Macromolecules **1995,** *28,* 5671−5675

Alkoxy-Substituted Titanium(IV) Chlorides as Lewis Acid Activators for Living Cationic Polymerization of Isobutyl Vinyl Ether: Control of Lewis Acidity in the Design of Initiating Systems[1]

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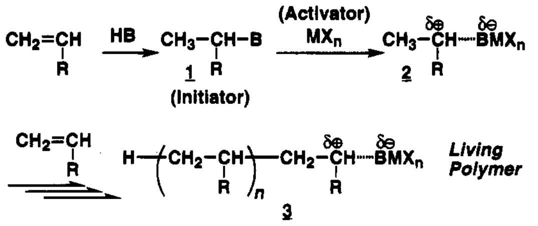
Received February 27, 1995; Revised Manuscript Received May 26, 1995[⊗]

ABSTRACT: Titanium(IV)-based new initiating systems for living cationic polymerization of isobutyl vinyl ether (IBVE) have been developed by using a series of isopropoxytitanium chlorides [$TiCl_{4-n}(O\textit{i}Pr)_n$; $n = 0-4$] in conjunction with the IBVE−HCl adduct in CH_2Cl_2 at −15 °C. The ^1H and ^{13}C NMR analysis of the titanium compounds showed that their Lewis acidity decreased with the increasing number (n) of isopropoxyl groups and affected the polymerizations accordingly. For example, $TiCl_4$ and $TiCl_3(O\textit{i}Pr)$, the strongest Lewis acids among the five, induced very rapid polymerizations to give polymers with broad molecular weight distributions (MWDs) ($\bar{M}_w/\bar{M}_n \sim 1.6$). In contrast, the reaction rate with $TiCl_2(O\textit{i}Pr)_2$, a weaker Lewis acid, was moderate. The MWDs of the polymers were narrow throughout the reaction ($\bar{M}_w/\bar{M}_n < 1.2$), and the number average molecular weights increased in direct proportion to monomer conversion. The polymerization with $TiCl(O\textit{i}Pr)_3$ was slower, and the MWDs became slightly broader. No polymer was obtained with a much weaker Lewis acid, $Ti(O\textit{i}Pr)_4$. Another modified titanium chloride, $TiCl_2(OPh)_2$, also led to a controlled polymerization of IBVE which is similar to the one with $TiCl_2(O\textit{i}Pr)_2$. These results indicate that living cationic polymerizations of IBVE can be achieved by controlling the Lewis acidity of the titanium(IV) activators with electron-donating groups.

Introduction

Living cationic polymerizations of vinyl monomers have been achieved with a variety of two-component initiating systems consisting of a protonic acid (HB) or its adduct (**1**) and a Lewis acid (MX_n),[4] as shown in eq 1. The protonic acids or the adducts generate polymer chains with a covalent C−B bond, and this component is thereby called an "initiator". The terminal C−B bond is dormant, incapable of initiating or propagating per se, and should be electrophilically activated by MX_n into carbocationic species (**2** and **3**) for living cationic polymerization. Thus, the second component MX_n is a Lewis acid, mostly a metal halide, and is accordingly called an "activator" or "coinitiator".



(1)

As shown in eq 1, the growing species derived from an HB/MX_n system consists of three components: the carbocation ($\sim\sim\sim C^+$) from the monomer, the counteranion (B^-) from the initiator HB, and the Lewis acid activator MX_n. Therefore, the judicious choice of the last two components to be suited for each monomer is important for the achievement of living cationic polymerizations. The effects of the counteranions have been systematically investigated in the polymerizations of vinyl ethers and isobutene with the use of a series of acetate and benzoate anions.[5−7] For example, we have shown that the counteranion (B^-) should be nucleophilic and may be halides, acetates, benzoates, and phosphates, etc. to form stable dormant species.

