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In-Situ ^{13}C and ^{1}H NMR Analysis of the Growing Species in Living Cationic Polymerization of Isobutyl Vinyl Ether by the $HCl/SnCl_4$ Initiating System in the Presence of a $n\text{Bu}_4NCl$ Salt[1]

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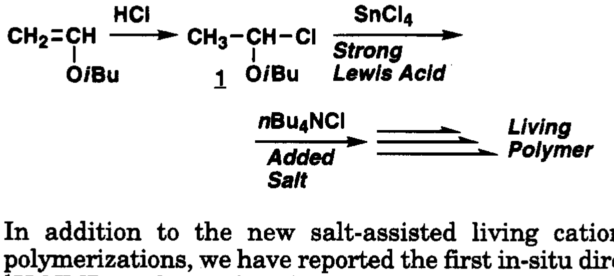
ABSTRACT: Model reactions of the living cationic polymerization of isobutyl vinyl ether (IBVE) with HCl–IBVE adduct [**1**: $CH_3CH(O\textit{i}Bu)Cl$]/$SnCl_4$ initiating system were directly analyzed by ^{13}C and ^{1}H NMR spectroscopy in CD_2Cl_2 at −78 °C to demonstrate the formation of carbocation from **1**. Under the polymerization condition, the **1**/$SnCl_4$ initiating system gave nonliving polymers, but in the presence of $n\text{Bu}_4NCl$, it induced living polymerization, and the spectral data were closely correlated with the salt-assisted transition from nonliving to living polymerization. For example, upon mixing $SnCl_4$ with **1**, the α-methine and the pendant methylene absorptions of **1** shifted remarkably downfield (e.g., up to 227 ppm in ^{13}C NMR for the former), and the extent of the downfield shifts increased with increasing $SnCl_4$ concentration. On further addition of the salt, the downfield signals returned to the original upfield positions close to those for the covalent adduct **1**. Thus, these changes and coupling constant ($^{1}J_{CH}$) analysis demonstrated that **1**/$SnCl_4$ generates an sp^2-type carbocationic species that is in a rapid and dynamic exchange equilibrium with the covalent precursor **1**, and adding $n\text{Bu}_4NCl$ suppresses the growing carbocation, thereby leading to living cationic polymerization.

Introduction

Recently we have found that living cationic polymerization of isobutyl vinyl ether (IBVE) can be achieved with the hydrogen chloride–IBVE adduct (**1**) as an initiator in conjunction with tin tetrachloride ($SnCl_4$) as an activator in the presence of various salts (e.g., $n\text{Bu}_4N^+Y^-$ and $n\text{Bu}_4P^+Y^-$; $Y^- = Cl^-, Br^-$, etc.) (eq 1).[3]



(1)

In addition to the new salt-assisted living cationic polymerizations, we have reported the first in-situ direct ^{1}H NMR analysis of model growing systems (mixtures of **1**, a metal halide, and a salt), which was primarily directed toward uncovering (i) the difference between Lewis acid activators (e.g., $ZnCl_2$ vs $SnCl_4$), (ii) the range of added salts ($n\text{Bu}_4N^+Y^-$) suited for living cationic polymerizations, (iii) the overall effects of the added $n\text{Bu}_4N^+Cl^-$, and, above all, (iv) the nature of the growing species in the living IBVE polymerizations. It has thus been indicated that $SnCl_4$, a strong Lewis acid, would generate a relatively high concentration of an ionic growing species from the covalent precursor **1**, whereas $ZnCl_2$ does not, that nucleophilic anions are required for Y^- in the added salts, and that the salt would reduce the concentration of the ionic intermediate.

Though clearly demonstrating the usefulness of in-situ NMR analysis in cationic processes, the previous ^{1}H NMR-based approach cannot directly tell the nature of the seemingly ionic species (carbocations?) arising from the **1**/$SnCl_4$ and related systems, and also it lacks a more detailed analysis of the effects of concentrations of the metal halide as well as the added salts upon the nature of the growing species, which are obviously relevant to the criteria for living cationic polymerizations.[4-10]

Following these leads, this study now employs not only ^{1}H NMR but ^{13}C NMR spectroscopy to the **1**/$SnCl_4$/$n\text{Bu}_4N^+Cl^-$ model system at systematically varied concentrations of the latter two components. The double nuclei NMR analysis will lead to a more direct insight

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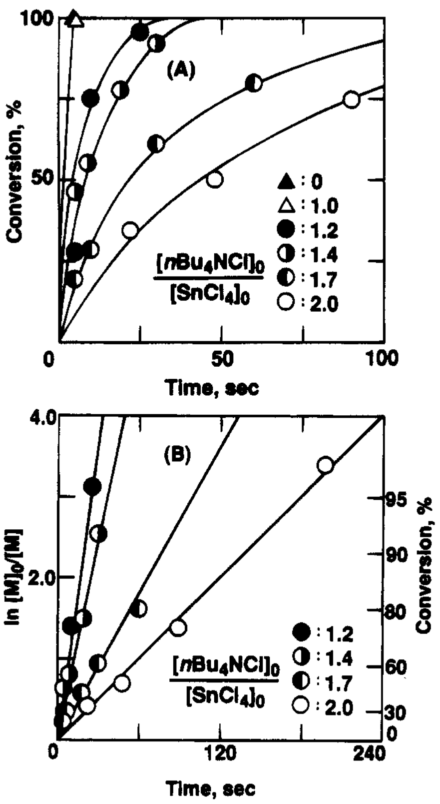


Figure 1. (A) Time-conversion curves and (B) first-order plots for the polymerization of IBVE with **1**/$SnCl_4$ in the absence and presence of $n$$Bu_4NCl$ in CH_2Cl_2 at −78 °C: $[M]_0 = 1.0$ M; $[\mathbf{1}]_0 = 20$ mM; $[SnCl_4]_0 = 10$ mM; $[nBu_4NCl]_0 = 0$ (▲), 10 (△), 12 (●), 14 (◑), 17 (◐), 20 (○) mM.

into the nature of the living and nonliving growing species and their difference, in relation to the roles of $SnCl_4$ and the added salt.

Results and Discussion

1. Polymerizations of IBVE with HCl–IBVE Adduct (1)/$SnCl_4$ in the Presence of $nBu_4N^+Cl^-$. (a) Polymerization. Prior to NMR investigations, IBVE was polymerized with **1** and $SnCl_4$ in the presence of an added salt, $nBu_4N^+Cl^-$, in CH_2Cl_2 at −78 °C.[5–10] Because it has not been clarified yet how the amount of the salt influences the polymerization, we herein investigated these initiated by **1**/$SnCl_4$ ($[M]_0/[\mathbf{1}]_0/[SnCl_4]_0 = 1000/20/10$ mM) in the presence of nBu_4NCl at varying concentrations ($[nBu_4NCl]_0 = 0–20$ mM). The detailed analysis of the effects of salt concentrations is of importance as a basis of our subsequent NMR study to be discussed later in this paper.

As shown in Figure 1A, in the absence of nBu_4NCl, an almost instantaneous polymerization proceeded and completed within 5 s. However, the addition of increasing amounts of the salt retarded the polymerization.[3a] At a high salt concentration, $[nBu_4NCl]_0 = 22$ mM, the polymerization was extremely slow, and no polymers were obtained even after 22 days. Figure 1B shows the logarithmic conversion data, $\ln([M]_0/[M])$ ([M] is the monomer concentration at time t), plotted against time t. The plots are linear up to high monomer conversion (~95%), indicating constant concentrations of the growing species during the polymerizations with varying amounts of the added salt.

