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In-Situ Direct Analysis of the Growing Species by ^{119}Sn NMR Spectroscopy: Living Cationic Polymerization of Isobutyl Vinyl Ether with HCl/$SnCl_4$/$n$$Bu_4NCl$[1]

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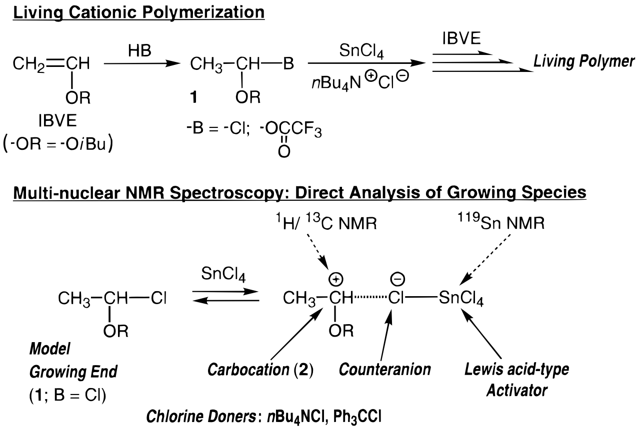
ABSTRACT: ^{119}Sn NMR spectroscopy was employed for analysis of the interaction and reaction of $SnCl_4$ with the HCl−IBVE adduct [**1**; CH_3CHCl(O*i*Bu)] in the presence of $n$$Bu_4NCl$ in CH_2Cl_2 solution at −78 °C, which are model reactions for the living cationic polymerization of isobutyl vinyl ether (IBVE). The addition of **1** to an $SnCl_4$ solution led to upfield shifts of the tin nucleus as the **1**/$SnCl_4$ mole ratio (<1) increases, which indicates the formation of $SnCl_5^-$, via the interaction between $SnCl_4$ and the chlorine atom in **1**. On further addition of **1**, the pentacoordinated anion is converted into the hexacoordinated $SnCl_6^{2-}$. These tin species are in fast equilibrium among each other, and the ^{119}Sn NMR analyses support the formation of a carbocation [**2**; CH_3CH^+(O*i*Bu)] from **1** and the dynamic equilibrium between **1** and **2**. More effective chloride-anion donors such as $n$$Bu_4NCl$ and Ph_3CCl can quantitatively convert $SnCl_4$ into $SnCl_5^-$, and then into $SnCl_6^{2-}$. Thus under the conditions where living cationic IBVE polymerization proceeds ($1 < n\mathrm{Bu_4NCl/SnCl_4} < 2$), $SnCl_4$ is fully converted into a weaker Lewis acid, $SnCl_5^-$, with the aid of added $n$$Bu_4NCl$. The suppression of the carbocationic species in the living system has thus been found due to the interaction between the added salt and $SnCl_4$.

Introduction

In the past decade, the scope of living cationic polymerizations has rapidly been expanding along with the developments of the initiating systems.[2] Most of the initiating systems consist of two components, an initiator and an activator (see Scheme 1). The initiator generates a carbocationic species and a nucleophilic counteranion, and the activator assists the carbocation formation via the interaction with the initiator or the polymer terminal with a covalent group (e.g., a carbon−chlorine bond) derived from the initiator and monomer. In such binary systems, a stable but potentially reactive adduct, which can be prepared from a protonic acid (HB) and a monomer, is employed as the initiator, along with a metal halide or Lewis acid (MX_n) as the activator. A typical initiator for vinyl ether polymerizations is the adduct (**1**) of hydrogen chloride with isobutyl vinyl ether (IBVE). The polymerization proceeds via the electrophilic activation (ionization) of the covalent C−B bond of the initiator or the dormant polymer terminal by MX_n, as shown in Scheme 1. However, it is still not fully understood and often controversial what the nature of the living propagating species is, and whether there is a difference in nature between living and nonliving species. The answers may be derived from in-situ, direct, and spectroscopic analysis of the model growing species under the conditions mimicking the actual polymerizations.

Scheme 1



One of the most suited analytical methods for this purpose may be multinuclear NMR spectroscopy, which permits one to analyze each component of the growing species.[3] As seen in Scheme 1, the living growing end **2** should consist of three components, (1) the growing carbocation (∼∼∼C^+) from the monomer, (2) the counteranion (B^-) from the initiator HB, and (3) the activator (MX_n) associating with B^-. The individual analysis of each component would reveal the mutual interactions among them and clarify the nature of the living ends and their propagation mechanism. We have recently applied ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy for the analysis of the former two components in the living cationic polymerizations of IBVE by the HCl/$SnCl_4$ or the CF_3CO_2H/$SnCl_4$ initiating system in conjunction with an added salt such as $n$$Bu_4NCl$;[4−6] the carbocationic part (∼∼∼C^+) can be analyzed by ^{1}H and ^{13}C NMR, whereas the counteranion (B^-) can be analyzed by ^{13}C and ^{19}F NMR in the CF_3CO_2H-based system. The interactions between the two components, both of which are originated from the initiator, have already been investigated.[4−6] These analyses have shown that the carbocationic intermediate is indeed generated, along with the formation of a counteranionic part via the activation of the C−B bond by $SnCl_4$, and that the added $n$$Bu_4NCl$ suppresses the ionic species, thereby leading to living cationic polymerization. Several other research groups also reported use of ammonium salts for living cationic polymerizations.[7]

This study is to analyze the third component, the Lewis acid ($SnCl_4$) by ^{119}Sn NMR spectroscopy, in the