In contrast to the relatively wide variation in the initiator/counterion components, far fewer Lewis acid components are known, which are primarily halides of zinc, boron, tin, and titanium.[4] Despite their relative paucity, the Lewis acid components are also known to play a critical role in initiating systems for living cationic polymerization.[8−10] In the vinyl ether polymerizations with HCl/MX_n systems, for example, mild Lewis acids such as $ZnCl_2$ and $SnBr_4$ lead to living processes, whereas stronger Lewis acids such as $SnCl_4$ and $TiCl_4$ result in uncontrolled polymerizations.[9,11] In our view, the primary factor in selecting Lewis acids is their Lewis acidity. However, for the metal halides thus far examined, the Lewis acidity depends primarily on the central metal and hence cannot be systematically controlled.

Noting that the Lewis acidity depends on substituents in metal halides and related Lewis acids as well, we herein employ a series of titanium compounds, $TiCl_{4-n}(OR)_n$ ($n = 0-4$, R = isopropyl, phenyl), as the Lewis acid components that may be coupled with hydrogen chloride or adduct **1** as an initiator for cationic polymerization of isobutyl vinyl ether (IBVE). The rationale for the use of these compounds is that their Lewis acidity may be modulated by varying the number (n) and the nature of the −OR groups to give an insight into the effects of Lewis acidity on living cationic polymerizations. Such modulation of Lewis acidity by substituents would be more systematic and straightforward than that by central metals (e.g., from zinc to titanium), as has been examined in our previous work.[9] In general, the Lewis acidity of metal halides can be decreased by replacing the chlorines with electron-donating alkoxyl or aryloxyl groups, and a variety of metal alkoxides have been widely used in organic chemistry.[12] However, there are only a few examples of the use of such metal alkoxides for cationic polymerizations. Butoxytitanium trichloride, $TiCl_3(O\textit{n}Bu)$, has recently been employed for the cationic polymerization

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[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1995.

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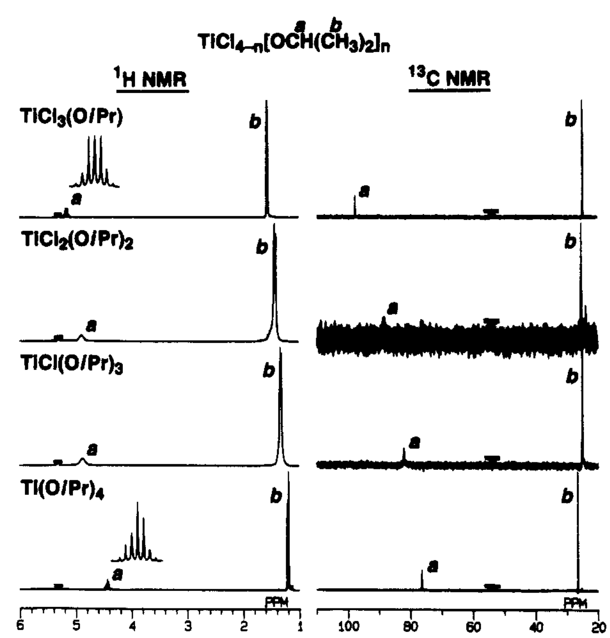

Figure 1. ^1H and ^{13}C NMR spectra of $TiCl_{4-n}(OiPr)_n$ ($n = 1-4$) in CD_2Cl_2 at −15 °C: $[TiCl_{4-n}(OiPr)_n] = 100$ mM.

of indene.[13] Quite recently, similiar attempts to decrease the Lewis acidity of $TiCl_4$ have been made for living block polymerization of styrene derivatives by in-situ mixing of titanium(IV) chloride and alkoxides.[14] Herein we prepared a series of well-defined isopropoxytitanium chlorides [$TiCl_{4-n}(OiPr)_n$; $n = 1-4$] and diphenoxytitanium dichloride [$TiCl_2(OPh)_2$] and investigated the effects of the number and the nature of the substituents on the polymerizations of IBVE.