Figure 2 shows the number-average molecular weight ($\bar{M}_n$), polydispersity ($\bar{M}_w/\bar{M}_n$), and molecular weight distributions (MWD) of the polymers obtained at varying salt concentrations. The polymerization without the salt gave the polymers with broad MWDs; however, in the presence of an excess amount of the salt ($[nBu_4NCl]_0 = 12–20$ mM; i.e., $1 < [nBu_4NCl]_0/[SnCl_4]_0 \leq 2$), the polymers had very narrow MWDs ($\bar{M}_w/\bar{M}_n \leq 1.1$). The $\bar{M}_n$ values increased in direct proportion to monomer conversion and were in good agreement with the calculated values assuming that one molecule of **1** generates one living polymer chain. These results suggest that the **1**/$SnCl_4$ initiating system induces the living polymerization of IBVE in the presence of nBu_4NCl, the amount of which ranges between 1.2 and 2 times that of $SnCl_4$. However, it cannot be described whether the polymerization in the absence and the presence of an equimolar amount of nBu_4NCl with $SnCl_4$ is living or not from these results.

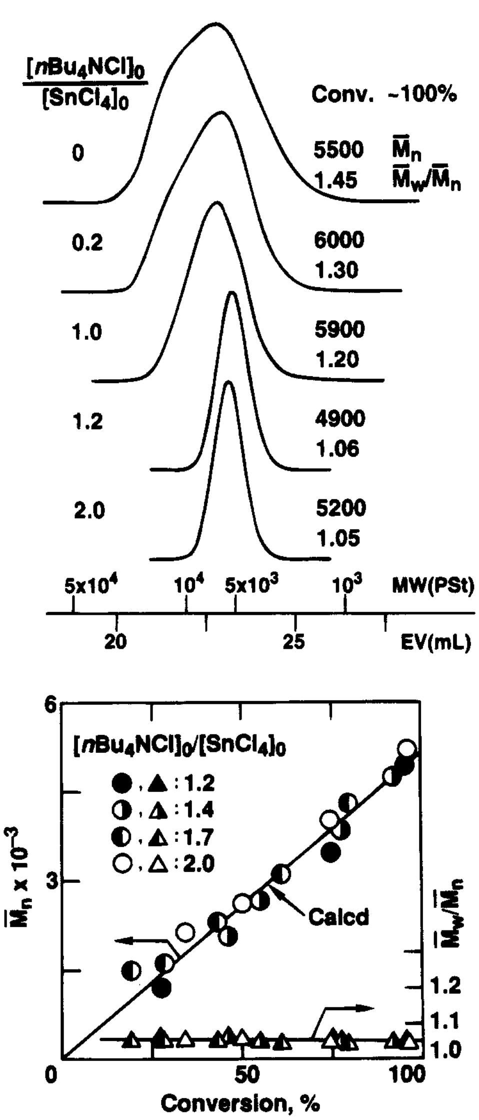


Figure 2. Effects of added nBu_4NCl on IBVE polymerization with **1**/$SnCl_4$ in CH_2Cl_2 at −78 °C: $[M]_0 = 1.0$ M; $[\mathbf{1}]_0 = 20$ mM; $[SnCl_4]_0 = 10$ mM; $[nBu_4NCl]_0 = 0$ (▲), 10 (△), 12 (●), 14 (◑), 17 (◐), 20 (○) mM. The "Calcd" solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **1** molecule.

(b) Monomer Addition Experiments. Thus, to examine the living nature of the polymerizations with **1**/$SnCl_4$ in the presence and the absence of the salt, a fresh feed of monomer was added to the reaction mixtures when the initial charge of the monomer had been consumed. For all cases shown in Figure 3, the added monomer feed was smoothly polymerized, and the

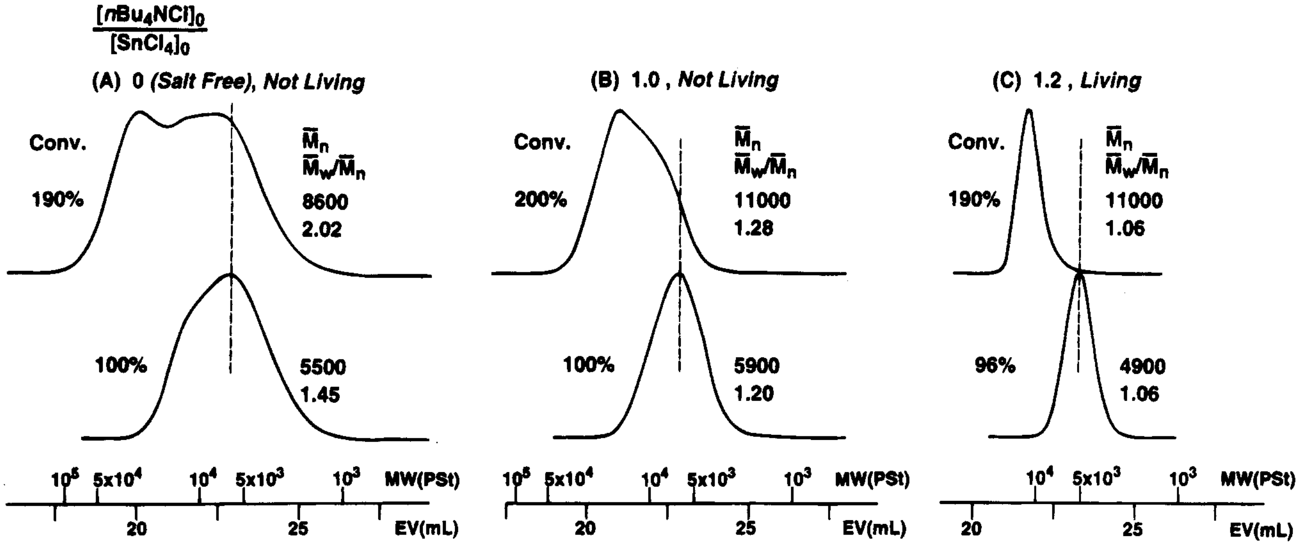


Figure 3. MWD curves of poly(IBVE) obtained in the monomer-addition experiments with **1**/SnCl$_4$ in CH$_2$Cl$_2$ at −78 °C: [M]$_0$ = [M]$_{add}$ = 1.0 M; [**1**]$_0$ = 20 mM; [SnCl$_4$]$_0$ = 10 mM; [*n*Bu$_4$NCl]$_0$ = 0 (A), 1.0 (B), 1.2 (C) mM. The calculated $\bar{M}_n$'s assuming the formation of one living polymer per **1** molecule, are 5100 (Conv. 100%) and 11 000 (Conv. 200%), before and after the monomer addition, respectively.