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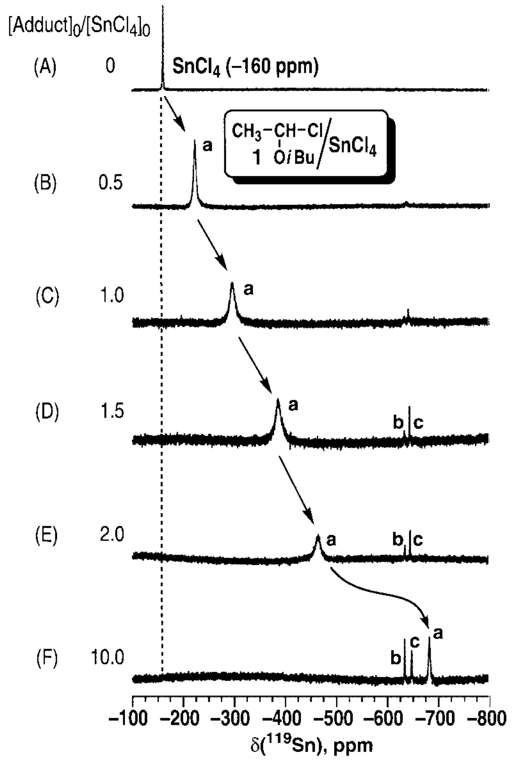


Figure 1. ^{119}Sn NMR spectra of the mixtures of **1**/$SnCl_4$ in CH_2Cl_2 at −78 °C: $[\mathbf{1}]_0/[SnCl_4]_0$ = 0/200 (A), 200/400 (B), 200/200 (C), 300/200 (D), 400/200 (E), 1000/100 (F) mM.

living cationic polymerization with HCl−IBVE adduct (**1**)/$SnCl_4$/$n$$Bu_4NCl$. The ^{119}Sn nucleus has a spin number of $^1/_2$ and a sensitivity to NMR 25.4 times higher than ^{13}C,[8] which will permit a direct and effective analysis of the Lewis acid part in our model reactions. There are a few examples of the ^{119}Sn NMR analysis of the interaction between $SnCl_4$ and $n$$Bu_4NCl$,[8,9] but the interaction with the model compound of the polymer terminal with a carbon−chlorine bond is still unknown. Similar analysis of the MX_n component has been carried out with use of ^{11}B NMR in the model reactions for the BCl_3-catalyzed living cationic polymerization of isobutene.[10] In this ^{119}Sn NMR study, we have investigated the interactions of $SnCl_4$ with **1** and/or $n$$Bu_4NCl$ as the model reactions of the living cationic polymerizations of IBVE.

Results and Discussion

1. Interaction between $SnCl_4$ and Chlorine Donors: Generation of $SnCl_5^-$ and $SnCl_6^{2-}$. ^{119}Sn NMR analysis was first directed to mixtures of $SnCl_4$ and the HCl−IBVE adduct (**1**) in CH_2Cl_2 at −78 °C (Figure 1). Adduct **1** is considered a model for the dormant poly(IBVE) terminal with a carbon−chlorine bond (cf. Scheme 1).[4−6] As reported in our previous paper,[6] $SnCl_4$ affords the carbocationic species from **1** at concentrations high enough to be readily detected by ^{1}H and ^{13}C NMR under the conditions where the IBVE polymerization is not living.

In the ^{119}Sn NMR analysis, $SnCl_4$ alone gave a sharp singlet at −160 ppm (Figure 1A). On addition of varying amounts of **1** into a cooled solution of $SnCl_4$, the spectra clearly changed, as seen in Figure 1B−F: the main peak (a) broadened and progressively shifted upfield with increasing $[\mathbf{1}]/[SnCl_4]$ ratio. It is reported that the ^{119}Sn nucleus shows a progressive upfield shift upon increasing coordination numbers: $SnCl_4$, −150 ppm; $SnCl_5^-$, −479 ppm; $SnCl_6^{2-}$, −732 ppm in CH_2Cl_2 at −30 °C.[8] The observed upfield shift thus indicates the generation of these tin=anionic species with higher coordination numbers via the interaction with the chlorine originated from **1**. The signal broadening also shows rapid interconversion among $SnCl_4$, $SnCl_5^-$, and $SnCl_6^{2-}$. These ^{119}Sn NMR spectra therefore supports the formation of ionic species from **1** and $SnCl_4$, as shown in Scheme 1 and in accordance with our former results by ^{1}H and ^{13}C NMR analyses.

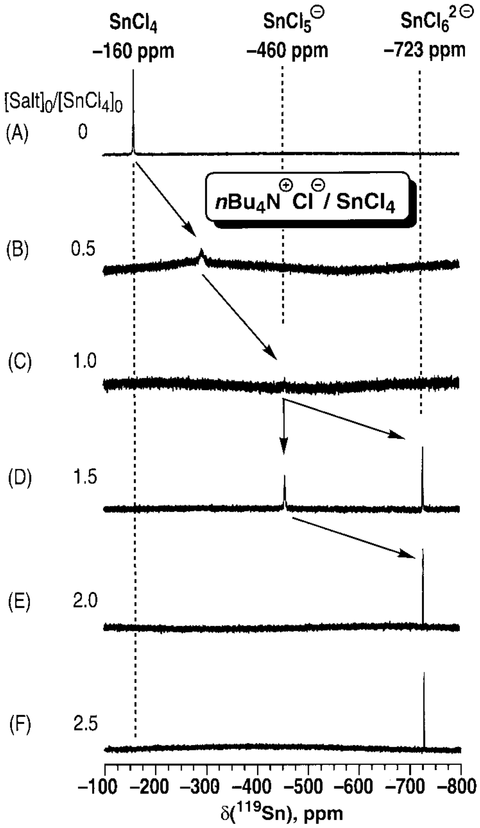


Figure 2. ^{119}Sn NMR spectra of the mixtures of $n$$Bu_4NCl$/$SnCl_4$ in CH_2Cl_2 at −78 °C: $[nBu_4NCl]_0/[SnCl_4]_0$ = 0/200 (A), 50/100 (B), 100/100 (C), 150/100 (D), 200/100 (E), 250/100 (F) mM.

