

Living Cationic Polymerization of Isobutyl Vinyl Ether by Protonic Acid/Zinc Halide Initiating Systems: Evidence for the Halogen Exchange with Zinc Halide in the Growing Species¹

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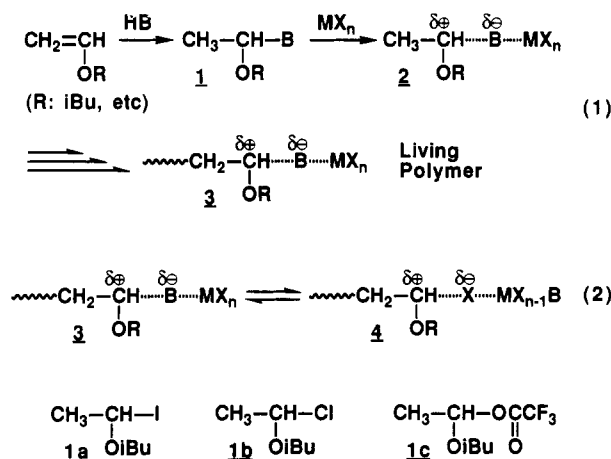
ABSTRACT: Living cationic polymerization of isobutyl vinyl ether (IBVE) was achieved by protonic acid/zinc halide (HB/ZnX₂; B = I, Cl, OCOCF₃, X = I, Br, Cl) initiating systems. The rate decreased in the order: HI/ZnI₂ > HI/ZnCl₂ ≈ HCl/ZnI₂ ≈ HCl/ZnBr₂ > HCl/ZnCl₂ >> CF₃CO₂H/ZnCl₂. The number-average molecular weight of the polymers was directly proportional to monomer conversion and in good agreement with the calculated value assuming that one polymer chain forms per HB molecule. The molecular weight distribution of the polymer was very narrow ($\bar{M}_w/\bar{M}_n \leq 1.1$). As model reactions of these living polymerizations, a series of mixtures of the HB-IBVE adduct 1 and ZnX₂ were directly analyzed by ¹H NMR spectroscopy. The two methylene protons (–OCH₂–) of 1 [CH₃C*H(OCH₂CH(CH₃)₂)B], which are not chemical shift equivalent because of the chiral α-carbon C*, are found interchangeable in the presence of ZnX₂ due to the interaction of the C–B bond with ZnX₂ in the activated form 3 (C^{δ+}...B^{δ–}...ZnX₂). When B in 1 and X in ZnX₂ are both halogens, the exchange reaction between B and X occurs to give another adduct [CH₃CH(OCH₂CH(CH₃)₂)X], whereas such an exchange was absent for the adduct with B = OCOCF₃. These observations by ¹H NMR were consistent with the results of the polymerizations of IBVE by the HB/ZnX₂ system and showed that the activated species 3 is at least partly ionic.

Introduction

Living cationic polymerization of vinyl compounds has been accomplished with a variety of initiating systems that are based on our concept of carbocation stabilized through nucleophilic interaction.^{2,3} One family of the typical initiating systems in this line involves combinations of a protonic acid [HB (B = halogen, CF₃CO₂, etc.)] and a weak Lewis acid [MX_n; I₂, ZnX₂ (X = halogen), etc.].^{4–7} As shown in eq 1, the HB/MX_n initiating systems invariably generate the initiating species 1 prior to polymerization, and MX_n then “activates” the inert carbon–B bond of 1 (as in 2) to commence living propagation via the growing species 3, which involves a similar activated structure (~~~C^{δ+}...B^{δ–}...MX_n). Thus, HB is called “initiator” and MX_n “activator”. According to this mechanism, the growing carbocation is considered to be stabilized by the nucleophilic binary counteranion, B^{δ–}...MX_n.³ Though differing in HB/MX_n combinations and sometimes in terminology, similar systems for living cationic polymerizations have been reported by other research groups.²

In parallel with these developments of various HB/MX_n initiating systems, attempts have been made to clarify the nature of the living propagating species generated therefrom. For example, we published the first spectroscopic and kinetic analysis on the living polymerization of isobutyl vinyl ether (IBVE) initiated with the HI/I₂ system⁸ and established the quantitative and selective formation of a HI-IBVE adduct [CH₃CH(OiBu)I; 1a] as well as the initiator/activator scheme (eq 1) where HI (initiator) forms an inert carbon–iodine terminal to be activated by coexisting molecular iodine (activator). Similar conclusions have been reached for the HI/ZnX₂ systems primarily by kinetic analyses.^{5,6}

