NCl.

In the presence of nBu$_4$NBr (Figure 9B), the methine proton b of 1 slightly broadened, and in the presence of nBu$_4$PBr (Figure 9F), a small signal appeared at 6.1 ppm, which is a characteristic absorption of the methine proton b'' of HBr–IBVE adduct 6.[13] Thus, the addition of the bromide anion led to conversion of a small portion of 1 into 6 via the ionic species 5. Such a halogen exchange was not observed with 1/nBu$_4$NBr in the absence of $SnCl_4$.

It is surprising that the spectrum for nBu$_4$NClO$_4$ (Figure 9D) is very similar to those for the salts with halogen anions, and the dissociation of the ionic species 5 is seemingly suppressed even in the presence of nBu$_4$NClO$_4$, which did not lead to living polymerization (cf. Figure 5). This perchlorate-based system, however, apparently differs from the others, as indicated by the coalescence of the diastereotopic methylene protons into a sharp doublet which was absent with the other salts (see also the next section). The sharp doublet indicates an extremely rapid exchange between methylene protons c_1 and c_2 through the ionic species; note that, with the other salts, the methylene signals still split, indicative of slower exchange processes. The system with nBu$_4$NClO$_4$ should be further studied.

(d) Effects of Temperature: Rapid Shuffling of Diastereomers. All the spectra have been recorded at −78 °C thus far. Subsequent analysis at varying temperature revealed that the spectrum of 1 alone did not change in the range of −90 to 0 °C. In contrast, when 1 was mixed with $SnCl_4$, the chemical shifts of the methine (b) and the methylene (c) signals varied with temperature, as shown in Figure 10A; the absorptions were more downfield-shifted at lower temperature. This means that the ionic dissociation of 1 assisted by $SnCl_4$ is more favorable at lower temperature, where the polarity (dielectric constant) of the solvent (CH_2Cl_2) increases.[30] The spectrum at −15 °C also demonstrates the generation of the ionic species under the conditions where the polymerization was carried out (cf. Figure 1). At 0 °C, the spectrum became complicated, which indicates decomposition of 1 due to its instability in the presence of a strong Lewis acid, $SnCl_4$.

Parts B and C of Figure 10 show the spectra with 1/$SnCl_4$/nBu$_4$NCl and 1/$SnCl_4$/nBu$_4$PCl, respectively, taken at varying temperatures. The methine proton b invariable absorbed at 5.7 ppm. Thus, the ionic dissociation was suppressed not only at −78 °C but also at −15 °C, where the living polymerization occurs. At higher temperature, the methylene signals (c_1 and c_2), which clearly split at −90 °C, became broader and finally coalesced. Such a change with temperature was more clearly observed with use of nBu$_4$PCl (Figure 10C), whose methylene signals $[(CH_3CH_2CH_2CH_2)_4PCl]$, unlike those of nBu$_4$NCl, did not overlap with the methylene peaks of 1. These observations indicate that the racemization of 1 (or the exchange between protons c_1 and c_2) occurs more frequently at higher temperature and that the propagating species derived from 1/$SnCl_4$/nBu$_4$NCl is stable even at 0 °C. The similar changes of spectra with temperature were observed in the systems with the other nucleophilic anions such as Br^- and $CH_3CO_2^-$.

The spectra of a 1/$SnCl_4$/nBu$_4$NClO$_4$ mixture (Figure 10D) were almost unchanged with temperature in the range of −90 to −40 °C, but side reactions clearly occurred at 0 °C as in the system without an added salt (cf. Figure 10A). This indicates the instability of the propagating species derived from 1/$SnCl_4$/nBu$_4$NClO$_4$, another difference from the systems with other salts like nBu$_4$NCl.