However, in addition to the predominant broad signals (a), due to the interaction of $SnCl_4$ with the chlorine in **1**, minor sharp signals appeared (b and c), and their relative intensity increased at a higher $[\mathbf{1}]_0/[SnCl_4]_0$ ratio. This suggests other interactions between **1** and $SnCl_4$, as discussed later.

To investigate the interaction between the chlorine anion and $SnCl_4$ in detail, mixtures of $SnCl_4$ with more efficient chloride anion donors, $n$$Bu_4NCl$ and Ph_3CCl, were examined. In contrast to the **1**/$SnCl_4$ system, these mixtures led to a series of much simpler spectra (Figures 2 and 3). For example, addition of $n$$Bu_4NCl$ to $SnCl_4$ led to upfield shifts of the tin signal, as observed in the system with adduct **1**, and the shifts were larger for $n$$Bu_4NCl$ (Figures 2B−F) than for **1** (Figures 1B−F) at the same ratios of the chlorides to $SnCl_4$. (The weak signals in spectra 2B and 2C were due to the low solubility of the compound ($nBu_4N^+SnCl_5^-$) generated from $n$$Bu_4NCl$ and $SnCl_4$.)

Ph_3CCl gave simple and well-resolved spectra (Figure 3), due to the high solubility of the resultant salts such as $Ph_3C^+SnCl_5^-$. The mixtures were homogeneous

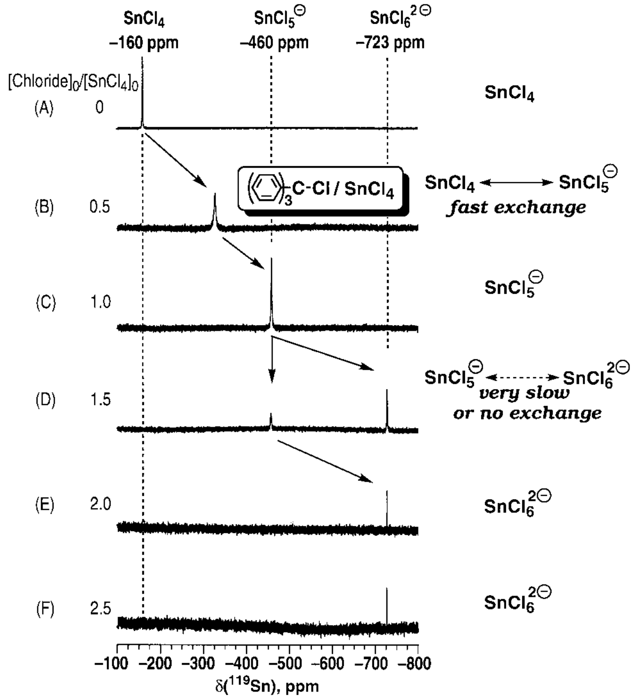


Figure 3. ^{119}Sn NMR spectra of the mixtures of $Ph_3CCl/SnCl_4$ in CH_2Cl_2 at −78 °C: $[Ph_3CCl]_0/[SnCl_4]_0 = 0/200$ (A), 100/200 (B), 200/200 (C), 300/200 (D), 400/200 (E), 500/200 (F) mM.

throughout all the $[Ph_3CCl]_0/[SnCl_4]_0$ ratios.

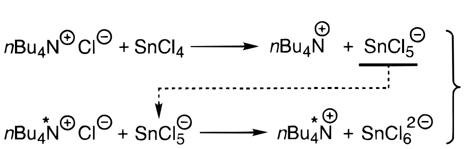
The results for both chloride donors (RCl) are thus virtually the same as summarized below:

(1) In the region where the initial amount of the donor is less than that of $SnCl_4$ ($[RCl]_0/[SnCl_4]_0 \leq 1$; spectra A−C, Figures 2 and 3), a single but broad signal is observed that progressively shifts upfield to reach the position for $SnCl_5^-$ at the ratio =1. Under these conditions, therefore, $SnCl_4$ reacts with the chloride anion of RCl to give $SnCl_5^-$. The broadened signals show a fast exchange equilibrium with $SnCl_4$.

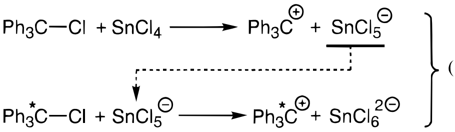
(2) When the donor is in excess over $SnCl_4$ (spectrum D), two signals appear, one for $SnCl_5^-$ and the other for $SnCl_6^{2-}$. In contrast to the $SnCl_4/SnCl_5^-$ pair, the penta- and hexa-coordinated species do not interconvert or, more likely, their interconversion is slow enough to be separately observed by ^{119}Sn NMR.

(3) Further addition of the salt ($[salt]_0/[SnCl_4]_0 \geq 2$; spectra E and F) converts all the tin species into $SnCl_6^{2-}$ to give a single and sharp signal at −723 ppm.

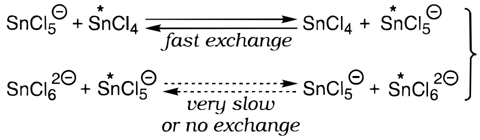
These interactions between $SnCl_4$ and Cl^- are summarized in eqs 1−3. The spectral changes in Figures 2 and 3 indicate that $SnCl_4$ quantitatively interacts with Cl^- arising from not only an ionic salt like nBu$_4$NCl but also covalent species such as Ph_3CCl to afford $SnCl_5^-$ and $SnCl_6^{2-}$ (eqs 1 and 2). With such stable cations as ammonium (nBu$_4$N$^+$) and trityl (Ph_3C^+), the exchange reaction between $SnCl_5^-$ and $SnCl_6^{2-}$ is slow, as indicated by two well-resolved sharp signals (−460 and −723 ppm), whereas the exchange between $SnCl_4$ and $SnCl_5^-$ is so fast that the two absorptions coalesced into one broad signal. The difference in the interconversion rate is probably due to the difference in the Lewis acidity between $SnCl_4$ and $SnCl_5^-$ (eq 3). A strong Lewis acid, $SnCl_4$, can easily abstract Cl^- from preformed $SnCl_5^-$ to induce the rapid interconversion. A weaker Lewis acid, $SnCl_5^-$, is not strong enough to rapidly abstract Cl^- from $SnCl_6^{2-}$.