Results and Discussion

1. Lewis Acidity of $TiCl_{4-n}(OiPr)_n$. In this study, it is crucial to use *well-defined* metal compounds for a systematic understanding of how Lewis acidity affects living cationic polymerization. Thus, a series of $TiCl_{4-n}(OiPr)_n$ compounds were prepared by the reactions of titanium(IV) tetrachloride and tetraisopropoxide at varying stoichiometries that determine the substitution number n (see the Experimental Section).[12] Figure 1 shows the ^1H and ^{13}C NMR spectra of the purified and recrystallized isopropoxyl compounds in methylene chloride at −15 °C (see the Experimental Section for characterization). The signals of the isopropoxyl groups can be seen in all the spectra. For example, in the ^1H NMR spectra of $TiCl_3(OiPr)$ and $Ti(OiPr)_4$, the methine (*a*) and methyl (*b*) signals are the characteristic septet and doublet, respectively. However, those signals in $TiCl_2(OiPr)_2$ and $TiCl(OiPr)_3$ slightly broadened, which is probably due to the aggregation of these compounds.[12] The same reason may hold for the relatively poor noise-to-signal ratios of their ^{13}C NMR spectra.

The chemical shifts of the methine protons and carbons were then plotted against the number of the isopropoxyl groups (n) (Figure 2). The ^1H and ^{13}C NMR resonances shift progressively upfield as the number of the isopropoxyl groups increases. This shows that the electron density on the titanium center increases with the increasing number of electron-donating isopropoxyl groups and, accordingly, that the Lewis acidity of $TiCl_{4-n}(OiPr)_n$ decreases in the same order: ($TiCl_4$>) $TiCl_3(OiPr)$ > $TiCl_2(OiPr)_2$ > $TiCl(OiPr)_3$ > $Ti(OiPr)_4$.

2. Living Cationic Polymerization with $TiCl_{4-n}(OiPr)_n$. Isobutyl vinyl ether (IBVE) was then polymerized with a series of the isopropoxytitanium chlorides [$TiCl_{4-n}(OiPr)_n$; $n = 0-4$] in conjunction with the HCl−IBVE adduct (**1**; R = OiBu, B = Cl) in CH_2Cl_2 at −15 °C. As seen in Figure 3, the overall polymerization rate followed their Lewis acidity order. The strongest two Lewis acids, $TiCl_4$ and $TiCl_3(OiPr)$, induced very rapid, almost instantaneous polymerizations. The reaction with a milder Lewis acid, $TiCl_2(OiPr)_2$, was slower and completed in 2 h. The rate is moderate, almost comparable to that with $ZnCl_2$ under the same conditions (time for 100% conversion = 10 min).[9] With the increasing number of isopropoxyl groups, the polymerization thus became progressively slower.[15] The weakest Lewis acid, $Ti(OiPr)_4$, did not induce polymerization at all under the same conditions. This indicates that the reaction rate can be controlled by the number of isopropoxyl groups in the compounds.

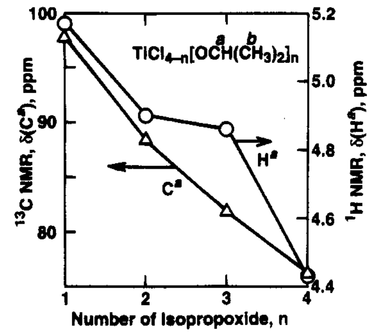

Figure 2. ^1H and ^{13}C NMR chemical shift of the methine proton *a* and carbon *a* as a function of the number (n) of isopropoxyl groups in CD_2Cl_2 at −15 °C: $[TiCl_{4-n}(OiPr)_n] = 100$ mM.