More recently, several research groups further studied, spectroscopically and kinetically, the cationic living polymerization and related model reactions with similar HB/MX_n initiating systems, where in most cases HB is employed in the form of the adduct (CH₃CHRB) with



such monomers as IBVE, 2-chloroethyl vinyl ether (CEVE), and styrene. The typical systems (monomer–HB adduct/activator) include IBVE–CF₃CO₂H/CF₃CO₂H (excess),⁹ IBVE–CF₃CO₂H/Zn(OCOCF₃)₂,¹⁰ CEVE–HX/ZnX₂ (X = I, Cl),^{11,12} styrene–CF₃CO₂H/CF₃CO₂H (excess),¹³ and styrene–CH₃CO₂H/BCl₃.¹⁴

While conflicting in some aspects, these studies have indeed shown in common the existence of an interaction of MX_n with the carbon–B terminal bond^{8–18} and suggested some ionic character of the growing species.^{11–13} However, the nature of the living growing end, often illustrated schematically as 3 (~~~C^{δ+}...B^{δ–}...MX_n), still remains obscure, specifically in terms of the role of the MX_n activator and the ionic versus covalent character of the activated species. Closely related to these is the possibility of counteranion exchange (eq 2), namely, the replacement of the anionic moiety –B with the halogen X of the MX_n in the activated growing end 3, as discussed recently.^{14–18} For example, this last problem has been quite recently studied by us with use of trimethylsilyl halide (Me₃SiY)/ZnX₂ systems, but the conclusions are obscured by the rather slow and incomplete initiation from Me₃SiCl.¹⁸

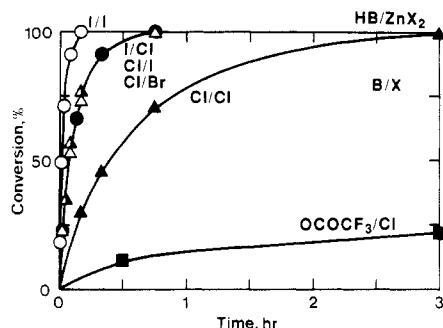


Figure 1. Time-conversion curves for the polymerization of IBVE by HB/ZnX₂ in toluene at -40 °C: [M]₀ = 0.38 M; [HB]₀ = 5.0 mM; [ZnX₂]₀ = 2.5 or 5.0 (only for CF₃CO₂H) mM. HB/ZnX₂ = HI/ZnI₂ (○); HI/ZnCl₂ (●); HCl/ZnI₂ (Δ); HCl/ZnBr₂ (▲); HCl/ZnCl₂ (▲); CF₃CO₂H/ZnCl₂ (■).

With such a current status of the understanding in mind, we herein analyzed a series of mixtures of the HB-IBVE adduct (1a-c) with ZnX₂ by ¹H NMR spectroscopy as well as by polymerization experiments [HB = HI (1a), HCl (1b), CF₃CO₂H (1c); ZnX₂ = ZnI₂, ZnBr₂, ZnCl₂]. These adduct 1/ZnX₂ systems are well-suited for the study of the living growing end 3 for the following reasons: (a) the 1/ZnX₂ systems can actually initiate living cationic polymerization of IBVE; (b) adduct 1 is a model compound for the living polymer with a ~CH(OiBu)-B terminal; and (c) various combinations of the anion B and the halogen X in the 1/ZnX₂ systems, particularly those where B differs from X, may give crucial evidence for the nature of the activated species 3 and the counteranion (halogen) exchange with ZnX₂ activator (eq 2).

Results and Discussion

1. Polymerization with HB/ZnX₂. Prior to ¹H NMR analysis, we examined the polymerization of IBVE by HB/ZnX₂ (B = I, Cl, OCOCF₃; X = I, Br, Cl) in toluene at -40 °C, where the concentrations of B and X are the same ([B] = [X] = 5.0 mM; [M]₀/[HB]₀/[ZnX₂]₀ = 380/5.0/2.5 mM) except for the CF₃CO₂H/ZnCl₂ system ([CF₃CO₂H]₀/[ZnCl₂]₀ = 5.0/5.0 mM). In all cases, the polymerizations were quantitative, without induction, and of first order with respect to monomer. The rate decreased in the order HI/ZnI₂ > HI/ZnCl₂ ≈ HCl/ZnI₂ ≈ HCl/ZnBr₂ > HCl/ZnCl₂ >> CF₃CO₂H/ZnCl₂ (Figure 1). Note that the CF₃CO₂H-based system led to the slowest process (100% conversion in 4 days), although it employs twice as much ZnCl₂ as for the other systems.