$$\left.\begin{array}{l} n\mathrm{Bu_4N^{\oplus}Cl^{\ominus}} + \mathrm{SnCl_4} \longrightarrow n\mathrm{Bu_4}\overset{\oplus}{\mathrm{N}} + \underline{\mathrm{SnCl_5^{\ominus}}} \\ n\mathrm{Bu_4}\overset{*}{\mathrm{N}}{}^{\oplus}\mathrm{Cl^{\ominus}} + \mathrm{SnCl_5^{\ominus}} \longrightarrow n\mathrm{Bu_4}\overset{*\oplus}{\mathrm{N}} + \mathrm{SnCl_6^{2\ominus}} \end{array}\right\} \quad (1)$$

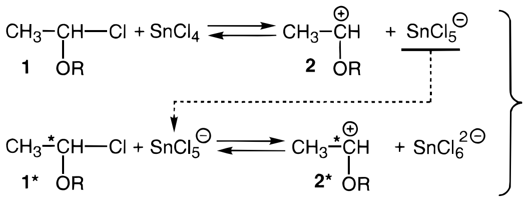


$$\left.\begin{array}{l} \mathrm{Ph_3C{-}Cl} + \mathrm{SnCl_4} \longrightarrow \mathrm{Ph_3C^{\oplus}} + \underline{\mathrm{SnCl_5^{\ominus}}} \\ \mathrm{Ph_3\overset{*}{C}{-}Cl} + \mathrm{SnCl_5^{\ominus}} \longrightarrow \mathrm{Ph_3\overset{*}{C}{}^{\oplus}} + \mathrm{SnCl_6^{2\ominus}} \end{array}\right\} \quad (2)$$



$$\left.\begin{array}{l} \mathrm{SnCl_5^{\ominus}} + \overset{*}{\mathrm{Sn}}\mathrm{Cl_4} \underset{\textit{fast exchange}}{\rightleftharpoons} \mathrm{SnCl_4} + \overset{*}{\mathrm{Sn}}\mathrm{Cl_5^{\ominus}} \\ \mathrm{SnCl_6^{2\ominus}} + \overset{*}{\mathrm{Sn}}\mathrm{Cl_5^{\ominus}} \underset{\textit{very slow or no exchange}}{\rightleftharpoons} \mathrm{SnCl_5^{\ominus}} + \overset{*}{\mathrm{Sn}}\mathrm{Cl_6^{2\ominus}} \end{array}\right\} \quad (3)$$

These observations on the two chlorides (Figures 2 and 3) will help the understanding of a series of the ^{119}Sn NMR spectra of the mixtures between **1** and $SnCl_4$ (Figure 1). The upfield shift in this series clearly shows the formation of ionic species such as $SnCl_5^-$ and $SnCl_6^{2-}$ via the interaction of $SnCl_4$ with the chlorine in **1** (eq 4). However, in contrast to the results with nBu$_4$NCl and Ph_3CCl, the extents of the upfield shift were small at the same ratios of the Cl-donors/$SnCl_4$. This indicates that a larger amount of **1** is needed for ionization of $SnCl_4$; i.e., **1** is a less effective Cl-anion donor than nBu$_4$NCl or Ph_3CCl due to the stronger covalent nature of its C−Cl bond.



$$\left.\begin{array}{l} \underset{\mathbf{1}}{\mathrm{CH_3{-}\underset{OR}{CH}{-}Cl}} + \mathrm{SnCl_4} \rightleftharpoons \underset{\mathbf{2}}{\mathrm{CH_3{-}\underset{OR}{\overset{\oplus}{CH}}}} + \underline{\mathrm{SnCl_5^{\ominus}}} \\ \underset{\mathbf{1^*}}{\mathrm{CH_3{-}\underset{OR}{\overset{*}{CH}}{-}Cl}} + \mathrm{SnCl_5^{\ominus}} \rightleftharpoons \underset{\mathbf{2^*}}{\mathrm{CH_3{-}\underset{OR}{\overset{*\oplus}{CH}}}} + \mathrm{SnCl_6^{2\ominus}} \end{array}\right\} \quad (4)$$

Interestingly, the main absorption (a) in the adduct **1** system is a single broad signal (E and F in Figure 1) even under the conditions where $SnCl_5^-$ and $SnCl_6^{2-}$ coexist; note that the systems with nBu$_4$NCl and Ph_3CCl gave the separate signals at the two tin species (D in Figures 2 and 3, respectively). This suggests a relatively rapid exchange reaction between $SnCl_5^-$ and $SnCl_6^{2-}$ in the presence of the carbocationic species derived from **1**. Because the alkoxycarbenium cation is more electrophilic than the stable nBu$_4$N$^+$ and Ph_3C^+, the chloride anion in $SnCl_6^{2-}$ can be readily abstracted by the carbocationic species and thereby $SnCl_6^{2-}$ is rapidly converted into $SnCl_5^-$, which in turn induces a rapid exchange reaction between them.

2. Interaction between $SnCl_4$ and Ether Oxygen. The spectra with **1**, D−F in Figure 1, exhibit two sharp signals (b and c) at −633 and −645 ppm, respectively, in addition to the main broad signal (a). These minor signals suggest the existence of other interactions of a tin nucleus with **1**, probably its ether oxygen. To clarify such possibility, mixtures of $SnCl_4$ and dibutyl ether (DBE), an ether without a reactive chlorine, were analyzed by ^{119}Sn NMR spectroscopy in CH_2Cl_2 at −78 °C (Figure 4).