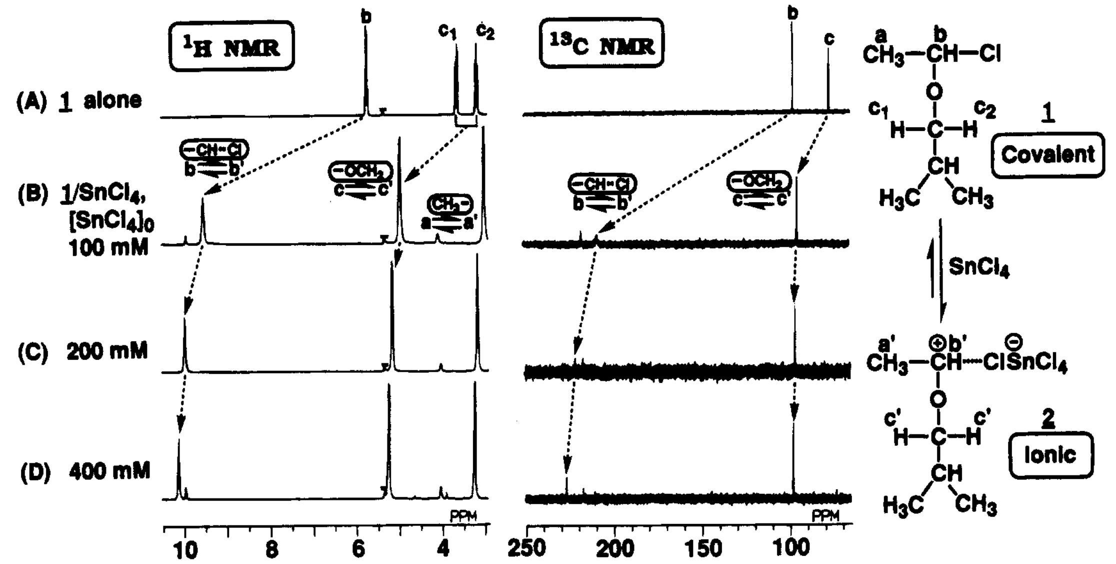


Figure 4. ^{1}H NMR and ^{13}C NMR spectra of the mixture of **1**/SnCl$_4$ at varying SnCl$_4$ concentration in CD$_2$Cl$_2$ at −78 °C: [**1**]$_0$ = 200 mM; [SnCl$_4$]$_0$ = 0 (A), 100 (B), 200 (C), 400 (D) mM.

$\bar{M}_n$ of the polymers increased with the monomer conversion. In the presence of the salt in a slight excess over SnCl$_4$ ([*n*Bu$_4$NCl]$_0$/[SnCl$_4$]$_0$ = 1.2; Figure 3C), the MWD remained as narrow as in the first-stage polymerization and was free from tailings. Thus, in this case nearly perfect living polymerization proceeded. However, such a living process was feasible neither under salt-free conditions (Figure 3A) nor in the presence of the salt equimolar to SnCl$_4$ (Figure 3B), as evidenced by the bimodal MWD in Figure 3A and the broadened distribution with the apparently overlapping two populations in Figure 3B, respectively, both of which indicate that a part of the growing species was dead.

2. Direct NMR Analysis. After detailed analysis of the effect of the [salt]/[SnCl$_4$] ratio, the interaction of **1** with SnCl$_4$ and the salt was directly analyzed by both ^{1}H and ^{13}C NMR spectroscopy. The objectives herein were to clarify the nature of the growing species in the **1**/SnCl$_4$-initiated polymerization and the roles of SnCl$_4$ and *n*Bu$_4$NCl, where **1** is considered as the simplest model of the polymer terminal. ^{1}H and ^{13}C nuclei were monitored under identical reaction conditions, so that their spectral correlations might be discussed.

(a) Salt-Free System: SnCl$_4$-Assisted Generation of Carbocations. Figure 4 shows the ^{1}H and ^{13}C 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 ([**1**]$_0$ = 200 mM, [SnCl$_4$]$_0$ = 0−400 mM). As shown in Figure 4A for the precursor **1** alone, the signals of the α-methine b, which is adjacent to the chlorine, appeared at 97 ppm in ^{13}C NMR and at 5.7 ppm in the ^{1}H NMR as a sharp quartet. The methylene carbon C^{c} (−*OCH*$_2$−) of the pendant isobutyl groups absorbs at 77 ppm. The two methylene protons c$_1$ and c$_2$ are chemical shift nonequivalent due to the asymmetric α-carbon to give a pair of resonances around 3.3 ppm.[3]

On mixing SnCl$_4$ to a cooled solution of **1**, the spectrum changed clearly, as seen in Figure 4B−D; the methine proton (H^{b}) and carbon (C^{b}) shifted downfield and broadened (Figure 4B). Along with this change, the

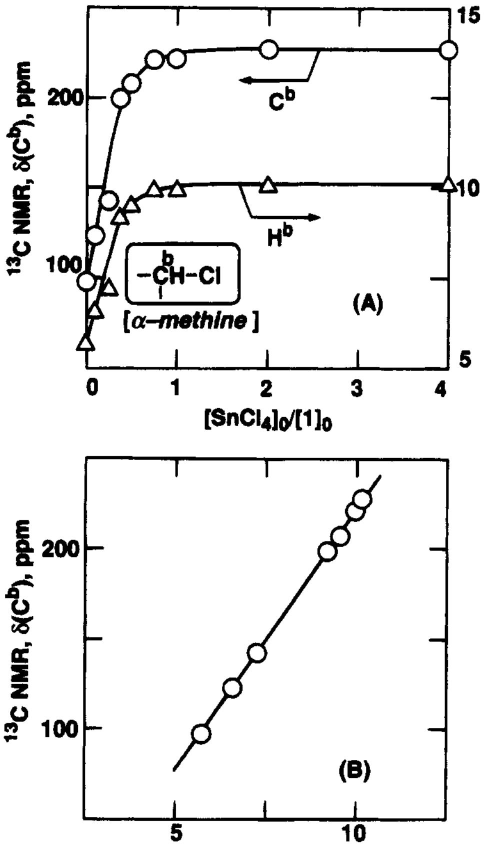


Figure 5. (A) Effects of $SnCl_4$ concentration on the ^{13}C and ^1H NMR chemical shifts of the α-methine of **1** [δ(C^b) and δ(H^b)] and (B) their correlation in CD_2Cl_2 at −78 °C: $[\mathbf{1}]_0 = 200$ mM; $[SnCl_4]_0 = 0-800$ mM.