Figure 2 shows the number-average molecular weight (\bar{M}_n) and the molecular weight distribution (MWD) of the polymers obtained with the six initiating systems. Without exceptions, the \bar{M}_n values of the polymers were directly proportional to monomer conversion and in good agreement with the calculated values assuming that one polymer chain forms per HB molecule. The MWD stayed very narrow throughout the reaction ($\bar{M}_w/\bar{M}_n \leq 1.1$). Thus, these HB/ZnX₂ systems all led to living polymerization of IBVE. Similar results have also been reported.^{5,6,11}

More important, as shown in Figure 1, the polymerization rate depends not only on HB but also on ZnX₂. With HB/ZnCl₂, the rate decreased with varying HB in the order HI > HCl > CF₃CO₂H, which reflects the order of the reactivity of the terminal dormant bond ~CH(OiBu)-B.^{6,11,18} With HCl/ZnX₂, on the other hand, the rate was in the order for three zinc halides ZnI₂ ≈ ZnBr₂ > ZnCl₂. Apart from the difference in the Lewis acidity of ZnX₂, this dependence on ZnX₂ may be explained by the occurrence of the halogen exchange between B in the

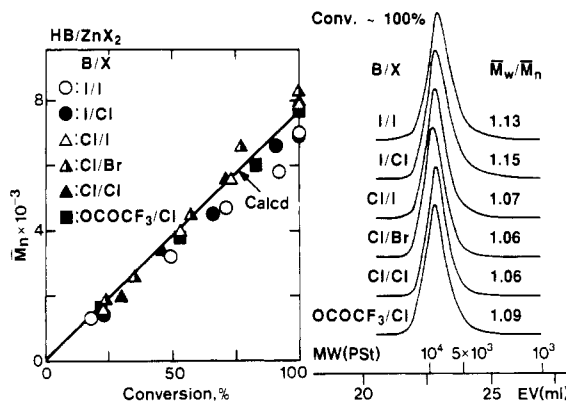


Figure 2. \bar{M}_n , \bar{M}_w/\bar{M}_n , and MWD curves of poly(IBVE) obtained with HB/ZnX₂ in toluene at -40 °C: [M]₀ = 0.38 M; [HB]₀ = 5.0 mM; [ZnX₂]₀ = 2.5 or 5.0 (only for CF₃CO₂H) mM. HB/ZnX₂ = HI/ZnI₂ (○); HI/ZnCl₂ (●); HCl/ZnI₂ (Δ); HCl/ZnBr₂ (▲); HCl/ZnCl₂ (▲); CF₃CO₂H/ZnCl₂ (■). The diagonal solid line indicates the calculated \bar{M}_n assuming the formation of one living polymer per HB molecule.

polymer terminal and X in the zinc halide; and with ZnI₂ and ZnBr₂, the exchange process will convert the C-Cl bond generated from HCl into the more reactive C-I or C-Br bond, respectively. Accordingly, if the halogen exchange occurs faster than the polymerization and if the distribution of halides does not depend on where they come from (HB or ZnX₂), then the HCl/ZnI₂ and HI/ZnCl₂ systems will give the same polymerization rate as long as the concentrations of B and X are the same. This expectation is indeed corroborated by the completely overlapping time-conversion curves for HCl/ZnI₂ (open triangles) and HI/ZnCl₂ (filled circles) shown in Figure 1. The possibility of the halogen exchange will be discussed more in detail later in this paper on the basis of ¹H NMR analyses.

2. ¹H NMR Analysis. Formation of Adducts 1. Previous studies have revealed that HB adds to vinyl ethers to give adducts 1 prior to polymerization (eq 1).^{7,8,11,19} We herein synthesized a series of adducts 1 [CH₃C*H(OCH₂-CH(CH₃)₂)B; B = I (1a), Cl (1b), OCOCF₃ (1c)] from HB and IBVE (see the Experimental Section). The ¹H NMR spectra of 1, along with peak assignments, are shown in Figure 3 (in toluene-d₈/n-hexane = 3/1, at -40 °C).²⁰ These spectra are similar to those reported for the adducts of HB (HI,^{8,19} HCl,¹¹ and CF₃CO₂H⁷) with IBVE and related vinyl ethers. It is worth noting that (1) the chemical shifts of the methine proton b adjacent to B are clearly dependent on B (OCOCF₃ ≥ I > Cl) and thus mutually distinguishable and that (2) the two methylene protons c₁ and c₂ (-OCH₂-) are not chemical shift equivalent because of the chiral α-carbon C*.^{9,21} These spectra indicate the formation of 1, though the upfield signals (1-2 ppm) of 1 overlapped with those of n-hexane as solvent.²⁰

Homo-Halogen Systems: CH₃CH(OiBu)-X/ZnX₂ (B = X). As a simple combination, a mixture of 1 [CH₃-CH(OiBu)B] and ZnX₂ where B and X are the same halogen ("homo" combination, B = X = Cl or I) was first analyzed by ¹H NMR spectroscopy at various temperatures in toluene-d₈ containing n-hexane (10 vol %) and diethyl ether (10 vol %).²² ([1]₀/[ZnX₂]₀ = 100/20 mM).