On mixing $SnCl_4$ and DBE, the signal of $SnCl_4$ changes into a sharp upfield signal at −596 ppm (Figure 4B). This absorption suggests the generation of a

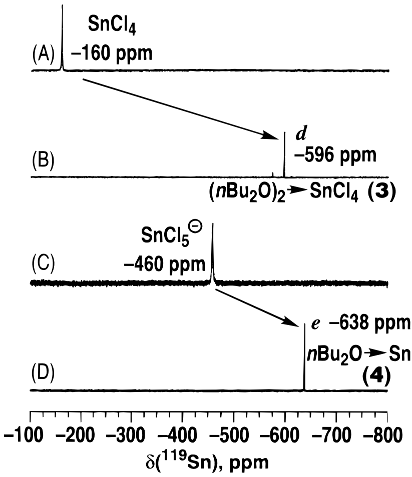
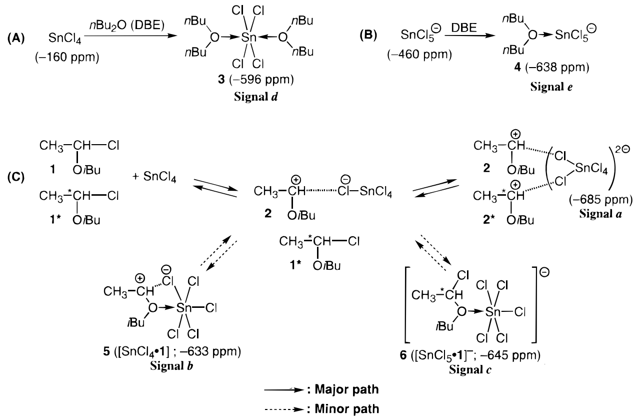


Figure 4. Interaction of the ether compound with $SnCl_4$ or $SnCl_5^-$: (A) $SnCl_4$ alone (200 mM); (B) DBE/$SnCl_4$ (1.0 M/200 mM); (C) $SnCl_4$/Ph_3CCl (200/200 mM); (D) DBE/$SnCl_4$/Ph_3CCl (1.0 M/200 mM/200 mM).

Scheme 2



compound like $SnCl_4(OBu_2)_2$ (**3** in Scheme 2A), where two molecules of DBE coordinate to one molecule of $SnCl_4$. Similar signals were also detected for diisobutyl ether and diethyl ether at −590 and −600 ppm, respectively. Such a hexacoordinated tin species with double ligands was also reported for a mixture of $SnCl_4$ and tributylphosphine, where $SnCl_4(PBu_3)_2$ absorbs at −573 ppm.[8] However, the signal of **3** is still more downfield than signals b and c in Figure 1. A possible signal of $SnCl_4(OBu_2)$ which has one molecule of ether coordinated to one $SnCl_4$ cannot be observed even under the conditions where the amount of DBE is equimolar to $SnCl_4$.

A similar analysis was also carried out for a mixture of $Ph_3C^+SnCl_5^-$ ($SnCl_4$/Ph_3CCl) and DBE. The anion $SnCl_5^-$ shows a sharp signal at −460 ppm (Figure 4C), which moves upfield into a sharp signal at −638 ppm on addition of DBE (Figure 4D). This can be ascribed to a hexacoordinated tin species, $Ph_3C^+[SnCl_5(DBE)]^-$ (**4** in Scheme 2B), by analogy of the chemical shift (−652 ppm) of a similar species, $n\mathrm{Bu}_4N^+[SnCl_5(PBu_3)]^-$,[8] and stands close to the signals b and c. Thus, the two sharp signals, b and c in Figure 1, are most probably ascribed to similar hexacoordinated species (**5** and **6** in Scheme 2C, respectively), where $SnCl_5^-$ interacts with the ether oxygen in either adduct **1** or its carbocation.

These ^{119}Sn NMR studies also suggest the interactions between $SnCl_4$ and the basic oxygen atoms of vinyl ether monomer and/or polymer in cationic polymerization. Such interactions will decrease the Lewis acidity of the metal halide to slow the polymerization. However, the concentration of such species is considered to be low as expected by their small peak intensity ratio. The main interaction between $SnCl_4$ and **1** occurs between the tin center and the chlorine in **1** to form $SnCl_5^-$ and $SnCl_6^{2-}$.

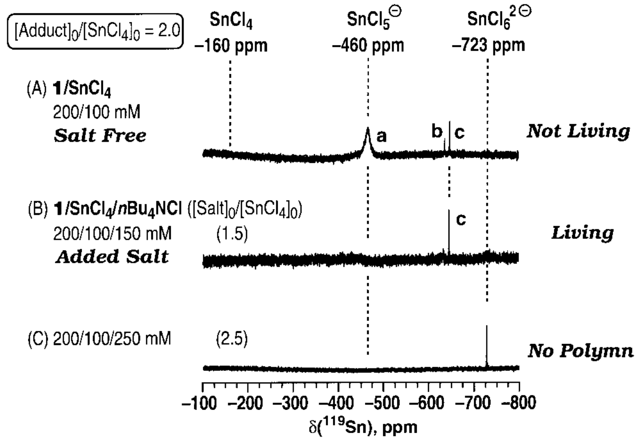


Figure 5. ^{119}Sn NMR spectra of the mixture of **1**/$SnCl_4$/$n\mathrm{Bu}_4NCl$ with varying $n\mathrm{Bu}_4NCl$ concentration in CH_2Cl_2 at −78 °C: $[\mathbf{1}]_0$ = 200 mM; $[SnCl_4]_0$ = 100 mM; $[n\mathrm{Bu}_4NCl]_0$ = 0 (A), 150 (B), 250 (C) mM.

