Macromolecules 1991, *24*, 3988-3992

Living Cationic Polymerization of Isobutyl Vinyl Ether by RCOOH/Lewis Acid Initiating Systems: Effects of Carboxylate Ions and Lewis Acid Activators[1]

Masami Kamigaito, Mitsuo Sawamoto, and Toshinobu Higashimura*

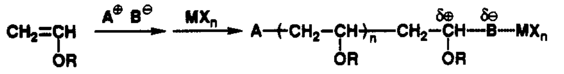
Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

Received November 27, 1990; Revised Manuscript Received February 25, 1991

ABSTRACT: A series of acetic acid derivatives (RCOOH; R = CF_3, CCl_3, $CHCl_2$, CH_2Cl, CH_3), coupled with zinc chloride ($ZnCl_2$), induced living cationic polymerization of isobutyl vinyl ether (IBVE) in toluene at 0 °C. Except for R = CH_3, the number-average molecular weights ($\bar{M}_n$) of the polymers were directly proportional to monomer conversion and in excellent agreement with the calculated values, assuming that one polymer chain forms per unit IBVE–RCOOH adduct [$CH_3CH(OiBu)OCOR$ (1)]. The molecular weight distribution of the polymers was very narrow ($\bar{M}_w/\bar{M}_n \leq 1.1$) for R = CF_3 and CCl_3; it gradually broadened ($\bar{M}_w/\bar{M}_n$ = 1.1 → 1.3) as the electron-withdrawing power of the substituent R decreased. The stronger RCOOH, the faster the reaction was. When a stronger Lewis acid activator, ethylaluminum dichloride ($EtAlCl_2$), was employed in place of $ZnCl_2$ in the 1/$ZnCl_2$ system, a fast, conventional, nonliving polymerization occurred. However, this system indeed led to living polymerization of IBVE in the presence of an excess of 1,4-dioxane. Thus, the living nature was clearly affected by the nucleophilicity of acetate ions and the acidity of Lewis acid activators. The effects of RCOOH (initiator) and Lewis acid (MX_n; activator) demonstrated the importance of the nucleophilic interaction between the growing carbocation and the counteranion ($^-OCOR\cdots MX_n$), and thereby the relation between "stabilization of a carbocation by a counteranion" and "stabilization of a carbocation by an externally added base", both of which are principles for living cationic polymerization proposed by us, was clarified.

Introduction

Recently we have reported that living cationic polymerization of vinyl ethers can be achieved by stabilization of a growing carbocation (1) with a suitably nucleophilic counteranion or (2) with an externally added Lewis base.[2] The system based on method 1 consists of an initiator AB that generates a nucleophilic anion B^- and a weak Lewis acid activator MX_n. With the A^+B^-/MX_n initiating system, living cationic polymerization may proceed via a binary counteranion, $B^-\cdots MX_n$ (eq 1), where the anion

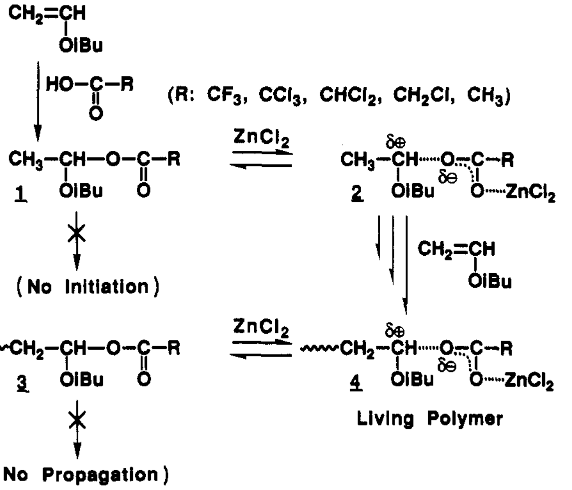


$$CH_2{=}\underset{\displaystyle OR}{CH} \xrightarrow{A^{\oplus}\ B^{\ominus}} \xrightarrow{MX_n} A\text{-}(CH_2\text{-}\underset{\displaystyle OR}{CH})_n\text{-}CH_2\text{-}\underset{\displaystyle OR}{\overset{\delta\oplus}{CH}}\cdots\overset{\delta\ominus}{B}\cdots MX_n \qquad (1)$$

B^- is modified by MX_n in such a way that the nucleophilicity of $B^-\cdots MX_n$ is suitably high to stabilize the growing carbocation. The HI/I_2,[3] HI/ZnX_2 or SnX_2 (X = I, Br, Cl),[4,5] and $HOP(O)(OPh)_2/ZnI_2$[6] initiating systems have been developed on the basis of this concept. However, the range of the nucleophilic anions B^- is rather limited, and, more important, it remains still unknown how nucleophilic these anions should be so as to be suited for living cationic polymerization.