Figure 4 shows the spectra (2.5-6 ppm) of the mixtures of the chloride with ZnCl₂ [1b (B = Cl)/ZnCl₂]. On addition of ZnCl₂ (in Et₂O) to a solution of 1b (Figure 4A) at -78 °C, any signals of 1b did not change, though the absorption of Et₂O interfered with the signals of 1b (Figure 4B). When the temperature of this solution was raised from -78 to -40 °C, however, the two methylene signals

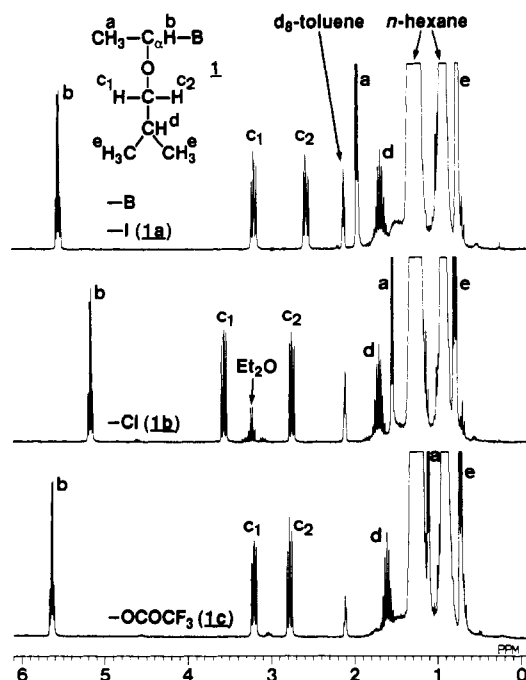


Figure 3. ^1H NMR spectra of $[1]_0 = 250$ mM in toluene- d_8 / n -hexane (3/1) at -40°C : 1a (B = I), 1b (B = Cl), 1c (B = OCOCF_3).

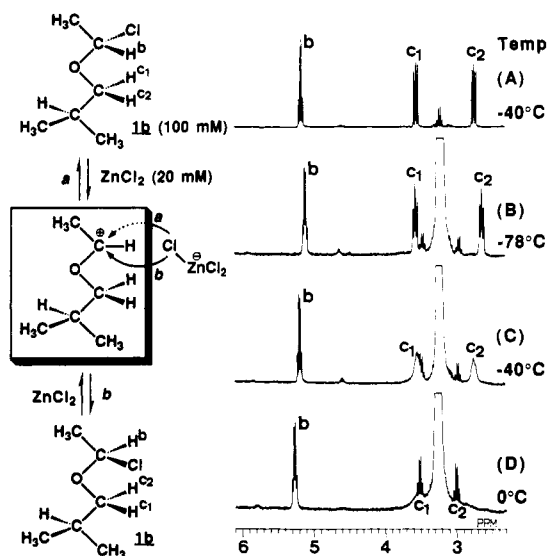


Figure 4. ^1H NMR spectra of $[1b]_0 = 250$ mM in toluene- d_8 / n -hexane (3/1) at -40°C (A) and the mixture of $[1b]_0 = 100$ mM and $[\text{ZnCl}_2]_0 = 20$ mM toluene- d_8 / n -hexane/ Et_2O (8/1/1) at -78°C (B), -40°C (C), and 0°C (D).

c_1 and c_2 became broader, whereas the others (e.g., H^b) remained unchanged (Figure 4C), and at 0°C the two signals became much broader (Figure 4D). In contrast, such broadening in the methylene signals of 1b was absent without ZnCl_2 , even at a temperature as high as 60°C .

These facts indicate that the two methylene protons interchange with each other in the presence of ZnCl_2 and, more important, that the interchange most likely accompanies the interconversion between the l and d isomers of 1. Because such a racemization should involve a weakening of the carbon–chlorine bond of 1 assisted by ZnCl_2 , the interchange is ascribed to the interaction of the C–Cl bond with ZnCl_2 in an at least partly ionic form $\text{C}^{\delta+}\cdots\text{Cl}^{\delta-}\cdots\text{ZnCl}_2$ (2, in eq 1). This type of interchange has been found in the system with 1c (B = OCOCF_3) and excess $\text{CF}_3\text{CO}_2\text{H}$,⁹ where $\text{CF}_3\text{CO}_2\text{H}$ serves in a similar manner as ZnCl_2 .