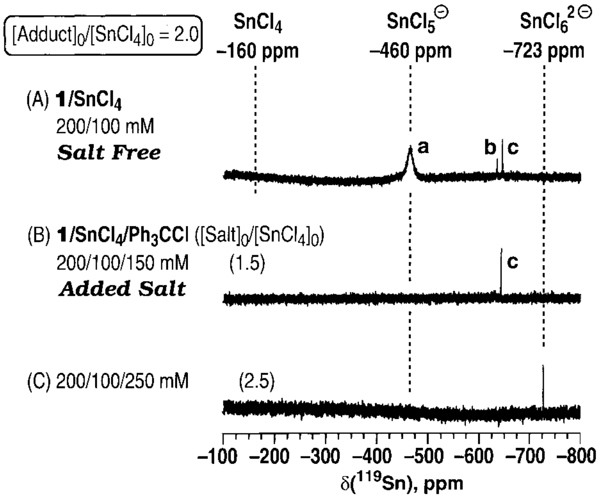


Figure 6. ^{119}Sn NMR spectra of the mixture of **1**/$SnCl_4$/Ph_3CCl with varying Ph_3CCl concentration in CH_2Cl_2 at −78 °C: $[\mathbf{1}]_0$ = 200 mM; $[SnCl_4]_0$ = 100 mM; $[Ph_3CCl]_0$ = 0 (A), 150 (B), 250 (C) mM.

3. Effects of Added Salts: Analysis of the Model Reaction for Living Polymerization (1/$SnCl_4$/$n\mathrm{Bu}_4NCl$ System). The addition of $n\mathrm{Bu}_4NCl$ can convert the **1**/$SnCl_4$-induced nonliving polymerization from nonliving to living or controlled, as demonstrated in our previous papers.[4,5] Also, our ^{1}H and ^{13}C NMR analysis of the model reaction revealed that the formation of the carbocationic species is suppressed under the conditions where living polymerization occurs.[4,5] However, it has not been shown why the cationic species is suppressed in the presence of $n\mathrm{Bu}_4NCl$. To clarify the effects of the added salt, mixtures of **1** with $SnCl_4$ in the presence of $n\mathrm{Bu}_4NCl$ or Ph_3CCl were analyzed by ^{119}Sn NMR (Figures 5−7). Herein it should be noted that in the salt-added polymerization of IBVE, the living nature depended on the $[n\mathrm{Bu}_4NCl]_0/[SnCl_4]_0$ ratio; in the region where $1 <$ the ratio < 2, the living polymerization

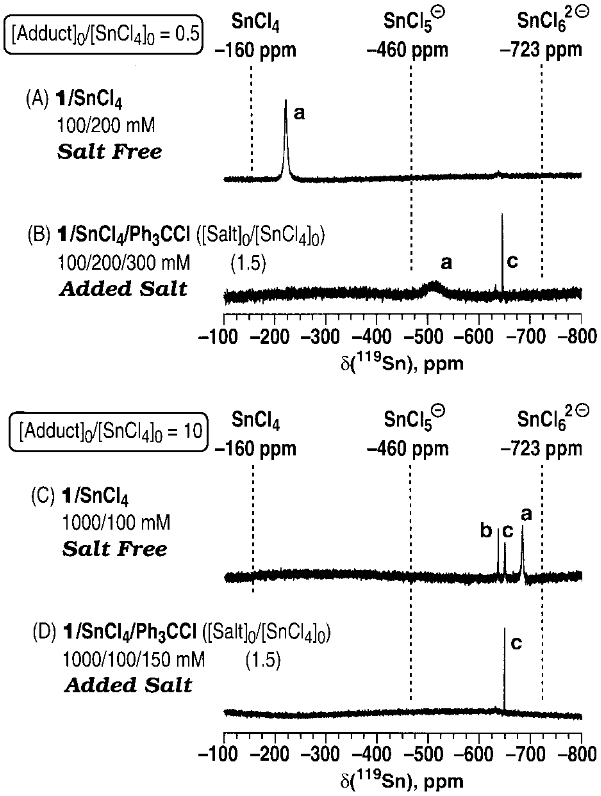
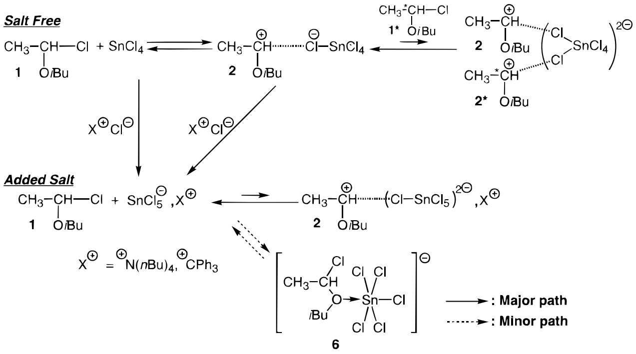


Figure 7. ^{119}Sn NMR spectra of the mixture of **1**/$SnCl_4$ in the absence and presence of Ph_3CCl in CH_2Cl_2 at −78 °C at two **1**/$SnCl_4$ mole ratios: $[\mathbf{1}]_0/[SnCl_4]_0 = 0.5$ (A and B), 10 (C and D); $[\mathbf{1}]_0 = 100$ mM (A and B), 1.0 M (C and D); $[SnCl_4]_0 = 200$ mM (A and B), 100 mM (C and D); $[Ph_3CCl]_0 = 300$ mM (B), 150 mM (D).

Scheme 3



proceeded, but when the ratio >2, no polymerization occurred. Namely, spectra A, B, and C in Figure 5 or 6 mimic the reagent concentrations for nonliving fast polymerization, living polymerization, and no monomer consumption, respectively.