3. Conclusions. The direct NMR analysis of the model reactions has demonstrated the following: (1) a carbocat-

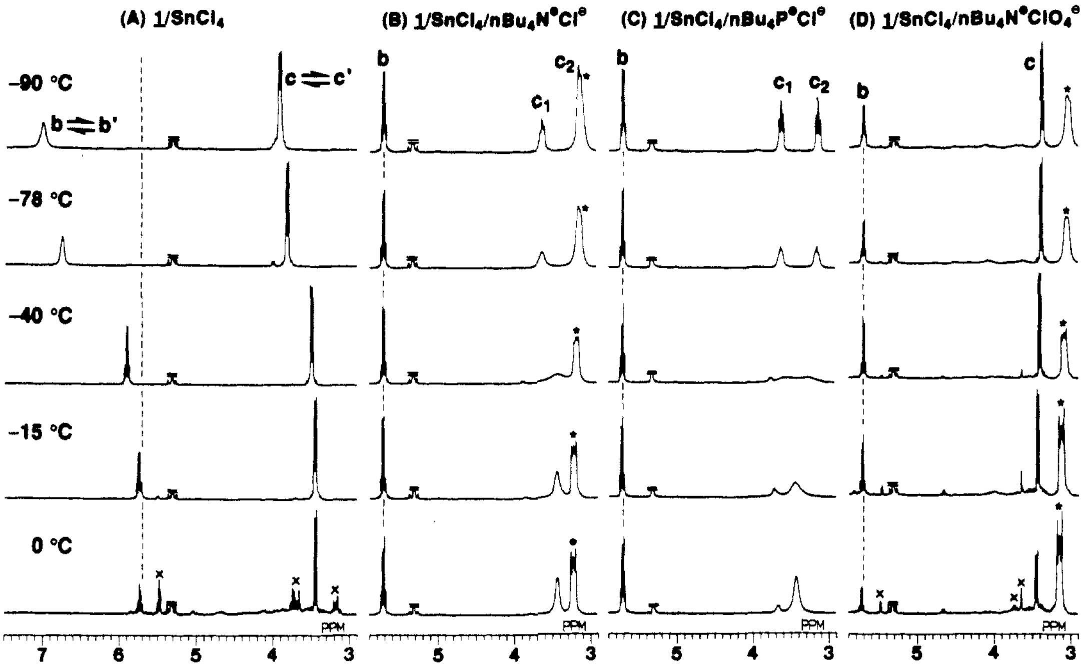
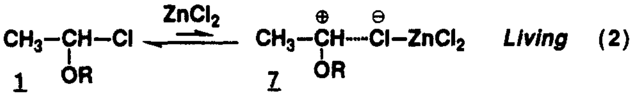


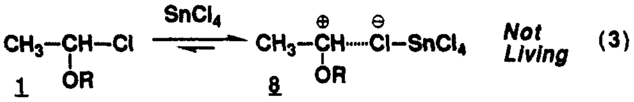
Figure 10. ^{1}H NMR spectra at varying temperature (from -90 to 0 °C) in CD_2Cl_2/n-hexane (9/1): $[1]_0 = 100$ mM; $[SnCl_4]_0 = 20$ mM; $[A^+Y^-]_0 = 40$ mM. 1/$SnCl_4$ (A); 1/$SnCl_4$/$n$$Bu_4N^+Cl^-$ (B); 1/$SnCl_4$/$n$$Bu_4P^+Cl^-$ (C); 1/$SnCl_4$/$n$$Bu_4N^+ClO_4^-$ (D). The signals marked with an asterisk: $(CH_3CH_2CH_2CH^*_2)_4NY$.

ionic species (5; Figure 6) is indeed generated from the covalent precursor 1 through the assistance of a Lewis acid under the conditions that simulate cationic polymerization; (2) the ionic species is in a fast equilibrium with the covalent counterpart 1; (3) the concentration of the ionic intermediate sharply decreases in the presence of the added salts; and (4) such a suppression is critical in achieving the living polymerization with the 1/$SnCl_4$ and 1/$TiCl_4$ initiating systems.