Thus, although any signals of the activated form 2 (eq 1) were not found in the ^1H NMR spectra, it probably has

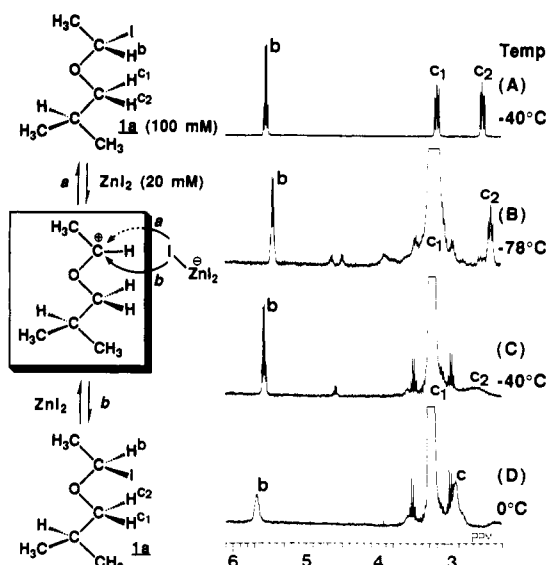


Figure 5. ^1H NMR spectra of $[1a]_0 = 250$ mM in toluene- d_8 / n -hexane (3/1) at -40°C (A) and the mixture of $[1a]_0 = 100$ mM and $[\text{ZnI}_2]_0 = 20$ mM in toluene- d_8 / n -hexane/ Et_2O (8/1/1) at -78°C (B), -40°C (C), and 0°C (D).

an ionic rather than covalent character. The reason of the failure to observe 2 is probably that the period where the dormant species is activated is very short; in other words, the time-averaged concentration of 2 is very low. That is consistent with the kinetics of the polymerization by HI/ZnX_2 .⁶

Another homo-halogen combination, 1a (B = I)/ ZnI_2 , was also analyzed by ^1H NMR. When ZnI_2 was mixed with 1a (Figure 5A), the methylene signal c_2 became slightly broader even at -78°C (Figure 5B). With the temperature raised to -40°C , it became far broader (Figure 5C), and at 0°C the two methylene peaks (c_1 and c_2) coalesced into a single broad peak (Figure 5D). Comparisons of Figure 5 (for HI/ZnI_2) with Figure 4 (for HCl/ZnCl_2) further showed that the methylene signals with the iodide (1a) broaden at a lower temperature than those with the chloride (1b). The faster the two methylene protons interchange, the broader the two signals, and finally they merged into a single signal. These observations are closely related to the fact that the polymerization with HI/ZnI_2 is faster than that with HCl/ZnCl_2 (see Figure 1).

Hetero-Halogen System: $\text{CH}_3\text{CH}(\text{OiBu})\text{-I}/\text{ZnCl}_2$ (B \neq X). A mixture of 1 and ZnX_2 , where B and X are different ("hetero" combination), was analyzed by ^1H NMR in the same manner.

In the spectrum of the 1a (B = I)/ ZnCl_2 system at -78°C (Figure 6A), there are clearly two quartets; one (5.6 ppm) is of course attributed to the methine proton b of 1a (B = I) originally present and the other (5.3 ppm) to the methine proton b' of another adduct, 1b (B = Cl). Similarly the methylene protons c_1' and c_2' of the chloride adduct 1b appeared. These assignments are based on Figure 1. It was proved that the exchange reaction between the iodine originating from 1a and the chlorine in ZnCl_2 occurs. When the temperature was raised to -40°C (Figure 6B), not only the methylene signals c_2 , c_1' , and c_2' but also the two methine peaks b and b' each broadened. When the temperature was further raised to 0°C (Figure 6C), the two methine signals merged into an averaged single broad peak, which is attributed to a rapid interchange of 1a and 1b. When the temperature was lowered to -40°C again (Figure 6D), the spectrum almost reverted to that in Figure 6B. This indicates that the ratio of 1a to 1b is

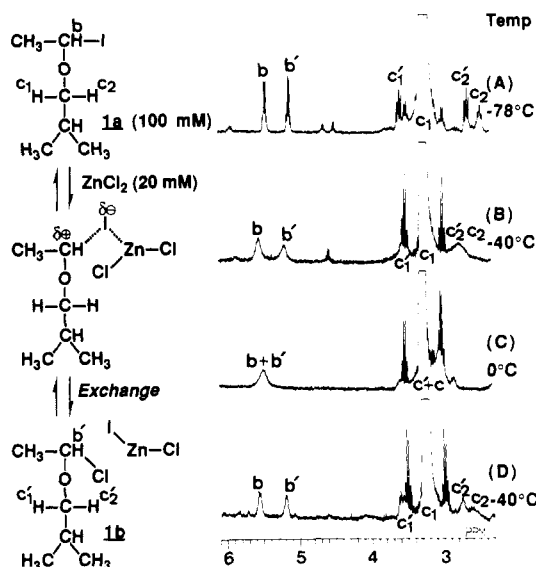


Figure 6. ¹H NMR spectra of the mixture of $[1a]_0 = 100$ mM and $[ZnCl_2]_0 = 20$ mM in toluene-*d*₈/*n*-hexane/Et₂O (8/1/1) at -78 °C (A), -40 °C (B), 0 °C (C), and -40 °C (D).