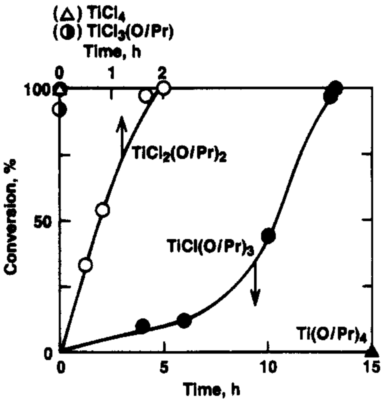

Figure 3. Polymerization of IBVE with $1/TiCl_{4-n}(OiPr)_n$ in CH_2Cl_2 at −15 °C: $[M]_0 = 0.38$ M; $[1]_0 = 5.0$ mM; $[TiCl_{4-n}(OiPr)_n]_0 = 2.0$ mM. $TiCl_{4-n}(OiPr)_n$: $n = 0$ (△); 1 (◐); 2 (○); 3 (●); 4 (▲).

As shown in Figure 4, the polymers obtained with the strongest two Lewis acids [$TiCl_4$ and $TiCl_3(OiPr)$] had broad molecular weight distributions (MWDs) ($\bar{M}_w/\bar{M}_n \sim 1.6$). In contrast, the diisopropoxide [$TiCl_2(OiPr)_2$] of milder Lewis acidity gave polymers with narrow MWDs ($\bar{M}_w/\bar{M}_n < 1.2$). The number-average molecular weights ($\bar{M}_n$) of these polymers increased in direct proportion to monomer conversion and agreed with the calculated values, if one molecule of **1** generates one living polymer chain. The MWDs of the polymers obtained with $TiCl(OiPr)_3$ were slightly broader ($\bar{M}_w/\bar{M}_n \sim 1.3$) than those with $TiCl_2(OiPr)_2$. Thus, the polymerizations can be controlled by substituting chlorine in strongly Lewis acidic $TiCl_4$ with electron-donating isopropoxyl groups.

To examine the living nature of the polymerization with $TiCl_2(OiPr)_2$, a fresh feed of IBVE was added to

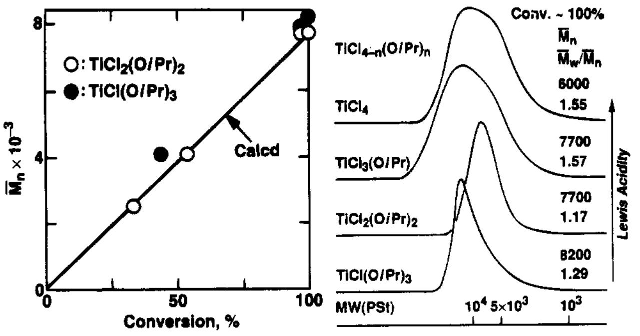

Figure 4. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(IBVE) obtained with 1/$TiCl_{4-n}(OiPr)_n$ in CH_2Cl_2 at −15 °C: $[M]_0$ = 0.38 M; $[1]_0$ = 5.0 mM; $[TiCl_{4-n}(OiPr)_n]_0$ = 2.0 mM. $TiCl_{4-n}(OiPr)_n$: n = 2 (○); 3 (●). The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **1** molecule.

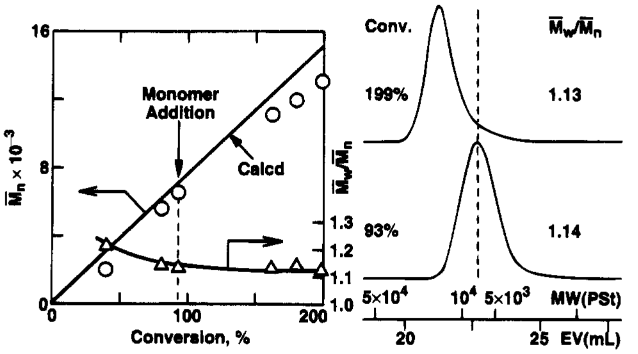

Figure 5. Monomer-addition experiments in the polymerization of IBVE with 1/$TiCl_2(OiPr)_2$ in CH_2Cl_2 at −15 °C: $[M]_0$ = $[M]_{add}$ = 0.38 M; $[1]_0$ = 5.0 mM; $[TiCl_2(OiPr)_2]_0$ = 2.0 mM. The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **1** molecule.