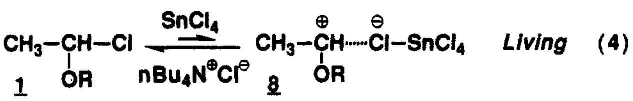
The results obtained from ^{1}H NMR analysis and polymerization were summarized in eqs 2–4. When adduct 1 is



$$\underset{\mathbf{1}}{CH_3-\underset{OR}{\underset{|}{CH}}-Cl} \underset{}{\overset{ZnCl_2}{\rightleftharpoons}} \underset{\mathbf{7}}{CH_3-\underset{OR}{\underset{|}{\overset{\oplus}{CH}}}\cdots\overset{\ominus}{Cl}-ZnCl_2} \quad \textit{Living} \qquad (2)$$



$$\underset{\mathbf{1}}{CH_3-\underset{OR}{\underset{|}{CH}}-Cl} \overset{SnCl_4}{\rightleftharpoons} \underset{\mathbf{8}}{CH_3-\underset{OR}{\underset{|}{\overset{\oplus}{CH}}}\cdots\overset{\ominus}{Cl}-SnCl_4} \quad \textit{Not Living} \qquad (3)$$



$$\underset{\mathbf{1}}{CH_3-\underset{OR}{\underset{|}{CH}}-Cl} \underset{nBu_4N^{\oplus}Cl^{\ominus}}{\overset{SnCl_4}{\rightleftharpoons}} \underset{\mathbf{8}}{CH_3-\underset{OR}{\underset{|}{\overset{\oplus}{CH}}}\cdots\overset{\ominus}{Cl}-SnCl_4} \quad \textit{Living} \qquad (4)$$

activated by a weak Lewis acid such as $ZnCl_2$, where living cationic polymerization occurs without additives, the ratio of the activated ionic species 7 to the covalent species 1 is very low; the equilibrium is shifted far to the covalent side (eq 2). In contrast, in conjunction with a strong Lewis acid, $SnCl_4$, where polymerization is not living, the ratio of ionic species 8 to 1 is relatively high (eq 3). Upon addition of $n$$Bu_4NCl$, where living polymerization indeed occurs, the ionic dissociation is suppressed, and the equilibrium is shifted to the covalent side (eq 4). Thus, eq 4 is comparable to eq 2. If we take a symbolism $\sim\sim\sim C^{\delta+}\cdots Cl^{\delta-}\cdots MX_n$ to represent a rapidly exchanging growing species where the concentration of the ionic species is very low, eqs 2–4 are probably summarized as Scheme I. It should be clarified, however, whether the "stabilization of the unstable carbocation"[2,8] is via an actual thermodynamic stabilization through an interaction with a binary nucleophilic counteranion $Cl^-\cdots MX_n$ during the activated period or via an "apparent" or "dynamic" stabilization by decreasing the concentration of the unstable ionic species.

Experimental Section

Materials. $SnCl_4$ (Wako Chemicals; purity >97%) was distilled under reduced pressure over phosphorus pentoxide. $TiCl_4$, $SnBr_4$, and $ZnCl_2$ (all Aldrich; 1.0 M solution in methylene chloride for $TiCl_4$ and $SnBr_4$ or in diethyl ether for $ZnCl_2$) and $EtAlCl_2$ (Kanto Chemicals; 0.95 M solution in n-hexane) were commercially supplied as solutions. $n$$Bu_4NCl$, $n$$Bu_4NBr$, $n$$Bu_4NI$, and $n$$Bu_4NClO_4$ (Tokyo Kasei; purity >98%) and $n$$Bu_4NOCOCH_3$, $n$$Bu_4NOSO_2CF_3$, $n$$Bu_4PCl$, and $n$$Bu_4PBr$ (Aldrich; purity 98%, 99%, 96%, and 98%, respectively) were all used as received. They were vacuum dried at least overnight just before use and dissolved in dry and distilled methylene chloride in a nitrogen-filled drybox. IBVE (Tokyo Kasei; purity >99%) was washed with 10% aqueous sodium hydroxide and then with water, dried overnight over potassium hydroxide (pellets), and distilled twice over calcium hydride before use. Deuterated methylene chloride (CD_2Cl_2) (Aldrich; 99.6 atom % D) was used as received. CH_2Cl_2 and n-hexane (solvents) and carbon tetrachloride (an internal standard for gas chromatography) were purified by the usual methods and distilled twice over calcium hydride before use.[3] Diethyl ether (Dojin; purity >99%, anhydrous) for $ZnCl_2$ solvent was distilled in the presence of $LiAlH_4$ before use.