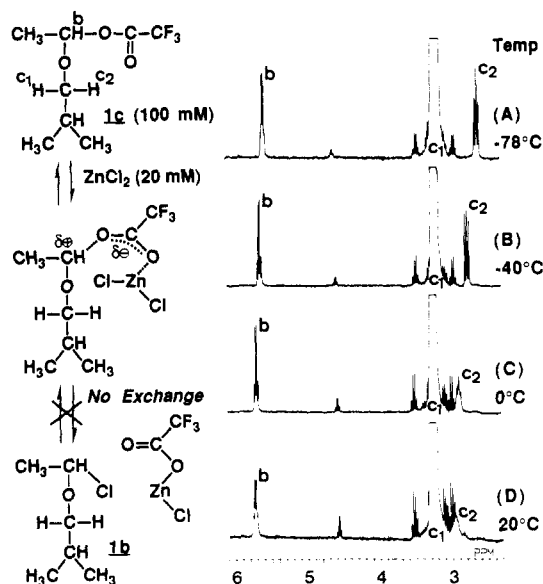


Figure 7. ¹H NMR spectra of the mixture of $[1c]_0 = 100$ mM and $[ZnCl_2]_0 = 20$ mM in toluene-*d*₈/*n*-hexane/Et₂O (8/1/1) at -78 °C (A), -40 °C (B), 0 °C (C), and 20 °C (D).

simply determined by temperature without a thermal hysteresis.

Hetero Systems: CH₃CH(OiBu)-OCOCF₃/ZnCl₂. As another hetero combination, the spectra of 1c (B = OCOCF₃)/ZnCl₂ were shown in Figure 7. Unlike the observation for the 1a (B = I)/ZnCl₂ system, 1c remained unchanged even in the presence of ZnCl₂ at -78 °C (Figure 7A). On raising the temperature from -78 °C through -40 °C up to +20 °C (Figure 7B–D), the single methine (–CHOCOCF₃) signal b was observed, and the absorption of 1b (B = Cl), which would generate from 1c and ZnCl₂, was not detected at all. However, the methylene protons became broader at a higher temperature (Figure 7D), as in the other systems (Figures 5 and 6). These facts demonstrate that the C–OCOCF₃ bond of 1c is indeed activated by (or in interaction with) ZnCl₂ but that the OCOCF₃ moiety is not substituted with the chlorine in ZnCl₂.

Extent of Counteranion Exchange. Other hetero combinations CH₃CH(OiBu)–B/ZnX₂ (B ≠ X) were also

Table I
Extent of Counteranion Exchange

		$\% \text{ Exchange} = \frac{[1'(C-X)]}{2[ZnX_2]_0} \times 100$			
		ZnX ₂	ZnI ₂	ZnBr ₂	ZnCl ₂
1 (C–B)					
1a (C–I)			—	70%	~100%
1b (C–Cl)			30%	10%	—
1c (C–OCOCF ₃)			0%	0%	0%

$[1(C-B)]_0 = 100$ mM; $[ZnX_2]_0 = 20$ mM; *d*₈-toluene, -40 °C, for 10 min.

analyzed in a similar way. From the peak intensity ratio of the two methine protons b and b' (e.g., Figure 6B), the extent of counteranion (halogen) exchange can be calculated by the following equation: $\text{Exchange} (\%) = [(b'/b + b')/(2[ZnX_2]_0/[1]_0)] \times 100$; herein 100% exchange implies that all of the halogen X in ZnX₂ has been incorporated in the adduct 1 to give CH₃CH(OiBu)–X. As seen from Table I, the C–I bond in adduct 1a is completely converted into C–Cl via the activation by ZnCl₂ and also into C–Br by ZnBr₂ to a considerable extent. In contrast, the C–Cl counterpart in 1b is hardly transformed into C–I or C–Br, and the C–OCOCF₃ bond of 1c cannot be replaced with a halogen (X = I, Br, Cl) at all even though the ester moiety is clearly in interaction with the ZnX₂ activator. Namely, the weaker the parent acid HB (CF₃CO₂H < HCl < HI) of 1 or the smaller the reactivity of the C–B bond, the less the C–B bond is substituted with X in ZnX₂. This order agrees with that of the nucleofugacity of B[–].²³ As for ZnX₂, the weaker the parent protonic acid HX (HCl < HBr < HI) of the zinc salt, the more X substitutes the C–B bond. Thus, the data in Table I may be systematically explained on the basis of the relative affinities of B and X toward carbon and zinc atoms.