the reaction mixture just before the initial charge of the monomer had completely been polymerized (1 h; see Figure 3). The added monomer feed was smoothly polymerized, and the $\bar{M}_n$ values further increased proportionally to monomer conversion and agreed with the calculated values, as shown in Figure 5. The MWDs stayed narrow throughout the two-stage reactions ($\bar{M}_w/\bar{M}_n$ < 1.2). This indicates the formation of living polymers with the 1/$TiCl_2(OiPr)_2$ initiating system. The introduction of the electron-donating alkoxy group onto the electron deficient titanium center of $TiCl_4$ permits us to modulate the Lewis acidity and thereby its interaction with the dormant C−Cl terminal. In this regard, the HCl/$TiCl_2(OiPr)_2$ system would be similar in nature to the zinc-based versions, such as HI/ZnI_2[8] and HCl/$ZnCl_2$[9] systems, in that all these involve mild Lewis acids and induce living cationic polymerizations of vinyl ethers without any additives.

3. Living Cationic Polymerization with $TiCl_2(OPh)_2$. The success in the living/controlled polymerization of IBVE with $TiCl_2(OiPr)_2$ encouraged us to investigate the polymerization with titanium(IV) dichlorides [$TiCl_2(OR)_2$] substituted with other groups. Herein, the diphenoxy compound [$TiCl_2(OPh)_2$] was investigated as a Lewis acid activator for IBVE polymerizations, where their Lewis acidity may depend not only on the number (n) but on the nature of the −OR groups. A bulkier group generally prevents the aggregation or the formation of μ-type complexes of neutral titanium compounds and thereby increases their Lewis acidity. Furthermore, phenoxy groups are much less basic than alkoxy groups. Therefore, the Lewis acidity of $TiCl_2(OPh)_2$ may be larger than that of $TiCl_2(OiPr)_2$.

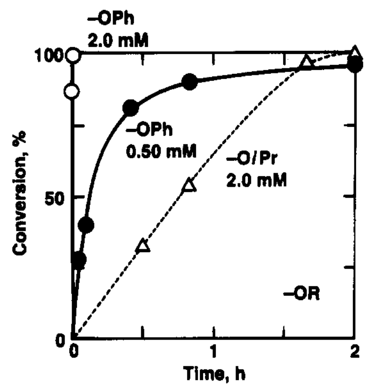

Figure 6. Polymerization of IBVE with 1/$TiCl_2(OR)_2$ in CH_2Cl_2 at −15 °C: $[M]_0$ = 0.38 M; $[1]_0$ = 5.0 mM; $[TiCl_2(OPh)_2]_0$ = 2.0 (○); 0.50 (●) mM; $[TiCl_2(OiPr)_2]_0$ = 2.0 (△) mM.

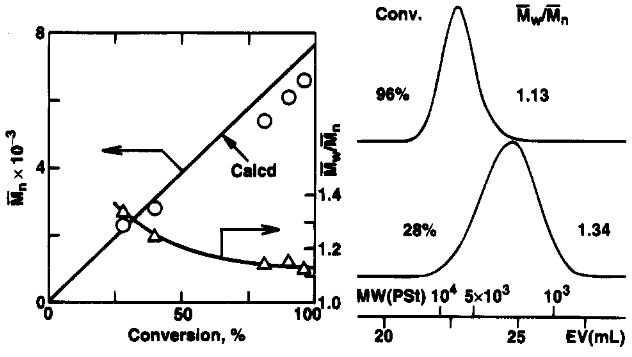

Figure 7. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(IBVE) obtained with 1/$TiCl_2(OPh)_2$ in CH_2Cl_2 at −15 °C: $[M]_0$ = 0.38 M; $[1]_0$ = 5.0 mM; $[TiCl_2(OPh)_2]_0$ = 0.50 mM. The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **1** molecule.