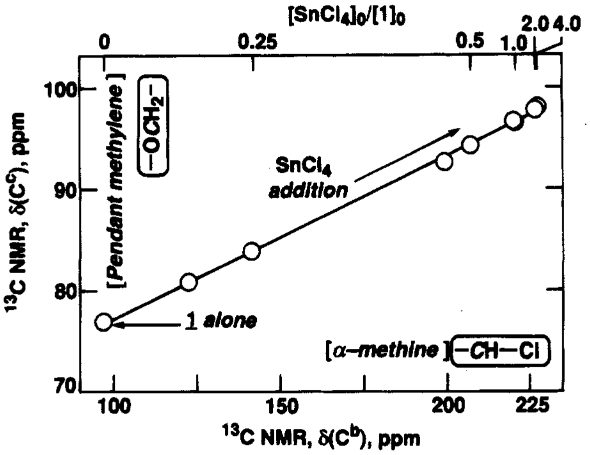


Figure 6. Relationship between the ^{13}C NMR chemical shift of α-methine carbon C^b and that of pendant methylene carbon C^c in CD_2Cl_2 at −78 °C: $[\mathbf{1}]_0 = 200$ mM; $[SnCl_4]_0 = 0-800$ mM.

two methylene proton resonances coalesced into a sharp doublet, that was also downfield shifted, and the methylene carbon also moved downfield accordingly. Equally important, with increasing concentration of $SnCl_4$, the signals progressively shifted downfield (Figure 4C); in particular, with an excess of $SnCl_4$ ($[SnCl_4]_0/[\mathbf{1}]_0 = 2$), the methine carbon C^b absorbed at the considerable downfield region, 227 ppm, as a sharp peak (Figure 4D). A series of these changes in the spectra shows that the covalent C−Cl bond in **1** is polarized by $SnCl_4$ to give a highly electron-deficient and most likely carbocationic species **2** and that the species thus formed are in rapid equilibrium with their covalent precursor **1**.[11,12] The latter conclusion is reached from the progressive downfield shift of the methine signal (b) with increasing $SnCl_4$ concentration and from the coalescence of the originally nonequivalent pairs of the methylene protons (c_1 and c_2) indicative of the racemization of the chiral carbon b.

Figure 5A shows the relationships between the concentration of $SnCl_4$ and the ^1H and ^{13}C NMR chemical shifts (δ values) of the methine signal b. Both nuclei shifted downfield as the concentration of $SnCl_4$ increased. These shifts continued progressively until $SnCl_4$ became a molar excess over the precursor where the chemical shifts stayed virtually constant. The chemical shift changes of the two different nuclei resemble each other and are closely correlated, as shown in the linear plots in Figure 5B. The progressive downfield shifts indicate an increase of the carbocationic species which are in fast equilibrium with the precursor **1**. In Figure 5A, beyond the point where $SnCl_4$ is molar equivalent to **1**, the saturation of the downfield shifts showed that the equilibrium is far shifted to the carbocationic species and that almost all the molecules of the covalent precursor **1** are ionized by an equimolar or more amount of $SnCl_4$.

On the other hand, in the region between $0 \le [SnCl_4]_0/[\mathbf{1}]_0 \le 1$, one molecule of $SnCl_4$ may ionize two molecules of **1** at most; namely, $SnCl_4$ interacts with one molecule of **1** to generate a cationic species and the $SnCl_5^-$ anion, the latter of which further interacts with another molecule of **1** to generate another cationic species and the $SnCl_6^{2-}$ dianion (eq 2). This is indicated by the

$$\sim\!\text{C}-\text{Cl} + \text{SnCl}_4 \xrightleftharpoons{K_1} \sim\!\text{C}^{\oplus}\cdots\text{SnCl}_5^{\ominus}$$

$$\sim\!\overset{*}{\text{C}}-\text{Cl} + \sim\!\text{C}^{\oplus}\cdots\text{SnCl}_5^{\ominus} \xrightleftharpoons{K_2} \sim\!\text{C}^{\oplus}\cdots\text{SnCl}_6^{2\ominus}\cdots\overset{*}{\text{C}}{}^{\oplus}\!\sim \qquad (2)$$

convex curve in this region of Figure 5A. If one $SnCl_4$ molecule was able to activate only one molecule of **1** and if the equilibrium was far shifted to the ionic species, the plot in the region would be a diagonal linear line, which disagrees with the observed convex dependence. Alternatively, if $SnCl_4$ was able to activate two molecules of **1** and if the equilibrium constants K_1 and K_2 (eq 2) were both very large, the plot would be a diagonal line in the region between $0 \le [SnCl_4]_0/[\mathbf{1}]_0 \le 0.5$ and then would level off to reach an asymptotic value (227 ppm for ^{13}C NMR) at higher $SnCl_4$ concentrations. As observed, however, the chemical shift does not level off yet so early at $[SnCl_4]_0/[\mathbf{1}]_0 = 0.5$. Thus, $SnCl_4$ ionizes two molecules of **1**, but the second equilibrium constant K_2 is smaller than K_1 because of the weaker Lewis acidity of $SnCl_5^-$.[13]

Figure 6 shows the relationship between the chemical shifts of the α-methine carbon b and the pendant methylene carbon c. The linearity indicates the downfield shifts of the two carbons are caused by only one factor, the ionization of the C−Cl bond of **1**. This also suggests that, along with the polarization of the C−Cl bond, the nonbonded electrons on the ether oxygen flow into the electron-deficient carbon b and that the electron density is decreased on the methylene carbon c adjacent to the oxygen.

The analysis of $^{13}C-^1H$ coupling constants ($^1J_{CH}$) also gives useful information about the interaction of **1** with $SnCl_4$ (Figure 7). The orbitals of the α-carbon of **1** are

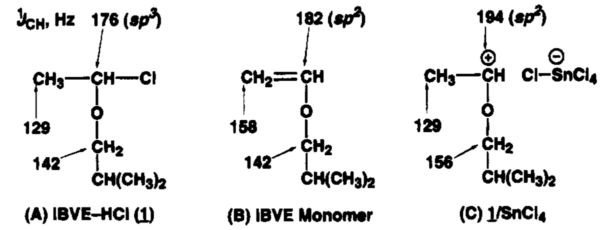
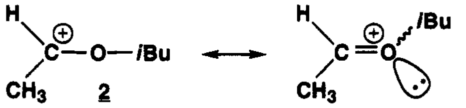


Figure 7. ^{13}C–^{1}H coupling constants $^1J_{CH}$ in CD_2Cl_2 at −78 °C: (A) **1** (500 mM), (B) IBVE monomer (200 mM), (C) **1**/$SnCl_4$ (500/1000 mM).

sp^3 hybridized, whereas the orbitals become sp^2 once the carbocation arises. It is well-known that the $^1J_{CH}$ increases with increasing *s*-character of the C–H bond and/or with substitution on the carbon atom of electron-withdrawing groups. For example, the $^1J_{CH}$ value of the sp^3-carbon of ethane is 125 Hz, which is smaller than those for the sp^2-carbons of ethylene (156 Hz) and the isopropyl cation (169 Hz).[14] The $^1J_{CH}$ values of the β-carbons of IBVE–HCl (**1**) (sp^3, 129 Hz; Figure 7A) and IBVE monomer (sp^2, 158 Hz; Figure 7B) are in good agreement with those of ethane and ethylene. Although both values of the α-carbon were quite different (sp^3, 176 Hz for **1**; sp^2, 182 Hz for IBVE monomer) from those of the corresponding β-carbons due to the adjacent heteroatoms (oxygen and chlorine), the value for the sp^2-CH carbon of IBVE monomer is still larger than that for the sp^3-carbon of **1**.