In conclusion, this study has demonstrated that zinc halide activator not only interacts with the terminal C–halogen bond of polymer 3 (eq 1) but also undergoes a rapid halogen (counteranion) exchange with the terminal halogen (cf. Figure 6 and Table I). Coupled with the ether methylene exchange (Figures 4–7), this observation strongly suggests that the activated species 3 is at least partly ionic; namely, when 3 reacts with a monomer, the living propagation proceeds via an ionic intermediate. Even for the 1c/ZnX₂ systems, where the OCOCF₃ part does not exchange with halogen, if the mechanism of the interchange of methylene protons were concerted, it would be much complicated. Therefore, it is also concluded that the activated species in the polymerization with 1c/ZnX₂ has an ionic character.

The ¹H NMR analysis also indicates that most of growing species exist in the form ~ ~ ~CH(OR)–B, which is per se incapable of propagating. Thus, the dormant species in the living polymerization based on “stabilization of a carbocation by a counteranion” is a neutral species, in contrast to the fact that the dormant species in the polymerization by CF₃SO₃H/alkyl sulfide, which is based on “stabilization of a carbocation by an externally added based”, is an onium ion.²⁴

Experimental Section

Materials. Hydrogen chloride (Aldrich; 1.0 M solution in diethyl ether) was used as received. CF₃CO₂H (Nacalai Tesque; purity >99%) was diluted with *n*-hexane, without further purification. Hydrogen iodide was obtained as an *n*-hexane solution by dehydration of commercial hydriodic acid (Wako

Chemicals) with phosphorus pentoxide.⁴ The concentrations of $\text{CF}_3\text{CO}_2\text{H}$ and HI were determined by titration just before use. Zinc halides ZnX_2 (Aldrich) were all used as received. Purity is as follows: ZnI_2 , >99.99%; ZnBr_2 , 99.999%; ZnCl_2 , 99.999%. They were vacuum dried at least overnight just before use and dissolved in dry and distilled diethyl ether 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. Toluene- d_8 (Aldrich; purity >99%) was dried overnight over baked molecular sieves (3 Å) just before use. Toluene 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 Diethylether (Dojin; purity >99%, anhydrous) 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 ZnX_2 (in diethyl ether; 0.50 mL) via dry syringes into a monomer solution (in toluene; 4.0 mL) containing IBVE (0.25 mL) and CCl_4 (0.25 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 10% aqueous sodium thiosulfate 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 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 M_n and M_w/M_n values of the polymers were calculated from size-exclusion eluograms on the basis of a polystyrene calibration.

Synthesis of the HB-IBVE Adduct (1). The HCl -IBVE adduct **1b** ($B = \text{Cl}$) was synthesized by magnetically stirring a mixture of HCl (in diethyl ether) and IBVE ($\text{HCl}/\text{IBVE} = 1.1/1$) at 0 °C for 10 min, the diethyl ether and unreacted HCl in excess were distilled off at ca. 0 °C under reduced pressure, and the isolated **1b** was diluted with n -hexane (ca. 0.8 M) and then sealed in brown ampules under nitrogen.¹¹ The concentration of **1b** was determined by titrating the chloride by the Volhard method.¹⁸ The HI -IBVE adduct **1a** ($B = \text{I}$) was prepared by an equimolar reaction of HI (in n -hexane) and IBVE in toluene- d_8 at -78 °C.^{8,19} The trifluoroacetate **1c** ($B = \text{OCOCF}_3$) was synthesized by magnetically stirring an equimolar mixture of $\text{CF}_3\text{CO}_2\text{H}$ (in n -hexane) and IBVE (in toluene- d_8) at 0 °C.⁷ The clean and quantitative formation of these adducts (**1a-c**) was confirmed by ^1H NMR spectroscopy (see Figure 3).

^1H NMR Spectroscopy. ^1H NMR spectra were recorded on a JEOL JNM-GSX270 spectrometer, operating without decoupling at 270.7 MHz (toluene- d_8 for locking). The main parameters were as follows: spectral width = 6002.4 Hz (22.17 ppm), pulse width = 4.3 μs (45°), acquisition time + pulse delay = 30 s, data points = 32 768, number of transients = 16 (8 min for one spectrum). The probe temperature was regulated with a variable-temperature apparatus NM-GVT3 (temperature fluctuation ≤ 1 deg). The reaction was started by adding a solution of ZnX_2 (in diethyl ether; 0.06 mL) to a prechilled solution of **1** (in toluene- d_8 / 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 ($[\text{ZnX}_2]_0 = 100/20$ mM). The tube was vigorously shaken at -78 °C and immediately placed in the thermostated probe. The chemical shifts were determined with reference to the methyl group of toluene- d_8 (2.09 ppm).