With these problems in mind, we herein employed a series of acetic acid derivatives (RCOOH; R = CF_3, CCl_3, $CHCl_2$, CH_2Cl, CH_3), in conjunction with zinc chloride ($RCOOH/ZnCl_2$ initiating systems), for living cationic polymerization of isobutyl vinyl ether (IBVE). These substituted acetic acids form ester-type adducts (1) with IBVE, but 1 by itself cannot polymerize IBVE.[7] It is expected that the activation of the ester linkage by $ZnCl_2$ gives a suitably nucleophilic counteranion ($^-OCOR\cdots ZnCl_2$) that would stabilize the growing carbocation to generate living polymers (Scheme I). Similar initiating systems consisting of carboxylic acids and metal halides have been reported for isobutene[8] and for styrene.[9] A feature of the $RCOOH/ZnCl_2$ systems is that the acidity of RCOOH, or the nucleophilicity of $RCOO^-$, can be systematically varied by the electron-withdrawing power of the substituent R. In this study, we investigated the effects of the nucleophilicity of $RCOO^-$ (as a function of R) and the acidity of Lewis acid activators with use of $EtAlCl_2$ in place of $ZnCl_2$.

Scheme I



Results and Discussion

1. Effects of Acetate Ions. Living Polymerization by $CH_3CH(OiBu)OCOR/ZnCl_2$. IBVE was polymerized by IBVE–acetic acid adducts 1 [$CH_3CH(OiBu)OCOR$; R = CF_3, CCl_3, CH_3] in conjunction with $ZnCl_2$ in toluene at 0 °C ($[M]_0/[1]_0/[ZnCl_2]_0$ = 380/5.0/2.0 mM). Regardless of the substituents R in the adducts 1, a quantitative polymerization occurred without an induction phase, and the reaction was faster as the substituent R was more electron withdrawing (Figure 1).

Figure 2 illustrates the molecular weight distribution (MWD) of the polymers obtained at conversions ~20, 40, and 100%. The molecular weights increased in all systems as the polymerizations proceeded. Strong acids (R = CF_3

0024-9297/91/2224-3988$02.50/0

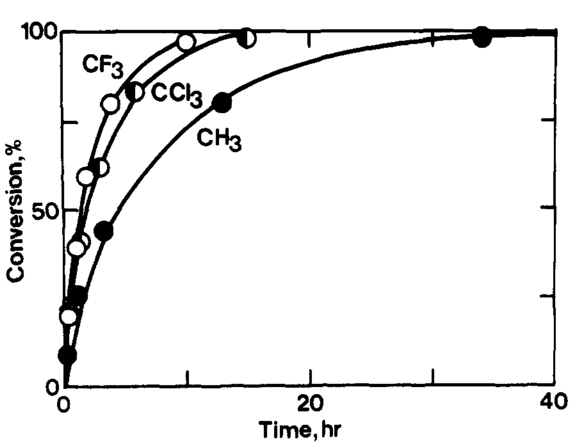


Figure 1. Time–conversion curves for the polymerization of IBVE by 1/$ZnCl_2$ in toluene at 0 °C: $[M]_0 = 0.38$ M; $[1]_0 = 5.0$ mM; $[ZnCl_2]_0 = 2.0$ mM. R = CF_3 (○), CCl_3 (◐), CH_3 (●).

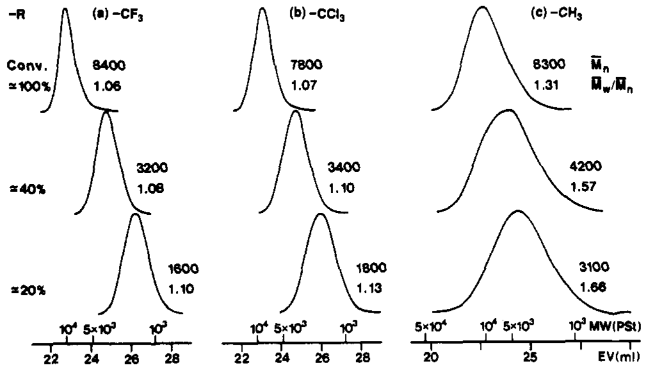


Figure 2. MWD curves of poly(IBVE) obtained with 1/$ZnCl_2$ in toluene at 0 °C (R = CF_3, CCl_3, CH_3). See Figure 1 for reaction conditions. Conversion ~20, 40, 100%.

or CCl_3) gave polymers with very narrow MWDs ($\bar{M}_w/\bar{M}_n \leq 1.1$), whereas acetic acid (R = CH_3) gave broader MWDs ($\bar{M}_w/\bar{M}_n \sim 1.3$).