$TiCl_2(OPh)_2$ was prepared by the equimolar reaction of $TiCl_4$ and $Ti(OPh)_4$ and then purified and recrystallized (see the Experimental Section). Polymerizations with the phenoxy compound were investigated in CH_2Cl_2 at −15 °C (initiator **1**; Figure 6). The polymerization with 1/$TiCl_2(OPh)_2$ was much faster than that with 1/$TiCl_2(OiPr)_2$ under the same conditions; the reaction completed in 30 s with 2.0 mM of $TiCl_2(OPh)_2$ but needed 2 h to complete at a lower concentration (0.50 mM).

Figure 7 shows the $\bar{M}_n$ values and MWDs of the polymers obtained with $TiCl_2(OPh)_2$. The $\bar{M}_n$ were directly in proportion to monomer conversion and in agreement with the calculated values, if one polymer chain is formed per one molecule of **1**. The MWDs became narrower as the polymerization proceeded ($\bar{M}_w/\bar{M}_n$ < 1.2). This indicates that living cationic polymerization of IBVE can be feasible also with the use of $TiCl_2(OPh)_2$ in conjunction with **1** and that the disubstituted titanium(IV) chlorides with alkoxy and aryloxy groups have the moderate Lewis acidity suited for the living cationic polymerizations of vinyl ethers.

The tacticity of the polymers obtained with the two titanium dichlorides in CH_2Cl_2 at −78 °C was investigated by ^{13}C NMR spectroscopy. Both polymers are *meso* rich (*meso* %): $TiCl_2(OiPr)_2$ (72), $TiCl_2(OPh)_2$ (70). Remarkable effects of structures of the titanium compounds on the stereoregularity of the polymers have not been observed under the examined conditions. The stereochemistry on living cationic polymerizations with various Lewis acids is now under study in our research group.

In conclusion, a series of well-defined titanium(IV) compounds, $TiCl_{4-n}(OiPr)_n$, permitted the modulation

Table 1. Polymerization of IBVE with 1/Titanium Complexes in CH_2Cl_2 at −15 °C

$TiCl_{4-n}(OR)_n$	polymerization
$TiCl_4$	not living
$TiCl_3(OiPr)$	not living
$TiCl_2(OPh)_2$	living
$TiCl_2(OiPr)_2$	living
$TiCl(OiPr)_3$	long lived
$Ti(OiPr)_4$	no polymn

of their Lewis acidity by successively replacing the chlorines with electron-donating isopropoxyl groups, so that the selected derivatives are suited for living cationic polymerizations of IBVE. The use of these titanium compounds has thus widened the variety in Lewis acids available for controlled cationic polymerization. Table 1 summarizes the relation between their Lewis acidity and the living nature of the IBVE polymerizations initiated with the $1/TiCl_{4-n}(OR)_n$ systems. Moderately Lewis acidic titanium compounds, $TiCl_2(OiPr)_2$ and $TiCl_2(OPh)_2$, both of which are disubstituted forms of $TiCl_4$ with alkoxyl or aryloxyl groups, are suited for living cationic polymerizations of IBVE coupled with the HCl−IBVE adduct (**1**) as an initiator. These compounds are rather similar to zinc halides (ZnX_2) or tin(II) halides (SnX_2).[8,9] The success in living polymerizations is probably due to the decrease in Lewis acidity, but the steric factor, which is increased by the replacement of chlorine by bulkier isopropoxy and phenoxy groups, should also be considered further. In addition, the introduction of alkoxyl and aryloxyl groups onto the titanium center therein will modify not only their Lewis acidity but the steric and perhaps chiral environment around the growing species, which would in turn allow finely controlled cationic polymerization that would be difficult to achieve with conventional metal halides.