On mixing $SnCl_4$ with **1**, the $^1J_{CH}$ of the α-methine of **1** increases from 176 to 194 Hz (Figure 7C). This indicates that $SnCl_4$ interacts with the chlorine of **1** to transform the methine carbon from sp^3 to sp^2 and thereby to generate a carbocationic species with an sp^2-hybrid orbital. Upon this interaction, however, the $^1J_{CH}$ of the β-carbon remained virtually unchanged, while the value of the pendant methylene carbon (sp^3) increases from 142 to 156 Hz. This suggests that the positive charge is not completely localized on the α-methine but is partly delocalized onto the ether oxygen; there is a contribution of an oxonium resonance structure (eq 3).[12]



(3)

Thus, the direct ^{1}H and ^{13}C NMR analysis of the **1**/$SnCl_4$ system has revealed that $SnCl_4$ and/or $SnCl_5^-$ interact with **1** to generate an sp^2-hybridized cationic species **2**, which is in rapid equilibrium with the covalent sp^3-type precursor **1**. This in turn shows that the growing species in the polymerization with **1**/$SnCl_4$ is the ionic species **2**, because any polymerization does not occur until the covalent precursor **1** is mixed with $SnCl_4$. However, it is important that such systems, which generate the cationic species at concentrations high enough to be readily detectable by ^{1}H and ^{13}C NMR, fail to achieve living IBVE polymerization, as discussed below.

(b) Effects of Added Salts: Suppression of Ionic Species. Mixtures of **1** with $SnCl_4$ at varying concentrations of nBu$_4$NCl were then analyzed in a similar way (Figure 8). On addition of nBu$_4$NCl (100 mM) to a mixture of **1**/$SnCl_4$ (200/100 mM; Figure 8B), the downfield-shifted methine peaks H^b and C^b moved upfield (Figure 8C), which, however, were still broad and downfield-shifted relative to those for the adduct **1** alone (Figure 8A). This shows that nBu$_4$NCl 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 NMR spectroscopy. As shown in Figure 2, the polymerization was not living yet, under these particular conditions ($[n\mathrm{Bu_4NCl}]_0/[\mathrm{SnCl_4}]_0 \le 1$).

Upon further addition of nBu$_4$NCl (Figure 8D), under which condition the living cationic polymerization occurred as shown in Figure 2, the methine carbon C^b absorbs as a sharp signal located at the original upfield position for the covalent precursor **1** alone. The methine proton H^b also returned to the original position as a sharp quartet. The $^1J_{CH}$ values were almost the same as those of **1** alone. $^1J_{CH}$ (Hz): the α-methine, 177; the pendant methylene, 142; the β-methyl, 129 (cf. Figure 7). These indicate that the equilibrium is far shifted to the covalent species.

Despite the close similarity in chemical shifts of the major peaks, the spectra A and D clearly differ in that the pair of signals of the nonequivalent pendant methylene protons (c_1 and c_2) seen in A coalesced into a broad signal in D that appeared at the middle position of them. The broadening shows the occurrence of racemization of diastereomeric **1** via the sp^2-hybridized cationic species **2**, and no detectable change in the chemical shifts implies an extremely low concentration of the ionic species.[3] Thus, under these salt-present conditions where the living polymerization proceeds, the sp^2-type carbocationic species is not only at an extremely low concentration but in a dynamic exchange equilibrium with the covalent precursor **1**.[15,16]

With the use of a higher concentration of nBu$_4$NCl (Figure 8E), the signals of the methylene protons are again split into sharp triplets and almost the same as those for the adduct **1** alone. This shows that, with excess salt present, the racemization is very slow or does not occur; namely, the ionic species is virtually absent or at a concentration too low to be detected by NMR. Under these conditions, any detectable polymerization did not occur even after 22 days.

Figure 9 shows the relationships between the chemical shifts of the α-methine C^b, the concentrations of nBu$_4$NCl, and the polymerization. When nBu$_4$NCl is added to a mixture of **1** and $SnCl_4$, the downfield-shifted resonances return progressively to upfield regions. The upfield shift continues until nBu$_4$NCl becomes equimolar to, or excess over, $SnCl_4$. In the range where the downfield shift is observable, the polymerizations are very fast to give polymers with broad MWDs. On further addition of nBu$_4$NCl, the signals reach their original upfield positions for the adduct **1**, which indicates that the suppression of the ionic species. In the region where $1 < [n\mathrm{Bu_4NCl}]_0/[\mathrm{SnCl_4}]_0 \le 2$, the two pendant methylene signals coalesce or broaden, and the living polymerization proceeded. When $[n\mathrm{Bu_4NCl}]_0/[\mathrm{SnCl_4}]_0 > 2$, where even the racemization was not observed, no polymerization occurs.

Thus, it is clarified that there are close relationships between the living nature of the salt-present polymerizations and the NMR spectra of model reactions of **1**; i.e., living polymerization occurs when the downfield chemical shifts, which indicate a relatively high concentration of the carbocationic species, are hardly observable by NMR in the model reactions. The added salt, nBu$_4$NCl, suppresses the ionic species generated by $SnCl_4$ and then induces living polymerization.[17]

(c) Polymerization and NMR Analysis at Very Low Concentrations of SnCl$_4$. In the preceding

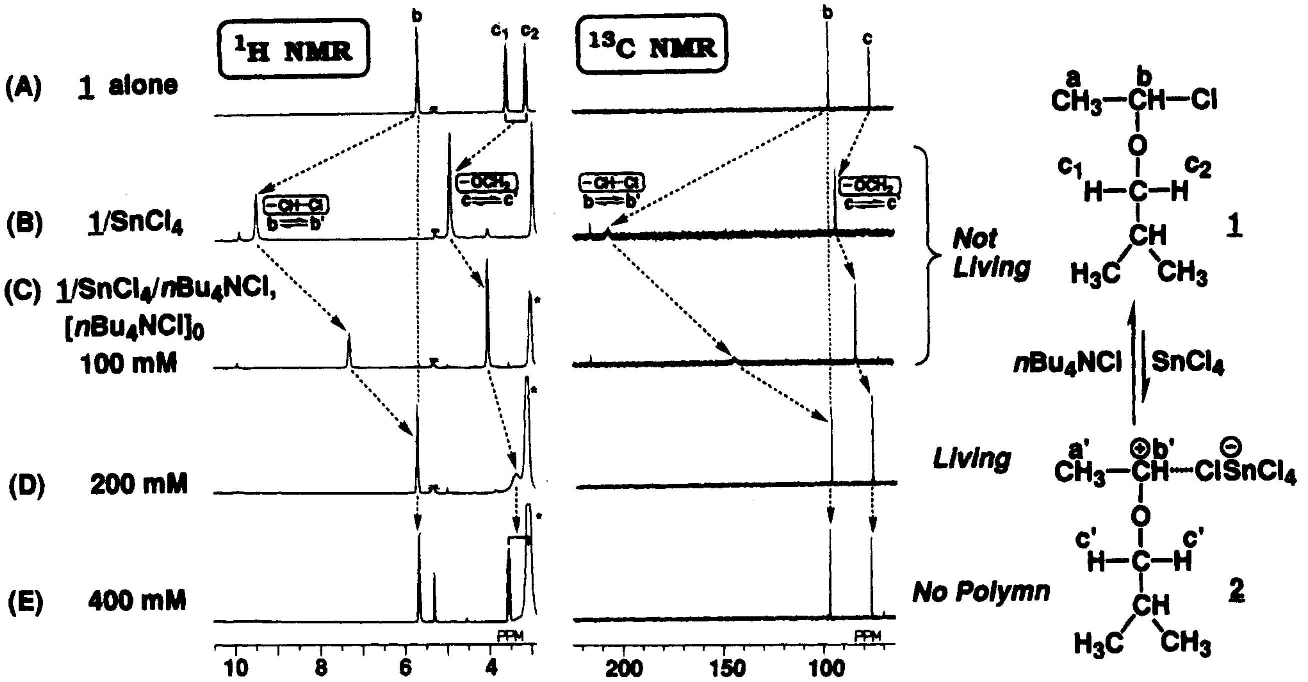


Figure 8. ^1H NMR and ^{13}C NMR spectra of **1** (A) and the mixture of **1**/$SnCl_4$/$n$$Bu_4NCl$ with varying $n$$Bu_4NCl$ concentration (B–E) in CD_2Cl_2 at −78 °C: $[\mathbf{1}]_0 = 200$ mM; $[SnCl_4]_0 = 100$ mM; $[nBu_4NCl]_0 = 0$ (B), 100 (C), 200 (D), 400 (E) mM. The asterisked signals are due to the α-methylene in $(CH_3CH_2CH_2CH^*_2)_4NCl$.