As shown in Figure 3A (for R = CF_3, CCl_3), the number-average molecular weights ($\bar{M}_n$) of the polymers increased in direct proportion to monomer conversion and were in good agreement with the calculated values, assuming that one polymer chain forms per adduct 1 molecule. For R = CH_3 (Figure 3B), the $\bar{M}_n$ values were higher than the calculated values at the early stage; as the polymerization proceeded, however, the $\bar{M}_n$'s came close to the calculated values, and the MWDs became narrower (see below).

The living nature of the 1/$ZnCl_2$-mediated polymerization was further demonstrated by so-called "monomer-addition" experiments, where a fresh feed of IBVE was added to the reaction mixture just before the initial charge of the monomer had completely been polymerized (Figure 4). The added IBVE feed was smoothly polymerized at nearly the same rate as in the initial stage. The polymer molecular weights further increased in direct proportion to monomer conversion and were in good agreement with the calculated values for living polymers, independent of the substituent R. Even after the monomer addition, the MWDs for R = CF_3 and CCl_3 stayed very narrow ($\bar{M}_w/\bar{M}_n \leq 1.1$), and those for R = CH_3 became somewhat narrower. These facts show that all these systems led to living polymers though different in MWD.

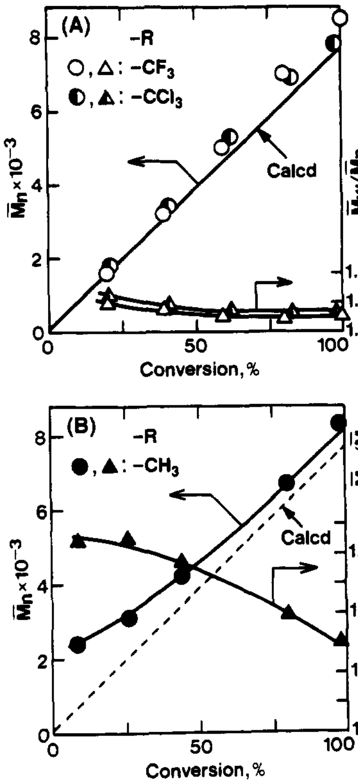


Figure 3. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of poly(IBVE) obtained with 1/$ZnCl_2$ in toluene at 0 °C: $[M]_0 = 0.38$ M; $[1]_0 = 5.0$ mM; $[ZnCl_2]_0 = 2.0$ mM. (A) R = CF_3 (○, △), CCl_3 (◐, ▲); (B) CH_3 (●, ▲). The "Calcd" lines indicate the calculated $\bar{M}_n$ assuming the formation of one living polymer per 1 molecule.

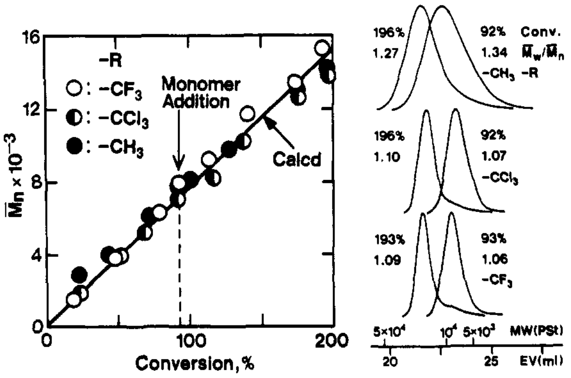


Figure 4. $\bar{M}_n$ and MWD curves of poly(IBVE) obtained with 1/$ZnCl_2$ in toluene at 0 °C: $[M]_0 = [M]_{add} = 0.38$ M; $[1]_0 = 5.0$ mM; $[ZnCl_2]_0 = 2.0$ mM. The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per 1 molecule. R = CF_3 (○), CCl_3 (◐), CH_3 (●).

Another series of polymerizations was carried out with use of the IBVE adducts of tri-, di-, and monochloroacetic acid and $ZnCl_2$ to examine further the effects of the nucleophilicity of $RCOO^-$ on the polymerizations. The more the adduct's acetate moiety is substituted with chlorine, the faster the polymerization ($CH_3 < CH_2Cl < CHCl_2 < CCl_3$). As shown in Figure 5, the $\bar{M}_n$ of the polymers obtained with 1 (R = CCl_3, $CHCl_2$, CH_2Cl)/$ZnCl_2$ was directly proportional to monomer conversion and in good agreement with the calculated value. The MWD gradually became broader as the nucleophilicity of $RCOO^-$ increased (less chlorine substituted). This fact suggests that the nucleophilicity of acetate anions affects the living polymerization by 1/$ZnCl_2$ systematically.