As already discussed (see Figure 1), a mixture of **1** and $SnCl_4$ (200/100 mM; Figure 5A) gives the broad signal of $SnCl_5^-$ (a) and two minor signals (b and c). On addition of *n*Bu_4NCl (150 mM; 1.5 equiv to $SnCl_4$) to this mixture, the $SnCl_5^-$ signal (a) disappeared along with peak b, but a sharp signal (c) at −645 ppm remained: This signal is assigned to the $SnCl_5^-$ species interacting with ether oxygen as in **6** (Scheme 3). The use of the same amount of Ph_3CCl in place of *n*Bu_4NCl gives a similar spectrum (Figure 6B). These indicate that the addition of these salts (chloride donors) in molar excess over $SnCl_4$ converts it completely into a weaker Lewis acid, $SnCl_5^-$, which is in a slow exchange reaction with $SnCl_6^{2-}$, and this causes the disappearance of the $SnCl_5^-$ signal in Figures 5B and 6B. The exchange rate is larger than that in Figures 2D and 3D, where the two sharp signals of $SnCl_5^-$ and $SnCl_6^{2-}$ can be observed separately, but lower than in Figure 1E. On further addition of *n*Bu_4NCl or Ph_3CCl, there is only one signal of $SnCl_6^{2-}$ (Figures 5C and 6C) that cannot react with Cl^- any longer.

Additionally, mixtures of **1**/$SnCl_4$ and Ph_3CCl were examined at varying $[\mathbf{1}]_0/[SnCl_4]_0$ ratio but at a constant $[Ph_3CCl]_0/[SnCl_4]_0$ ratio (=1.5) (Figure 7). In Figure 7B (for the system with Ph_3CCl), there appears the broad signal (a) that indicates the existence of the exchange reaction between $SnCl_5^-$ and $SnCl_6^{2-}$, but could not be clearly observed in the salt-added system with a lower concentration of $SnCl_4$ (Figures 5B and 6B). The appearance of the broad signal is therefore due to the higher concentration (200 mM) of the tin species that promote the exchange reaction.

On the other hand, there is almost no significant difference among the spectra in the presence of 1.5 mol equiv of *n*Bu_4NCl or Ph_3CCl to $SnCl_4$ (Figures 5B, 6B, 7B, and 7D), in contrast to the spectra in the absence of the salts (Figures 5A, 6A, 7A, and 7C) that clearly differ from each other depending on the **1**/$SnCl_4$ ratio. This indicates that $SnCl_4$ preferentially interacts with the chloride donors, rather than **1**, to generate the weaker Lewis acid, $SnCl_5^-$, which subsequently interacts with **1** to induce living polymerization. Under these conditions where $[RCl]_0/[SnCl_4]_0 = 1.5$ (Figures 5B, 6B, 7B, and 7D; RCl = *n*Bu_4NCl or Ph_3CCl), there can be seen no sharp signal (b) at −633 ppm assigned to **5** where $SnCl_5^-$ interacts with the ether oxygen of the carbocationic species **2**. This also shows the suppression of the generation of the cationic species.

The ^{119}Sn NMR spectra under the conditions where the living polymerization proceeds (Figure 5B) have revealed that $SnCl_4$ is fully converted into higher coordinated species such as $SnCl_5^-$ and $SnCl_6^{2-}$. The suppression of the carbocationic species on addition of *n*Bu_4NCl is due to the substantial disappearance of the strong Lewis acid, $SnCl_4$, that can generate carbocationic species from **1** at relatively high concentration. As shown in Scheme 3, the added *n*Bu_4NCl serves as an efficient Cl^- donor and reacts with $SnCl_4$ to give $SnCl_5^-$ and/or with **2** to give **1**. Under such conditions, **1** is activated by a weaker Lewis acid, $SnCl_5^-$, where the concentration of **2** is very low.

4. Polymerization of IBVE with 1 in Conjunction with $SnCl_5^-$.

The above-described results for model reactions suggest the possibility of living polymerization with $SnCl_5^-$ because it can work as a weak Lewis acid. The polymerization of IBVE with **1** and *n*$Bu_4N^+SnCl_5^-$ was then investigated in CH_2Cl_2 at −78 °C. The salt was synthesized from $SnCl_4$ and *n*Bu_4NCl and used after purification (see Experimental Section).

The polymerization occurred rapidly and completed in 25 s. As shown in Figure 8, the number-average molecular weight of the polymers (M_n) increased in direct proportion to monomer conversion and agreed with the calculated values assuming that one molecule of **1** generates one living polymer chain. The molecular weight distributions of the polymers were narrow ($M_w/M_n = 1.1$) throughout the reaction. The molecular weights further increased in direct proportion to monomer conversion with keeping narrow MWDs even

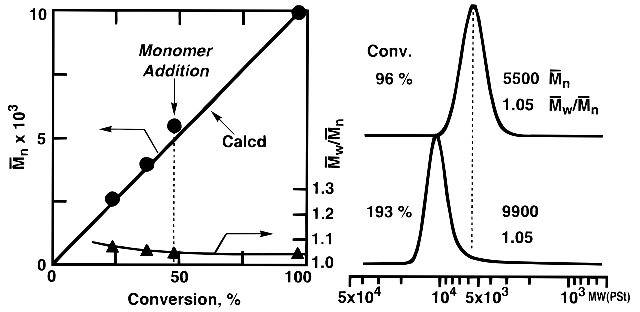
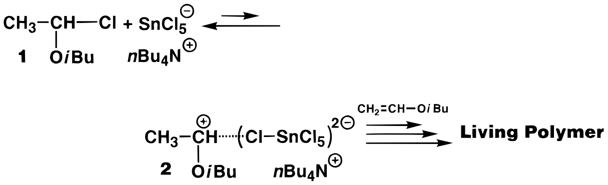