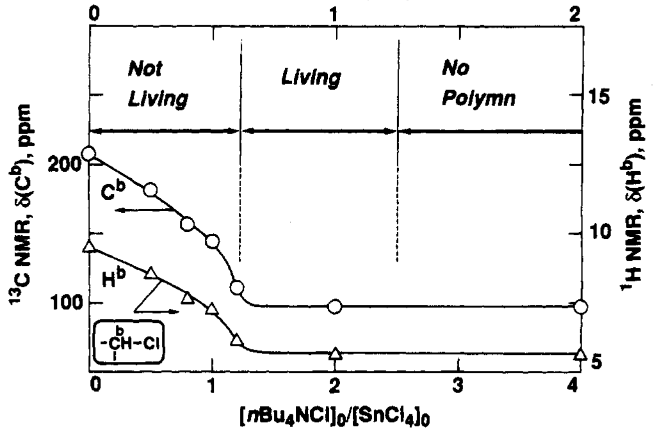


Figure 9. Effects of $n$$Bu_4NCl$ concentration on the ^{13}C and ^1H NMR chemical shifts of α-methine of **1** [$\delta(C^b)$ and $\delta(H^b)$] in CD_2Cl_2 at −78 °C: $[\mathbf{1}]_0 = 200$ mM; $[SnCl_4]_0 = 100$ mM; $[nBu_4NCl]_0 = 0$–400 mM.

sections, the results showed that the concentration of the ionic species increases with that of $SnCl_4$, and it should be very low to effect living polymerization. This suggests that, at a very low concentration of $SnCl_4$, the carbocation concentration be so low as to permit living polymerization possible even in the absence of the salt. Then, IBVE was polymerized with **1** in conjunction with a very small amount of $SnCl_4$ without $n$$Bu_4NCl$, and the corresponding model reactions were analyzed by ^1H and ^{13}C NMR spectroscopy.

On addition of a small amount of $SnCl_4$ (2 mM) to the adduct **1** (200 mM), both the α-methine carbon C^b and the methine proton H^b absorbed still at the original positions, and the two pendant methylene signals broadened (Figure 10D). The corresponding IBVE polymerization proceeded in the living process (Figure 12C). These spectral changes show the generation of the carbocationic species at a very low concentration as in the system with a large amount of $SnCl_4$ (100 mM) and in the presence of $n$$Bu_4NCl$ (200 mM) (Figure 10C). However, there is a difference in the shape of the methylene peaks; the peaks coalesced into a broad peak in the salt-present system (Figure 10C), whereas the two peaks broaden but do not coalesce yet in the salt-free system (Figure 10D). This indicates that, in the salt-free system, the carbocation indeed intervenes but that the exchange reaction between the ionic species and the covalent precursor is slower than in the salt-present system. As will be discussed later, such a difference in the rate of the ion-covalent exchange affects the MWD of the obtained polymers.

Figures 11 and 12 show the results for the polymerizations at low $SnCl_4$ concentrations, corresponding to the model reactions (Figure 10B–D). As already discussed above, **1** with a large amount of $SnCl_4$ (salt free) induced a very rapid polymerization to give polymers with broad MWDs, but in the presence of $n$$Bu_4NCl$, the rate was reduced, and polymers with narrow MWDs were obtained. In the absence of the salt, in contrast, the system with the same molar ratio of $SnCl_4$ to **1** ($[SnCl_4]_0/[\mathbf{1}]_0 = 1/100$) as in the model reaction in Figure 10D led to a rapid polymerization (filled circles in Figure 11), which is, however, slower than that with a large amount of $SnCl_4$ ($[SnCl_4]_0/[\mathbf{1}]_0 = 1/2$; open triangle in Figure 11).

As shown in Figure 12C, the $\bar{M}_n$ of the polymers obtained at a very low concentration of $SnCl_4$ increased in direct proportion to monomer conversion and agreed with the calculated values assuming that one polymer chain forms per **1** molecule, despite the absence of the added salt. The MWDs were unimodal and became narrower ($\bar{M}_w/\bar{M}_n = 1.10$) as the polymerization proceeded. However, they were still slightly broader than those obtained in the salt-present polymerizations (Figure 12B). This is due to the slower exchange between the ionic species and the dormant species as shown by the preceding NMR analysis. These relationships among the polymerization, the concentration of the carbocationic species, and the rapidness of the covalent-ionic exchange are collected in Table 1.