Thus, as the nucleophilic anion, not only the iodide[4,5] and the phosphate[6] anions but also carboxylate anions were found to induce living cationic polymerization of IBVE in the presence of $ZnCl_2$. As in the polymerization by the HI/ZnX_2 initiating systems,[4,5] the $\bar{M}_n$ of the polymers is determined by the $[M]_0/[1]_0$ mole ratio but independent of the $ZnCl_2$ concentration; the latter, however, increases the overall polymerization rate. Therefore,

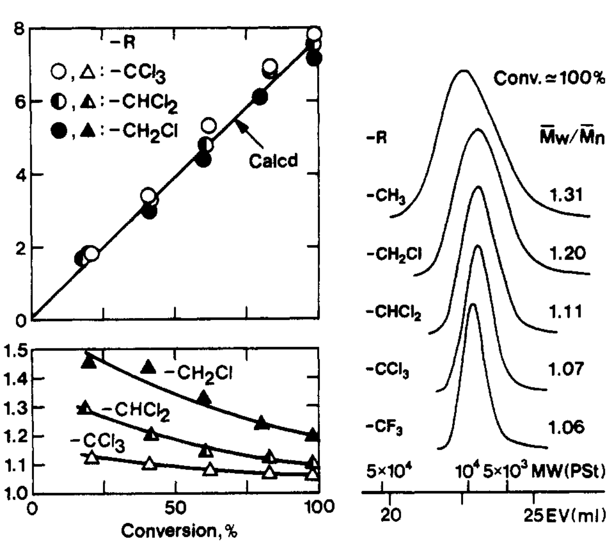


Figure 5. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(IBVE) obtained with 1/$ZnCl_2$ in toluene at 0 °C: $[M]_0 = 0.38$ M; $[1]_0 = 5.0$ mM; $[ZnCl_2]_0 = 2.0$ mM. The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per 1 molecule. R = CCl_3 (○, △), $CHCl_2$ (◐, ▲), CH_2Cl (●, ▲).

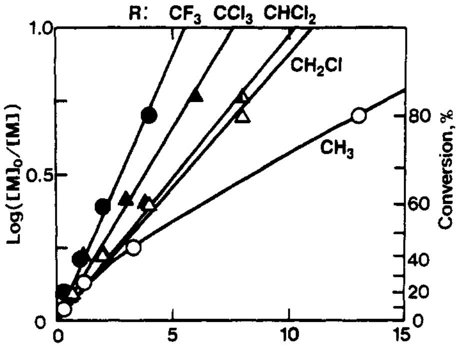


Figure 6. First-order plots for the IBVE polymerization by 1/$ZnCl_2$ in toluene at 0 °C. $[M]_0 = 0.38$ M; $[1]_0 = 5.0$ mM; $[ZnCl_2]_0 = 2.0$ mM. R = CF_3 (●), CCl_3 (▲), $CHCl_2$ (▲), CH_2Cl (△), CH_3 (○).

the living polymerization by 1/$ZnCl_2$ may proceed as shown in Scheme I, where 1 is the initiator that generates the growing end, whereas $ZnCl_2$ is the Lewis acid activator that activates the terminal C–OCOR linkage to form the living species 4.

Effects of the Nucleophilicity of RCOO⁻. Kinetic and NMR study was then carried out to clarify the effects of the nucleophilicity of RCOO⁻ on the polymerizations.

Figure 6 shows the logarithmic conversion data, log ($[M]_0/[M]$) ([M] is the monomer concentration at time *t*), plotted against *t*. The polymerization proved to be almost first order with respect to monomer ($-d[M]/dt = k[M]$) in all systems but one with R = CH_3, and the first-order rate constant, *k*, was obtained (see below).