Polymerization Procedures. Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. The reaction was initiated by sequential addition of prechilled solutions of 1 (in n-hexane; 0.50 mL) and MX_n (in CH_2Cl_2 or diethyl ether only for $ZnCl_2$; 0.50 mL) via dry syringes into a monomer solution (in CH_2Cl_2; 4.0 mL) containing IBVE (0.25 mL) and CCl_4 (0.25 mL). For polymerizations in the presence of a salt, it was dissolved in MX_n solution prior to addition. After predetermined intervals, the polymerization was terminated with prechilled methanol (2.0 mL) containing a small amount of ammonia. Monomer conversion was determined from its residual concentration measured by gas chromatography with CCl_4 as an internal standard. The polymer yield by gravimetry was in good agreement with the gas-chromatographic conversion of the monomer.

The quenched reaction mixture was washed with dilute hydrochloric acid, aqueous sodium hydroxide solution, and then water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum dried to give the product polymers.

The MWD of the polymers was measured by size-exclusion chromatography in chloroform at room temperature on a Jasco Trirotar-V chromatograph equipped with three polystyrene gel columns (Shodex K-802, K-803, and K-804). The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of the polymers were calculated from size-exclusion eluograms on the basis of a polystyrene calibration.

Synthesis of HCl–IBVE Adduct (1). The HCl–IBVE adduct 1 was synthesized by bubbling dry HCl gas through a solution of IBVE (in *n*-hexane; 1.00 M) at 0 °C. The gas was generated by dropping concentrated sulfuric acid into powdery sodium chloride and dried by passing it through a column packed with calcium chloride. After 30 min, the excess HCl in the reaction mixture was removed by bubbling dry nitrogen gas, and the clean and quantitative formation of adduct 1 was confirmed by ^{1}H NMR spectroscopy. The concentration of 1 was determined by titrating the chloride by the Volhard method;[13] the observed value (1.06 M) further confirmed the quantitative formation of 1 from IBVE.

^{1}H NMR Spectroscopy and Model Reactions. ^{1}H NMR spectra were recorded on a JEOL JNM-GSX270 spectrometer, operating at 270.2 MHz (CD_2Cl_2 for locking). The main parameters were as follows: spectral width = 6002.4 Hz (22.22 ppm), pulse width = 4.3 μs (45°), acquisition time + pulse delay = 30 s, data points = 32 768, number of transients = 8 (4 min for one spectrum). The probe temperature was regulated with a variable-temperature apparatus JEOL NM-GVT3 (temperature fluctuation ≤ 1 °C). The reaction was started by adding a solution of MX_n (in CD_2Cl_2; 0.06 mL) to a prechilled solution of 1 (in CD_2Cl_2/*n*-hexane = 8/1; 0.54 mL) in a septum-capped NMR tube (5-mm o.d.) under dry nitrogen via dry syringes at −78 °C. For the reaction in the presence of a salt, it was dissolved in the solution of 1 prior to addition of MX_n. The tube was vigorously shaken at −78 °C and immediately placed in the thermostated probe. The chemical shifts were determined with reference to the signal of the residual CH_2Cl_2 (5.32 ppm) in the deuterated solvent.

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(20) The order of rates in the presence of various anions Y^- is probably related to the possible formation of other tin Lewis acids such as $SnCl_3Y$, $SnCl_4Y^-$, etc., the Lewis acidity of which is different from that of $SnCl_4$. See also ref 21.

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(27) The large absorption at 3.5 ppm is due to the methylene protons of Et_2O which was used as a solvent for $ZnCl_2$. It has already been shown that the added ether does not affect the nature of the living polymerization (cf. ref 13).

(28) It has been proposed that the inversion may not occur via contact (intimate) ion pairs but occurs via solvent-separated ion pairs (cf. ref 21). Thus, the intermediate derived from a weak Lewis acid is probably more dissociated than contact ion pairs.

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