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References and Notes

- (1) Living Cationic Polymerization of Vinyl Ethers by Electrophile/Lewis Acid Initiating Systems. Part 9. For part 8: see ref 25. This work was presented in part at the following symposia: (a) The 40th Symposium on Macromolecules, the Society of Polymer Science, Japan, Okayama, Japan, Nov 1991; Paper 3C06: Kamigaito, M.; Yamaoka, K.; Sawamoto, M.; Higashimura, T. *Polym. Prepr. Jpn., Engl. Ed.* 1991, 40 (2), E822. (b) The 10th International Symposium on Cationic Polymerization and Related Processes, Hungary, Aug 1991: Sawamoto, M.; Higashimura, T. *Makromol. Chem., Macromol. Symp.*, in press.
- (2) For reviews on living cationic polymerizations, see: (a) Sawamoto, M.; Higashimura, T. *Encyclopedia of Polymer Science and Engineering*, 2nd ed. (supplement); John Wiley & Sons: New York, 1989; p 399. (b) Sawamoto, M. *Prog. Polym. Sci.* 1991, 16, 111. (c) Kennedy, J. P. *Makromol. Chem., Macromol. Symp.* 1990, 32, 119. (d) Kennedy, J. P. *Makromol. Chem., Macromol. Symp.* 1991, 47, 55.
- (3) For reviews, see: (a) Higashimura, T.; Aoshima, S.; Sawamoto, M. *Makromol. Chem., Macromol. Symp.* 1988, 13/14, 457. (b) Sawamoto, M.; Higashimura, T. *Makromol. Chem., Macromol. Symp.* 1990, 31, 131.
- (4) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1984, 17, 265, 2228.
- (5) Sawamoto, M.; Okamoto, C.; Higashimura, T. *Macromolecules* 1987, 20, 2693.
- (6) Kojima, K.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1989, 22, 1552.
- (7) Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1991, 24, 3988.
- (8) Higashimura, T.; Miyamoto, M.; Sawamoto, M. *Macromolecules* 1985, 18, 611.
- (9) Kim, Y. H. *Macromolecules* 1991, 24, 2122.
- (10) Kim, Y. H.; Heitz, T. *Makromol. Chem., Rapid Commun.* 1990, 11, 525.
- (11) Schappacher, M.; Deffieux, A. *Macromolecules* 1991, 24, 2140.
- (12) (a) Schappacher, M.; Deffieux, A. *Macromolecules* 1991, 24, 4221. (b) Völkel, T.; Schappacher, M.; Deffieux, A. The 10th International Symposium on Cationic Polymerization and Related Processes, Hungary, Aug 1991; Paper C-03.
- (13) Matyjaszewski, K.; Lin, C. H. *J. Polym. Sci., Part A: Polym. Chem.* 1988, 26, 3031.
- (14) Matyjaszewski, K.; Lin, C. H. *J. Polym. Sci., Part A: Polym. Chem.* 1991, 29, 1439.
- (15) Kaszas, G.; Puskas, J. E.; Chen, C. C.; Kennedy, J. P. *Macromolecules* 1990, 23, 3909.
- (16) Iván, B.; Kennedy, J. P. *Macromolecules* 1990, 23, 2880.
- (17) Faust, R.; Iván, B.; Kennedy, J. P. *J. Macromol. Sci., Chem.* 1991, A28, 1.
- (18) Kamigaito, M.; Sawamoto, M.; Higashimura, T. *J. Polym. Sci., Part A: Polym. Chem.* 1991, 29, 1909.
- (19) Nuyken, O.; Kröner, H. *Makromol. Chem.* 1990, 191, 1.
- (20) The hexane came from the solvent for hydrogen iodide employed in the synthesis of **1a**. The same amount of this solvent was deliberately added to the other systems to keep the solvent composition identical to each other.
- (21) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley & Sons: New York, 1981; p 207.
- (22) Zinc halides are insoluble in toluene, other nonpolar solvents, and even polar chlorinated hydrocarbons. They dissolve only in ethers (Et_2O , THF, etc.), acetone, etc., among which Et_2O was used to mimic the solvent for the living polymerization with HB/ZnX_2 systems (see the Experimental Section). The methylene proton peaks of Et_2O interfered with those of **1**; however, the spectra have given satisfactory results for drawing the conclusions about the exchange reaction, as discussed in the text.
- (23) Stirling, C. J. M. *Acc. Chem. Res.* 1979, 12, 198.
- (24) (a) Cho, C. G.; Feit, B. M.; Webster, O. W. *Macromolecules* 1990, 23, 1918. (b) Lin, C. H.; Matyjaszewski, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1990, 31 (1), 599.
- (25) Sawamoto, M.; Kojima, K.; Higashimura, T. *Makromol. Chem.* 1991, 192, 2479.

Registry No. **1a**, 95314-34-4; **1b**, 19865-33-9; **1c**, 131301-12-7; IBVE (homopolymer), 9003-44-5; IBVE, 109-53-5; ZnI_2 , 10139-47-6; ZnCl_2 , 7646-85-7; HCl , 7647-01-0; ZnBr_2 , 7699-45-8; $\text{CF}_3\text{CO}_2\text{H}$, 76-05-1; HI , 10034-85-2.