The adduct 1 per se is stable and incapable of polymerizing IBVE in the absence of $ZnCl_2$. Figure 7 shows the representative ^1H NMR spectra of adducts 1 (R = CF_3, $CHCl_2$, CH_3). The structure of 1 was confirmed by ^1H and ^{13}C NMR spectroscopy. Notably, the absorption of the methine proton b, which is adjacent to RCOO group, shifted upfield as the electron-withdrawing power of R decreased; $\delta(H^b)$, ppm: 6.06 (CF_3) > 6.02 (CCl_3) > 5.99 ($CHCl_2$) > 5.97 (CH_2Cl) > 5.89 (CH_3). The ^{13}C NMR chemical shift of carbon b changed in a similar order; $\delta(C^b)$, ppm: 102.9 (CCl_3) > 101.9 (CF_3) > 100.4 ($CHCl_2$) > 98.6 (CH_2Cl) > 96.2 (CH_3), though the values for CF_3 and CCl_3 were opposite in order to those from the ^1H NMR data. These orders indicate that the more electron withdrawing the substituent R, the more polarized the ester linkage, and the more electron deficient the α-carbon.

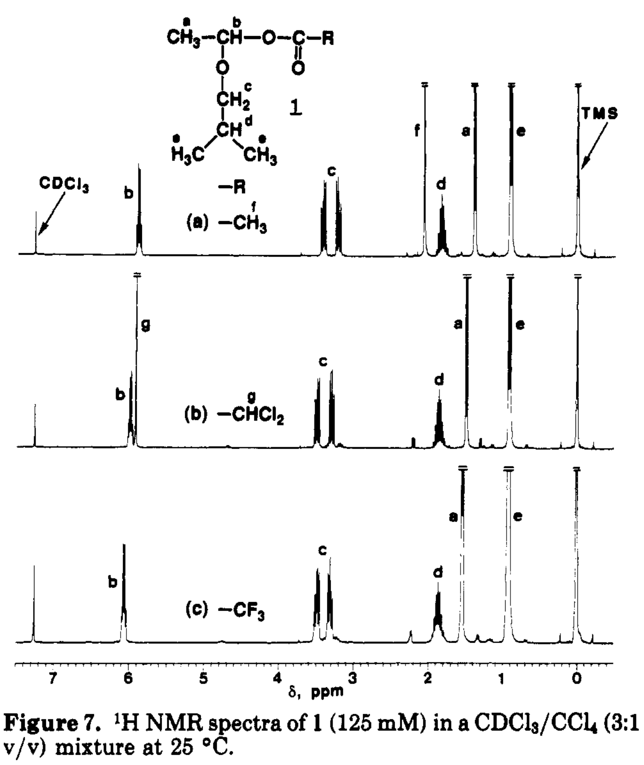


Figure 7. ^1H NMR spectra of 1 (125 mM) in a $CDCl_3/CCl_4$ (3:1 v/v) mixture at 25 °C.

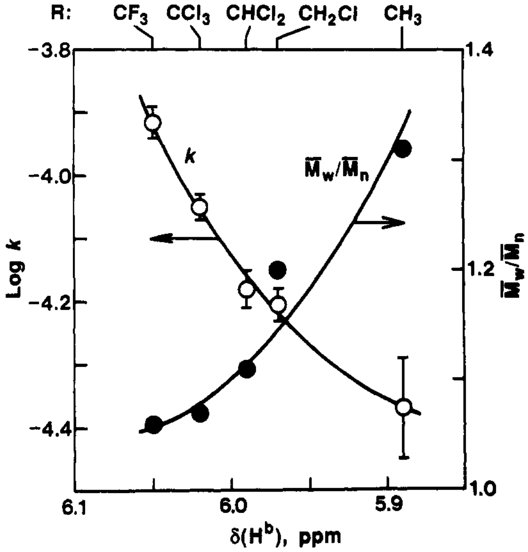


Figure 8. Logarithmic values of first-order rate constant (*k*) and $\bar{M}_w/\bar{M}_n$ values at conversion ~100% for the IBVE polymerization by 1/$ZnCl_2$ in toluene at 0 °C, as a function of ^1H NMR chemical shifts [$\delta(H^b)$] of the methine proton b in 1 (cf. Figure 7): (○) log *k*; (●) $\bar{M}_w/\bar{M}_n$.

The logarithmic first-order rate constant *k* values (log *k*) and the $\bar{M}_w/\bar{M}_n$ values of the polymers obtained at nearly 100% conversion were then plotted against the ^1H NMR chemical shifts [$\delta(H^b)$] of the methine proton of 1 (Figure 8). The polymerization rate (*k*) is greater for 1 with a more electron-withdrawing substituent R, most likely because the anion RCOO⁻ is less nucleophilic, to give a more dissociated growing end (4; Scheme I).