Experimental Section

Materials. 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. $TiCl_4$ (Aldrich, 1.0 M solution in CH_2Cl_2), $TiCl(OiPr)_3$ (Merck, > 99%), and $Ti(OiPr)_4$ (Kanto Chemicals, > 97%) were used as received. $TiCl_2(OiPr)_2$, $TiCl_3(OiPr)$, and $TiCl_2(OPh)_2$ were prepared and purified as below.[12]

Preparation of $TiCl_2(OiPr)_2$. All the synthetic procedures were carried out under dry nitrogen in baked glassware equipped with three-way stopcocks. All solvents were used after purification and distillation. Titanium(IV) chloride (5.6 mL, 50 mmol) was slowly added to a solution of titanium(IV) isopropoxide (14.9 mL, 50 mmol) in *n*-hexane (15 mL) at room temperature. On addition of $TiCl_4$, heat was evolved. After stirring for 10 min, the mixture was allowed to stand at room temperature for another 1 h, during which period a white solid precipitated from the mixture. After being washed with *n*-hexane (8 mL × 2), the precipitate was dissolved in *n*-hexane (10 mL) at 60 °C and then recrystallized at room temperature. The white crystal [$TiCl_2(OiPr)_2$] was then filtered off and dried under reduced pressure at room temperature and then dissolved in CH_2Cl_2 to give a 1.0 M solution. The solution was sealed in brown ampules and stored in the dark in a freezer.

Preparation of $TiCl_3(OiPr)$. All the synthetic procedures were carried out under dry nitrogen in baked glassware equipped with three-way stopcocks. All solvents were used after purification and distillation. Titanium(IV) chloride (8.2 mL, 75 mmol) was slowly added to a solution of titanium(IV) isopropoxide (7.4 mL, 25 mmol) in *n*-hexane (17.6 mL) at room temperature. On addition of $TiCl_4$, heat was evolved. After stirring for 10 min, the mixture was allowed to stand at room temperature for another 1 h, during which period a pale yellow powder precipitated from the solution. CH_2Cl_2 (30 mL) was added, and the heterogeneous mixture was warmed to 60 °C to become a yellow homogeneous solution. The solution was cooled and allowed to stand for 2.5 h at room temperature to precipitate yellow crystals [$TiCl_3(OiPr)$]. After the solvent was filtered off, the crystalline product was washed with *n*-hexane (10 mL × 2), dried under reduced pressure at room temperature, and then dissolved in CH_2Cl_2. The solution was immediately sealed in brown ampules and stored in the dark in a freezer. The concentration of the solution was determined by titrating the chloride by the Volhard method.[9]

Preparation of $TiCl_2(OPh)_2$. This compound was prepared by the reaction of titanium(IV) chloride with titanium(IV) phenoxide [$Ti(OPh)_4$]. 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. For the synthesis of $Ti(OPh)_4$,[12f] a mixture of titanium(IV) isopropoxide (7.4 mL, 25 mM) and distilled phenyl acetate (13.3 mL, 105 mM) was warmed to 135 °C in a round bottom flask fitted with a magnetic stirrer and a reflux condenser. The solution was stirred for 30 min at this temperature, and then cooled to room temperature. The volatile material was removed under reduced pressure at 110 °C for 2 h to give a red solid. It was dissolved in a mixture of toluene (10 mL) and *n*-hexane (10 mL) at 50 °C. Slow cooling to 0 °C gave the precipitation of red crystals, which were separated by filtration and then dried under reduced pressure to give 6.25 g of $Ti(OPh)_4$ (yield = 60%).