Figure 8. Polymerization of IBVE with $\mathbf{1}/n\mathrm{Bu_4N^+SnCl_5^-}$ in CH_2Cl_2 at −78 °C: $[M]_0 = 1.0$ M; $[\mathbf{1}]_0 = 20$ mM; $[n\mathrm{Bu_4N^+SnCl_5^-}]_0 = 10$ mM. The calculated M_n assuming the formation of one living polymer per **1** molecule is 5100.

after the addition of monomer. This indicates that $n\mathrm{Bu_4N^+SnCl_5^-}$ indeed induces living polymerization of IBVE (eq 5). The $\mathbf{1}/n\mathrm{Bu_4N^+SnCl_5^-}$ system indeed



(5)

employs an ammonium salt, but it acts as a Lewis acid ($SnCl_5^-$), unlike $n\mathrm{Bu_4NCl}$ in the $\mathbf{1}/SnCl_4$ system, which acts as a chlorine donor to give $SnCl_5^-$ from $SnCl_4$.

5. Conclusions. The in-situ direct ^{119}Sn NMR analysis of the model reactions has derived the following results. (1) A strong Lewis acid, $SnCl_4$, interacts with the chlorine atom in **1** to form higher coordinated tin species such as $SnCl_5^-$ and $SnCl_6^{2-}$ along with the formation of the carbocationic counterpart. (2) $SnCl_4$ interacts with **1** also via the other ways, where the tin center coordinates to the ether oxygen, but the interaction is minor in comparison to that with Cl^-. (3) $SnCl_4$ reacts quantitatively with an equimolar amount of an efficient Cl^- donor like $n\mathrm{Bu_4NCl}$ and Ph_3CCl to give $SnCl_5^-$ that also reacts quantitatively with another equimolar amount of the salts to generate $SnCl_6^{2-}$. (4) Under the conditions where the living polymerization proceeds, $SnCl_4$ is converted into a weakly acidic $SnCl_5^-$ via assistance of the added Cl^- donors, which ensures the suppression of the formation of the carbocationic species from **1**.

Experimental Section

Materials. $SnCl_4$ (Wako Chemicals, purity >97%) was distilled under reduced pressure over phosphorus pentoxide. $n\mathrm{Bu_4NCl}$ (Tokyo Kasei; purity >98%), Ph_3CCl (Wako Chemicals, purity >97%), and $n\mathrm{Bu_2O}$ (Wako Chemicals, purity >98%) were all used as received. $n\mathrm{Bu_4NCl}$ and Ph_3CCl 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. 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.[4]

Synthesis of the HCl−IBVE Adduct (1).[5] 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 CH_2Cl_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 CH_2Cl_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;[4,5] the observed value (∼1 M) further confirmed the quantitative formation of **1** from IBVE.

Synthesis of $n\mathrm{Bu_4N^+SnCl_5^-}$.[11] This compound was prepared by the reaction of $SnCl_4$ with $n\mathrm{Bu_4NCl}$. All the procedures were carried out under dry nitrogen in baked glassware equipped with three-way stopcocks. All solvents were used after purification and distillation. $n\mathrm{Bu_4NCl}$ (4.56 g, 16.4 mmol) was dissolved in CH_2Cl_2 (21 mL), and then $SnCl_4$ (1.92 mL, 16.4 mmol) was added to the solution at 0 °C. A small amount of CH_2Cl_2 was evaporated under reduced pressure. On addition of CCl_4 (60 mL) to the mixture, white solid ($n\mathrm{Bu_4N^+SnCl_5^-}$) precipitated from the solution. The precipitate was filtered off, washed with CCl_4 (20 mL × 2), and dried in vacuo at room temperature to give 7.74 g of $n\mathrm{Bu_4N^+SnCl_5^-}$ (yield = 88%). The salt was dissolved in CH_2Cl_2 and used for the IBVE polymerizations as an activator. Anal. Calcd for $C_{16}H_{36}NCl_5Sn$: C, 35.7; H, 6.74; N, 2.60. Found: C, 35.6; H, 6.88; N, 2.66.

^{119}Sn NMR Spectroscopy and Model Reactions. ^{119}Sn NMR spectra were recorded on a JEOL JNM-GSX270 spectrometer, operating at 100.7 MHz (acetone-d_6 for locking). The main parameters were as follows: spectral width = 161 290.3 Hz (1608 ppm), pulse width = 5.0 ms (45°), acquisition time + pulse delay = 3.0 s, data points = 65 536, number of transients = 1600 (80 min for one spectrum), complete decoupling from ^{1}H. The probe temperature was regulated with a variable-temperature apparatus JEOL NM-GVT3 (temperature fluctuation ≤1 deg). The reaction was started by adding a solution of **1** (in CH_2Cl_2; 0.6 mL) to a prechilled solution of $SnCl_4$ (in CH_2Cl_2; 2.4 mL) in a septum-capped NMR tube (10-mm o.d.) under dry nitrogen via dry syringes at −78 °C. For the reaction in the presence of a $n\mathrm{Bu_4NCl}$ 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 Me_4Sn (0 ppm as a singlet) as an external standard dissolved in acetone-d_6 in a capillary.

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 the $n\mathrm{Bu_4N^+SnCl_5^-}$ salt (in CH_2Cl_2; 0.50 mL) via dry syringes into a monomer solution (in CH_2Cl_2; 4.0 mL) containing IBVE (0.66 mL) and CCl_4 (0.20 mL). 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 with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymers. The MWD, M_n, and M_w/M_n ratios of the polymers were measured by size-exclusion chromatography (SEC) in chloroform at room temperature on three polystyrene gel columns (Shodex K-802 + K-803 + K-804) that were connected to a JASCO PU-980 precision pump and a JASCO 830-RI refractive index detector. The columns were calibrated against 10 standard polystyrene samples (M_n = 800−300 000; M_w/M_n = 1.03−1.10) as well as styrene oligomers (tetramer, trimer, and dimer) and monomer.

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