As described above, the 1/$ZnCl_2$ initiating systems induce living cationic polymerizations through quantitative initiation, while the amount of the activator ($ZnCl_2$) is smaller than that of the initiator (RCOO⁻ moiety). It implies, in turn, (1) that, for quantitative initiation from

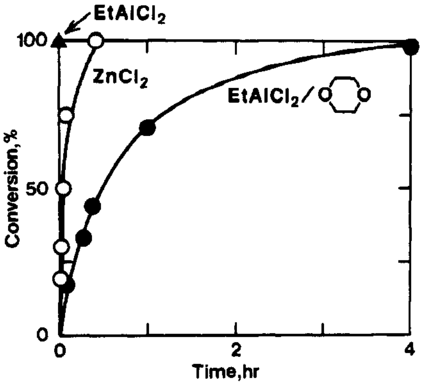


Figure 9. Time-conversion curves for the polymerization of IBVE by 1(R = CF$_3$)/MX$_n$ in toluene at 0 °C: [M]$_0$ = 0.38 M; [1]$_0$ = 5.0 mM; [MX$_n$]$_0$ = 10 mM; [1,4-dioxane]$_0$ = 1.2 M (10 vol %). MX$_n$: (▲) EtAlCl$_2$; (○) ZnCl$_2$; (●) EtAlCl$_2$ in the presence of 1,4-dioxane.

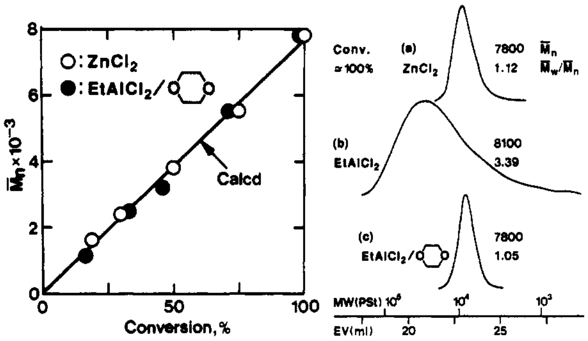


Figure 10. $\bar{M}_n$ and MWD curves of poly(IBVE) obtained with 1(R = CF$_3$)/MX$_n$ in toluene at 0 °C. See Figure 9 for reaction conditions. The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per 1 molecule. MX$_n$: (○) ZnCl$_2$; (●) EtAlCl$_2$ in the presence of 1,4-dioxane.

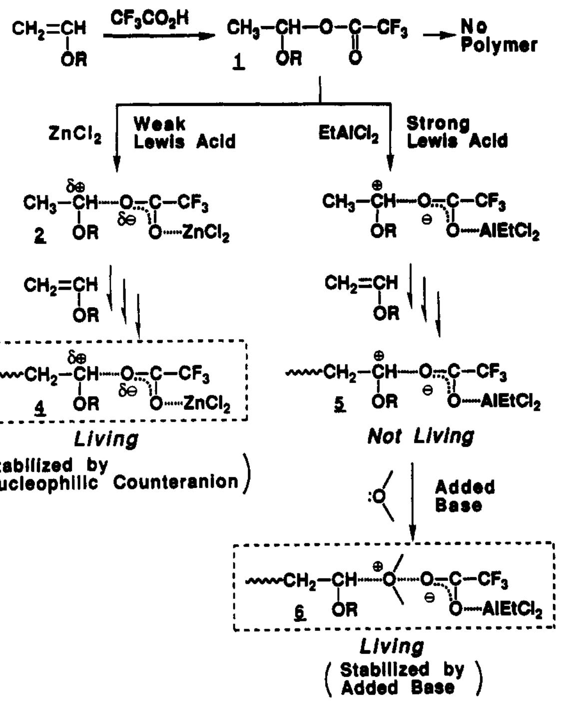
1, the active species (2 or 4; Scheme I) and the dormant species (1 or 3) should be in equilibrium and (2) that, for very narrow MWDs, the interconversion between the active and dormant species should be more frequent than the initiation and propagation. The relatively broad MWD (Figure 2c) with the nucleophilic acetate ion (R = CH$_3$), therefore, may be due to that such interconversions (1 $\rightleftharpoons$ 2; 3 $\rightleftharpoons$ 4) are not fast enough.[10]

In any case, the observed systematic effects of RCOOH further supports a strong interaction between the carboxylate moiety (RCOO$^-$) and the growing carbocation.

2. Effects of Lewis Acid Activators. Besides the structure of the anion part (B$^-$; eq 1), the choice of Lewis acid activators (MX$_n$) seems important for attaining living cationic polymerization by electrophile/Lewis acid activator systems. IBVE was then polymerized with use of a strong Lewis acid, ethylaluminum dichloride (EtAlCl$_2$), in place of ZnCl$_2$ in the CH$_3$CH(OiBu)OCOCF$_3$/ZnCl$_2$ system in toluene at 0 °C. The monomer was consumed instantly (Figure 9) and a conventional, nonliving polymerization occurred to give polymers with a very broad MWD ($\bar{M}_w/\bar{M}_n$ = 3.4) (Figure 10b). That is in sharp contrast to the narrow MWD (Figure 10a) obtained under the same conditions but with the weaker Lewis acid (ZnCl$_2$).