The titanium(IV) phenoxide (3.4 g, 8.2 mmol) was dissolved in a mixture of toluene (10 mL) and *n*-hexane (10 mL) at 80 °C, and then titanium(IV) chloride (0.89 mL, 8.2 mmol) was added to the solution. After stirring for 20 min at 80 °C, the mixture was allowed to stand for an additional 30 min. Blackish red crystals [$TiCl_2(OPh)_2$] precipitated from the solution. The precipitate was washed with *n*-hexane (5 mL × 2), dissolved in toluene (20 mL) at 100 °C, and then recrystallized at room temperature. The resultant crystal was filtered off and dried under reduced pressure at room temperature to give 3.0 g of $TiCl_2(OPh)_2$ (yield = 60%). The crystalline compound was then dissolved in CH_2Cl_2 into a 0.15 M solution, which was immediately sealed in brown ampules and stored in the dark in a freezer. Anal. Calcd for $C_{12}H_{10}O_2Cl_2Ti$: C, 47.3, H, 3.3, Cl, 23.2. Found: C, 44.5, H, 4.0, Cl, 22.2.

Synthesis of HCl−IBVE Adduct (1). The HCl−IBVE adduct **1** was synthesized by bubbling dry HCl gas through a solution of IBVE (9.0 mL IBVE in 60 mL *n*-hexane; 1.0 M) at −78 °C. The gas was generated by dropping concentrated sulfuric acid into powdery sodium chloride and dried by passing it through a column packed with calcium chloride. After 30 min, the excess HCl in the reaction mixture was removed by bubbling dry nitrogen gas at 0 °C for 30 min, and the clean and quantitative formation of adduct **1** was confirmed by ^1H NMR spectroscopy. The concentration of **1** was determined by titrating the chloride by the Volhard method; the observed value (~1 M) further confirmed the quantitative formation of **1** from IBVE.

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 titanium compound (in CH_2Cl_2, 0.50 mL) via dry syringes into a monomer solution (in CH_2Cl_2; 4.0 mL) containing IBVE (0.25 mL) and CCl_4 (0.25 mL) at −15 °C. 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.

Measurements. The MWD, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ 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 Trirotar-V precision pump and a JASCO 830-RI refractive index detector. The columns were calibrated against 10 standard polystyrene samples ($\bar{M}_n = 800-300\,000$; $\bar{M}_w/\bar{M}_n = 1.03-1.10$) as well as styrene oligomers (tetramer, trimer, and dimer) and monomer. ^{1}H NMR and ^{13}C NMR spectra of the compounds were recorded in CD_2Cl_2 at −15 °C on a JEOL JNM-GSX270 spectrometer, operating at 270.7 MHz (^{1}H) and 67.9 MHz (^{13}C).

Acknowledgment. M.K. is grateful to the Japan Society for the Promotion of Sciences for the Fellowships for Japanese Junior Scientists and the partial support of this work by the Grant-in-Aid for Scientific Research (No. 00051943) from the Ministry of Education, Science, and Culture, Japan.

References and Notes

(1) This work was presented in part at the following meetings. (a) The 43rd Annual Meeting of the Society of Polymer Science, Nagoya, Japan, May 1994; Paper I-4-16: Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Polym. Prepr. Jpn., Engl. Ed.* **1994**, *43* (1), E57. (b) The 35th IUPAC International Symposium on Macromolecules, Akron, OH, July 1994: Sawamoto, M.; Kamigaito, M. *Macromol. Symp.*, in press.

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(15) The increase of the rate with time in the polymerization with $TiCl(O\textit{i}Pr)_3$ is probably due to the exchange reaction between the isopropoxyl groups in the compound and the chlorine at the polymer terminal derived from **1**, which causes the generation of stronger Lewis acids like $TiCl_2(O\textit{i}Pr)_2$. The exchange reaction may occur also in the polymerization with $TiCl_2(O\textit{i}Pr)_2$, which gives $TiCl_3(O\textit{i}Pr)$. This also suggests the formation of polymer terminated with acetal. This is under investigation by NMR analysis of the model reactions between **1** and the titanium compounds.

MA950249E