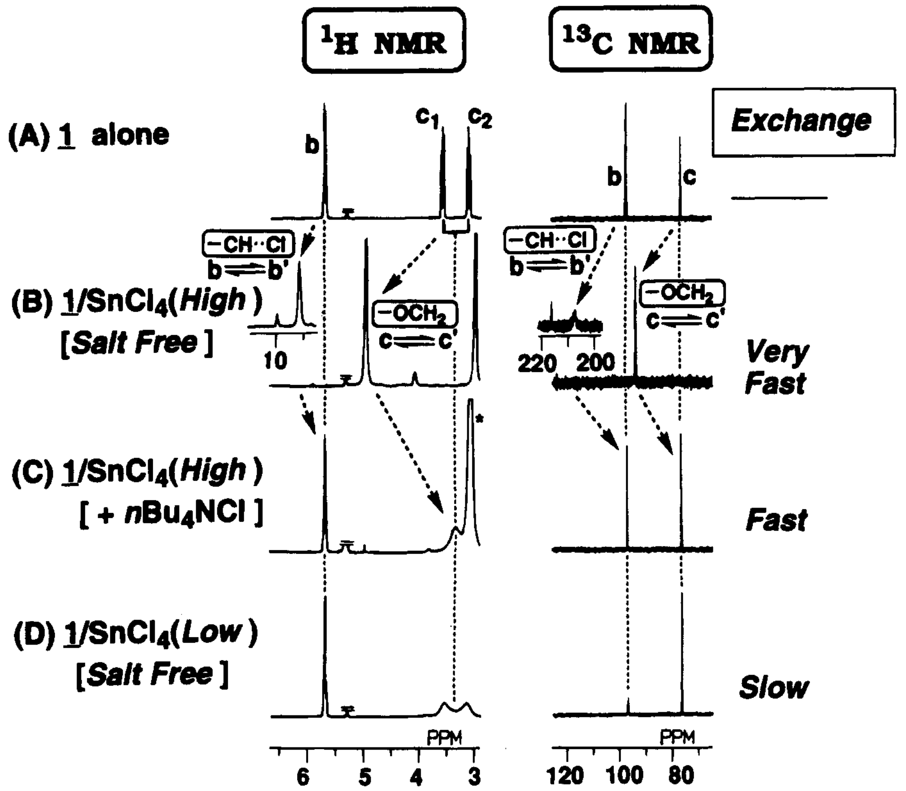


Figure 10. ^{1}H NMR and ^{13}C NMR spectra of **1** (A) and the mixture of **1**/SnCl$_4$ in the absence and the presence of *n*Bu$_4$NCl (B–D) in CD$_2$Cl$_2$ at −78 °C: (A) $[\mathbf{1}]_0$ = 200 mM; (B) $[\mathbf{1}]_0/[\mathrm{SnCl_4}]_0$ = 200/100 mM; (C) $[\mathbf{1}]_0/[\mathrm{SnCl_4}]_0/[n\mathrm{Bu_4NCl}]_0$ = 200/100/200 mM; (D) $[\mathbf{1}]_0/[\mathrm{SnCl_4}]_0$ = 200/2.0 mM. The asterisked signals are due to the α-methylene in $(\mathrm{CH_3CH_2CH_2C}H^*{}_2)_4\mathrm{NCl}$.

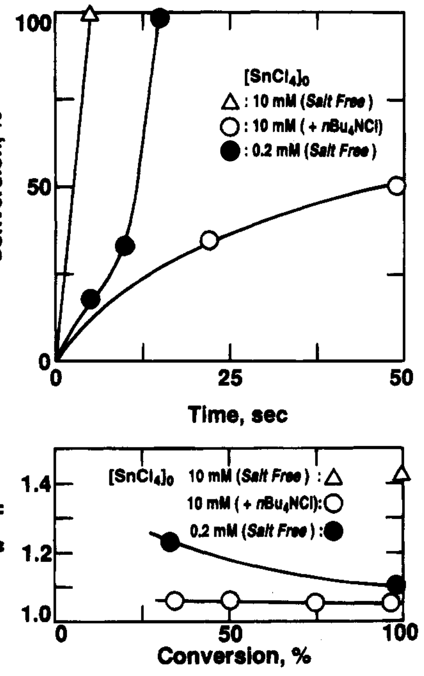


Figure 11. Polymerization of IBVE with **1**/SnCl$_4$ in the absence and the presence of *n*Bu$_4$NCl in CH$_2$Cl$_2$ at −78 °C: $[\mathrm{M}]_0$ = 1.0 M; $[\mathbf{1}]_0$ = 20 mM; $[\mathrm{SnCl_4}]_0/[n\mathrm{Bu_4NCl}]_0$ = 10/0 (△), 10/20 (○), 0.2/0 (●) mM.

Figure 13 shows the MWD curves of poly(IBVE) obtained in monomer-addition experiments at low SnCl$_4$ concentrations ($[\mathrm{M}]_0/[\mathbf{1}]_0$ = 1000/20 mM; $[\mathrm{SnCl_4}]_0$ = 0.2, 0.5, 2.0 mM). A fresh feed of monomer was added to the reaction mixture when the initial charge of the monomer had almost been consumed. The added monomer feed was smoothly polymerized, and the $\bar{M}_n$ of the polymers increased with monomer conversion in all cases. At an extremely low concentration of SnCl$_4$ (0.2 mM; Figure 13C), the MWD became narrower ($\bar{M}_w/\bar{M}_n \le 1.1$) even after the monomer addition with a linear increase in $\bar{M}_n$. This demonstrates the living character of the polymerization. However, at higher concentrations of SnCl$_4$ (Figure 13A,B), the MWD after the monomer addition broadened with a tailing and showed apparently overlapping populations indicative of dead polymers (e.g., Figure 13A). Thus, the livingness was lost with increasing the SnCl$_4$ concentration. Comparison between Figures 3 and 13 indicates that the effects

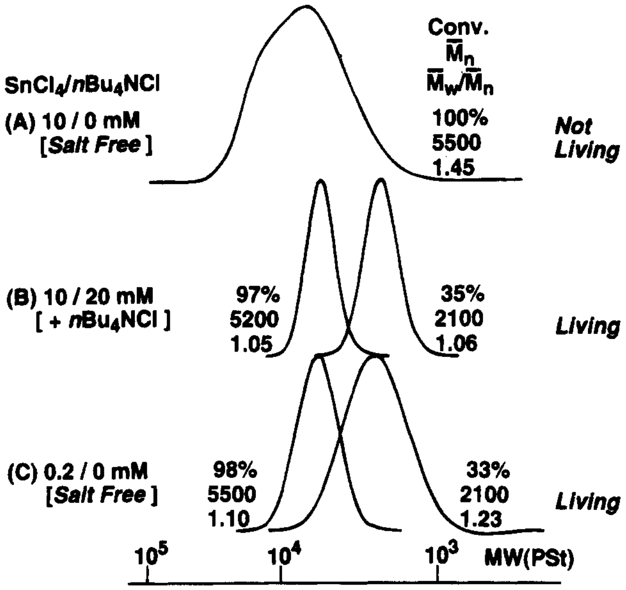


Figure 12. MWD curves of poly(IBVE) obtained with **1**/SnCl$_4$ in the absence and the presence of *n*Bu$_4$NCl in CH$_2$Cl$_2$ at −78 °C, as a function of IBVE conversion: $[\mathrm{M}]_0$ = 1.0 M; $[\mathbf{1}]_0$ = 20 mM. $[\mathrm{SnCl_4}]_0/[n\mathrm{Bu_4NCl}]_0$ = 10/0 (A), 10/20 (B), 0.2/0 (C) mM. The calculated $\bar{M}_n$ assuming the formation of one living polymer per **1** molecule is 5100.

Table 1. Characterization in Polymerization of IBVE 1/SnCl$_4$/*n*Bu$_4$NCl

system	1/SnCl$_4$/ *n*Bu$_4$NCl, mM	polymn	C$^+$ conc	covalent–ionic exchange
(A) adduct **1** alone	200/0/0^a (20/0/0)^b	no polymn		
(B) high [SnCl$_4$]$_0$ salt free	200/100/0^a (20/10/0)^b	not living broad MWD	high	very fast
(C) high [SnCl$_4$]$_0$ salt added	200/100/200^a (20/10/20)^b	living very narrow MWD	low	fast
(D) low [SnCl$_4$]$_0$ salt free	200/2/0^a (20/0.2/0)^b	living narrow MWD	low	slow

^{a} For model reaction, in CD$_2$Cl$_2$, at −78 °C. ^{b} For polymerization, [M]$_0$ = 1.0 M, in CH$_2$Cl$_2$, at −78 °C.