As already reported in part,[11] however, the polymerization by CH$_3$CH(OiBu)OCOCF$_3$/EtAlCl$_2$ proceeded slowly when carried out in the presence of an excess of an externally added base such as 1,4-dioxane. Interestingly, the $\bar{M}_n$ of the polymers obtained with the added base now increased in direct proportion to monomer conversion and agreed with the calculated value, assuming that one polymer chain forms per unit 1 (Figure 10c). It is important that the quite different initiating systems, 1/ZnCl$_2$ and 1/EtAlCl$_2$/1,4-dioxane, led to living polymers with the same molecular weights that were determined by the [M]$_0$/[1]$_0$ mole ratio.

Scheme II



These effects of the Lewis acid activators are summarized in Scheme II. Although the polymerizations with EtAlCl$_2$ and ZnCl$_2$ start from a common species [CH$_3$CH(OiBu)OCOCF$_3$], their living nature is clearly affected by the Lewis acid activators. With EtAlCl$_2$, the stronger Lewis acid, the ester linkage of 1 may be "activated" so strongly as in 5 that the resulting counteranion ($^-$OCOCF$_3\cdots$AlEtCl$_2$) is less nucleophilic than the ZnCl$_2$-derived counterpart in 4 ($^-$OCOCF$_3\cdots$ZnCl$_2$), and thus the growing species 5 is no longer stabilized by the counteranion. Addition of 1,4-dioxane leads to a living polymerization, most likely via an intermediate like 6, where the carbocationic center is now stabilized by the added base.[12] Note that living species 4 is based on the stabilization of the propagating end by a suitably nucleophilic counteranion (method 1), whereas living species 6 is based on an externally added nucleophile (method 2).

In conclusion, CH$_3$CH(OiBu)OCOR/ZnCl$_2$ initiating systems led to living cationic polymerization of vinyl ethers. The effects of CH$_3$CH(OiBu)OCOR (initiator) and Lewis acid (MX$_n$; activator) demonstrate the importance of the nucleophilic interaction between the growing carbocation and the counteranion ($^-$OCOR$\cdots$MX$_n$) and thereby support the mechanism (Scheme II) proposed by us. Furthermore, these results have revealed that our two methods (1) and (2) for living cationic polymerization, i.e., stabilization of a growing carbocation by a counteranion and stabilization of a growing carbocation by an externally added base, though apparently different, can be understood comprehensively on the basis of the varying nucleophilicity of the counteranion (B$^-\cdots$MX$_n$; eq 1) generated from an initiator and a Lewis acid activator.

Experimental Section

Materials. ZnCl$_2$ (Aldrich, 1.0 M solution in diethyl ether) and EtAlCl$_2$ (Kanto Chemicals, 0.95 M solution in *n*-hexane) were commercially supplied as solutions, which were diluted with Et$_2$O and toluene, respectively. IBVE (Tokyo Kasei) was washed with 10% aqueous sodium hydroxide solution and then water, dried overnight over potassium hydroxide, and distilled twice over calcium hydride before use. Toluene (solvent), 1,4-dioxane, and carbon tetrachloride (internal standard for gas chromatography) were purified by the usual methods and distilled twice over calcium hydride before use.[3] Diethyl ether (Dojin, purity >99%, anhydrous) was distilled in the presence of $LiAlH_4$ before use.

Synthesis of the RCOOH–IBVE Adduct (1). The adduct 1 with R = CH_3 was synthesized and purified as previously reported.[7] The other four adducts (R = CH_2Cl, $CHCl_2$, CCl_3, CF_3) were synthesized by stirring magnetically an equimolar mixture of RCOOH (purity >98%; as received) and IBVE (500 mM each) in CCl_4 at 0 °C for ca. 10 min, and their quantitative formation was confirmed by ^1H and ^{13}C NMR spectroscopy (see Figure 7 for representative ^1H NMR spectra). $CH_2ClCOOH$ was used as a diethyl ether solution because of its insolubility in CCl_4.

Polymerization Procedures. Polymerization was carried out under dry nitrogen in baked glass tubes equipped with three-way stopcocks. The reaction was initiated by adding, via dry syringes, a solution of $ZnCl_2$ (in Et_2O; 0.50 mL) or $EtAlCl_2$ (in toluene; 0.50 mL) into a monomer solution (in toluene; 4.5 mL) containing 1. For the polymerization in the presence of 1,4-dioxane (0.50 mL, 10 vol %, 1.2 M), it was added prior to initiation to the monomer solution. The polymerization was terminated with prechilled methanol (ca. 2 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 (for $1/ZnCl_2$) or with dilute hydrochloric acid (for $1/EtAlCl_2$) and then with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum dried to give the product polymers.

Measurements. The MWD of polymers was measured by size-exclusion chromatography in chloroform at room temperature on a Jasco Trirotar-V chromatograph equipped with three polystyrene gel columns (Shodex K-802, K-803, and K-804). The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of the polymers were calculated from size-exclusion eluograms on the basis of a polystyrene calibration. ^1H and ^{13}C NMR spectra (270 and 67.5 MHz, respectively) were recorded in a mixture of solvents ($CDCl_3$:CCl_4 = 3:1 and 1:4, respectively) at 25 °C on a Jeol GSX-270 spectrometer.

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research (No. 02453107) from the Ministry of Education, Science and Culture, Japan.

References and Notes

(1) Living Cationic Polymerization of Vinyl Ethers by Electrophile/Lewis Acid Initiating Systems. Part 6. For Part 5: see ref 13. This work was presented in part at the following symposia: (a) The 39th Annual Meeting of the Society of Polymer Science, Japan, Kyoto, May 1990; Paper II-4-10. Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Polym. Prepr. Jpn., Engl. Ed.* **1990**, *39* (1), E107. (b) SYMPOL 90, IUPAC International Symposium on Mechanisms and Kinetics of Polymerization Reactions and Their Use in Polymer Synthesis, Paris, Sept 1990. Sawamoto, M.; Higashimura, T. *Makromol. Chem., Macromol. Symp.*, in press.

(2) For reviews, see: (a) Higashimura, T.; Aoshima, S.; Sawamoto, M. *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 457. (b) Sawamoto, M.; Higashimura, T. *Ibid.* **1990**, *31*, 131.

(3) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265, 2228.

(4) Sawamoto, M.; Okamoto, C.; Higashimura, T. *Macromolecules* **1987**, *20*, 2693.

(5) Kojima, K.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1989**, *22*, 1552.

(6) Sawamoto, M.; Kamigaito, M.; Higashimura, T. *Polym. Bull.* **1988**, *20*, 407.

(7) Aoshima, S.; Higashimura, T. *Macromolecules* **1989**, *22*, 1009.

(8) (a) Faust, R.; Kennedy, J. P. *Polym. Bull.* **1986**, *15*, 317. (b) Faust, R.; Kennedy, J. P. *J. Polym. Sci., Part A, Polym. Chem.* **1987**, *25*, 1847. (c) Faust, R.; Kennedy, J. P. *Polym. Prepr., Div. Polym. Chem., Am. Chem. Soc.* **1988**, *29* (2), 69; *J. Macromol. Sci., Chem.* **1990**, *A27*, 649.

(9) (a) Matyjaszewski, K. *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 433. (b) Lin, C. H.; Matyjaszewski, K. *Polym. Prepr., Div. Polym. Chem., Am. Chem. Soc.* **1987**, *28* (1), 176; **1988**, *29* (2), 67.

(10) An exchange reaction between chloride in $ZnCl_2$ and carboxylate derived from the initiator 1 might occur, and in these polymerizations this possibility cannot be excluded. This point is now under investigation.

(11) Kishimoto, Y.; Aoshima, S.; Higashimura, T. *Polym. Bull.* **1987**, *18*, 111; *Macromolecules* **1989**, *22*, 3877.

(12) The polymerization mixture with $ZnCl_2$ contained 10 vol % (0.96 M) of diethyl ether (Et_2O) as solvent for the zinc salt (see Experimental Section). However, our separate experiments show that the polymerization by 1(R = CF_3)/$ZnCl_2$ (5.0/2.0 mM), even in the presence of as small as 0.2 vol % (19 mM) of Et_2O, was indeed living ($\bar{M}_w/\bar{M}_n < 1.2$). On the other hand, the polymers obtained with $1/EtAlCl_2$ in the presence of 10 vol % of Et_2O had broad MWDs (cf. ref 11). These facts suggest that 10 vol % of Et_2O cannot stabilize the growing carbocations under these conditions, whether they are generated with $ZnCl_2$ or $EtAlCl_2$.

(13) Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1990**, *23*, 4896.