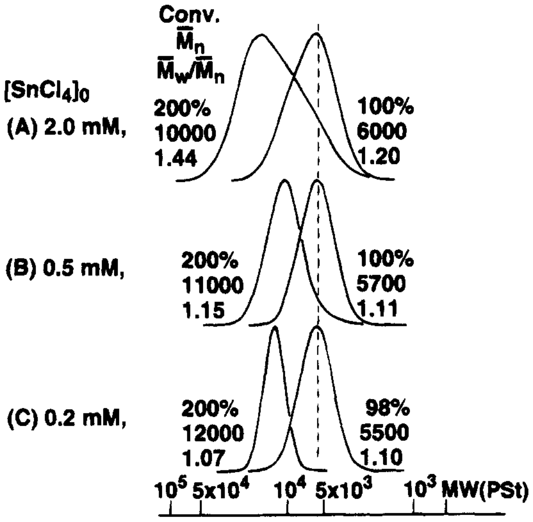


Figure 13. MWD curves of poly(IBVE) obtained in monomer-addition experiments in the polymerization with **1**/SnCl$_4$ in CH$_2$Cl$_2$ at −78 °C at low SnCl$_4$ concentrations in the absence of *n*Bu$_4$NCl: [M]$_0$ = [M]$_{add}$ = 1.0 M; [**1**]$_0$ = 20 mM; [SnCl$_4$]$_0$ = 2.0 (A), 0.5 (B), 0.2 (C) mM. The calculated $\bar{M}_n$'s, assuming the formation of one living polymer per **1** molecule, are 5100 (Conv. 100%) and 11 000 (Conv. 200%), before and after the monomer addition, respectively.

of increasing salt concentration (Figure 3) and lowering SnCl$_4$ concentration (Figure 13) are similar.

These results indicate that the **1**/SnCl$_4$-initiated polymerization of IBVE, even in the absence of the added salt, proceeded in a living fashion only at an extremely low SnCl$_4$ concentration.

3. Conclusions. Cationic polymerizations of IBVE were carried out with the **1**/SnCl$_4$ system in the presence and the absence of *n*Bu$_4$NCl, and the corresponding model reactions were directly investigated by ^{1}H and ^{13}C NMR spectroscopy. The in-situ direct NMR analysis, particularly the ^{13}C NMR analysis, has demonstrated the following: (1) the sp^2-type carbocationic species (**2**: Figure 4) are formed from the sp^3-type covalent precursors **1** by the assistance of SnCl$_4$, as evidenced by ^{13}C NMR chemical shifts and $^1J_{CH}$ constants; (2) the carbocationic intermediates thus formed are in rapid and dynamic exchange equilibrium with the covalent (dormant) precursor; (3) the added salt dramatically suppresses the generation of the carbocationic species, which is one of the critical conditions to achieve the living cationic polymerization; (4) with use of an extremely low concentration of SnCl$_4$, similar conditions may be achievable but the slow ion-covalent exchange broadens polymer MWD; and (5) even under such conditions, the carbocationic species, though at a very low concentration they may be, are definitely involved in the propagation process.

However, it is not clarified yet whether the structure of the carbocationic intermediates in the controlled or living polymerizations is the same as in the uncontrolled or nonliving ones, and the structure of the counteranionic part in the growing species is still unknown. The total analysis of the growing species by multinuclear NMR spectroscopy is now under investigation to uncover these points.

Experimental Section

Materials. SnCl$_4$ (Wako Chemicals; purity > 97%) was distilled under reduced pressure over phosphorus pentoxide. *n*Bu$_4$NCl (Tokyo Kasei; purity > 98%) were all used as received. It was 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$_2$Cl$_2$) (Wako Chemicals; 99.75 atom % D) was dried overnight over baked molecular sieves (3 Å) just before use. CH$_2$Cl$_2$ 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.[18]

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 SnCl$_4$ (in CH$_2$Cl$_2$) via dry syringes into a monomer solution (in CH$_2$Cl$_2$; 4.0 mL) containing IBVE (0.66 mL) and CCl$_4$ (0.20 mL). For polymerizations in the presence of a salt, it was dissolved in a SnCl$_4$ 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, an aqueous sodium hydroxide solution, and then with 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 (SEC) 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 SEC 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; 1.0 M) at 0 °C, which was used for the polymerizations; the adduct synthesized in CD$_2$Cl$_2$ (1.0 M) at −78 °C was used for the model reactions. 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. In *n*-hexane after 30 min and in CD$_2$Cl$_2$ after 10 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;[3] the observed value (~1 M) further confirmed the quantitative formation of **1** from IBVE.

^{1}H NMR and ^{13}C NMR Spectroscopy and Model Reactions. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX270 spectrometer, operating at 270.7 MHz (^{1}H) and 67.9 MHz (^{13}C) (CD$_2$Cl$_2$ for locking). The main parameters were as follows: for ^{1}H, spectral width = 6002.4 Hz (22.17 ppm), pulse width = 4.3 μs (45°), acquisition time + pulse delay = 30 s, data points = 16 384, number of transients = 8 (4 min for one spectrum); for ^{13}C, spectral width = 20 000.0 Hz (294.38 ppm), pulse width = 4.0 μs (45°), acquisition time + pulse delay = 3.0 s, data points = 32 768, number of transients = 500–2000 (30–120 min for one spectrum), completely decoupling from ^{1}H. The probe temperature was regulated with a variable-temperature apparatus JEOL NM-GVT3 (temperature fluctuation $\leq$ 1 deg). The reaction was started by adding a solution of **1** (in CD_2Cl_2; 0.12 mL) to a prechilled solution of $SnCl_4$ (in CD_2Cl_2; 0.48 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 $SnCl_4$ prior to addition of **1**. 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 as a singlet in ^{1}H NMR and 55.8 ppm as a quintet in ^{13}C NMR: both from TMS) in the deuterated solvent. ^{13}C–^{1}H coupling constants ($^1J_{CH}$ values) were obtained from the ^{13}C NMR spectra with the protons nondecoupled, where some of the main parameters for the spectra with the protons completely decoupled (see above) were changed as follows; acquisition time + pulse delay = 9.0 s, number of transients = 200 (30 min for one spectrum), and the concentrations of **1** and $SnCl_4$ were increased to 500 and 1000 mM, respectively, to compensate the low S/N ratios.

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References and Notes

(1) This work was presented in part at the following meetings: (a) The 42nd Symposium on Macromolecules, the Society of Polymer Science, Tokyo, Japan, Sept 1993; Paper 20D15: Kamigaito, M.; Katayama, H.; Sawamoto, M.; Higashimura, T. *Polym. Prepr. Jpn., Engl. Ed.* **1993**, *42* (2), E866. (b) International Conference on "Frontiers in Polymerization", Liège, Belgium, Oct 1993: Sawamoto, M. *Macromol. Symp.* **1994**, *88*, 105.

(2) Research Fellow of the Japan Society for the Promotion of Science.

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(4) Similar but limited uses of added salts (mostly $n\mathrm{Bu_4N^+Cl^-}$) have been reported for living polymerizations[5] of *p*-methoxystyrene,[6,7] styrene,[8] isobutylene,[9] and isobutyl vinyl ether.[5b,10]

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(11) There were numerous studies on the generation of carbocations with use of SbF_5 in superacid media. For reviews, see: Olah, G. A. *Science* **1970**, *168*, 1298; *Angew. Chem., Int. Ed. Engl.*, **1973**, *12*, 175.

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(15) It has been proposed that the inversion may not occur via contact (intimate) ion pairs but may occur via solvent-separated ion pairs.[16] Thus, the carbocationic intermediate in the living cationic polymerization is probably more dissociated than contact ion pairs. However, it still remains unknown that the degree of the dissociation of the ionic species in the controlled polymerization is the same as that of the sp^2-carbocationic species in the uncontrolled polymerization, because the former cannot be directly observable by ^{1}H and ^{13}C NMR spectroscopy.

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