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Living Cationic Isomerization Polymerization of β-Pinene. 1. Initiation with HCl−2-Chloroethyl Vinyl Ether Adduct/$TiCl_3(O\textit{i}Pr)$ in Conjunction with $n\mathrm{Bu_4NCl}$[1]

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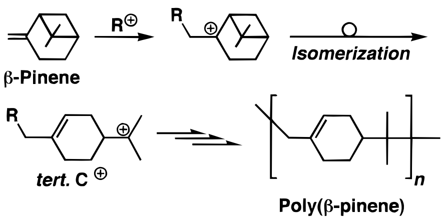
ABSTRACT: The first example of living cationic isomerization polymerization of β-pinene was achieved with an initiating system that consists of the HCl−2-chloroethyl vinyl ether adduct [**1a**; $CH_3CH(OCH_2CH_2Cl)Cl$] and isopropoxytitanium trichloride [$TiCl_3(O\textit{i}Pr)$] in the presence of tetra-*n*-butylammonium chloride ($n\mathrm{Bu_4NCl}$) in CH_2Cl_2 at −40 and −78 °C. The number-average molecular weight of the polymers ($\bar{M}_\mathrm{n} \leq 5 \times 10^3$) increased in direct proportion to monomer conversion, and the molecular weight distribution of the polymers was relatively narrow ($\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n} \sim 1.3$). The living nature of the polymerization was further demonstrated by monomer-addition experiments. A similar living polymerization was also feasible with the HCl−styrene adduct or 1-phenylethyl chloride [**1b**; $CH_3CH(Ph)Cl$] in conjunction with $TiCl_3(O\textit{i}Pr)$ and $n\mathrm{Bu_4NCl}$. ^{1}H NMR analysis of the polymers from **1a** showed that **1a** serves as an initiator and generates poly(β-pinene) chains consisting of the 1-(2-chloroethoxy)ethyl head group, a *tert*-chloride tail group, and isomerized β-pinene repeat units with a cyclohexene ring.

Introduction

β-Pinene is one of the main constituents of natural turpentine, and the polymers are used commercially as resins in many applications.[3,4] It is known as a reactive monomer that undergoes cationic isomerization polymerization to give polymers of moderate molecular weights ($\bar{M}_\mathrm{n} \sim 2000$) (eq 1).[5] Its cationic reactivity is higher than that of isobutene, which generates a tertiary aliphatic carbocation structurally similar to the isomerized β-pinene growing cation.[6] Factors contributing to the high reactivity of the bicyclic monomer include (1) the reactive *exo*-methylene double bond, (2) strain release via the opening of the fused cyclobutane ring, and (3) formation of a stable tertiary cation by growing-end ring-opening isomerization. Cationic polymerizations of β-pinene with a variety of Lewis acids ($AlCl_3$, $SnCl_4$, $ZnCl_2$, etc.) have been known for about a half-century,[3,4] but their control has not been achieved yet in terms of molecular weights and polymer terminal structures. Previously, Kennedy and his associates reported the selective synthesis of tertiary chloride-capped poly(β-pinene) by the so-called “inifer” technique, where the polymerization was initiated with the H_2O/BCl_3 system in the presence of an aromatic tertiary chloride.[7,8]

Recent developments show that living or controlled cationic polymerizations are now possible for a wide variety of vinyl and related monomers including vinyl ethers, isobutene, and styrenes.[9,10] As mentioned above and elsewhere,[4] the growing poly(β-pinene) terminal is a tertiary carbocation [$\sim C^+(CH_3)_2$] (eq 1) that is derived from the in-situ isomerization of the cyclic β-pinene cation and is virtually the same as the counterpart from isobutene, although β-pinene monomer per se has a complicated bicyclic structure. This suggests possible living cationic polymerization of β-pinene with designed initiating systems consisting of a protonic acid or its adduct with a vinyl monomer (as an initiator) and a Lewis acid (as an activator or coinitiator). In fact, it has been reported that the $HI/EtAlCl_2$ initiating system gave long-lived polymers from β-pinene but that control of molecular weights was difficult.[11]



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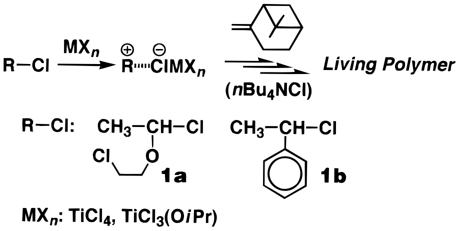
In this study, we have therefore investigated living cationic polymerization of β-pinene with a series of two-component initiating systems (R−Cl/MX_n in eq 2) that are effective for vinyl ethers,[12,13] styrene,[14−16] *p*-methylstyrene,[15] and α-methylstyrene.[17] With the HCl−2-chloroethyl vinyl ether adduct (**1a**)/$TiCl_3(O\textit{i}Pr)$ system, the first example of living cationic polymerization of β-pinene was achieved in the presence of $n\mathrm{Bu_4NCl}$ in CH_2Cl_2 at −40 and −78 °C.



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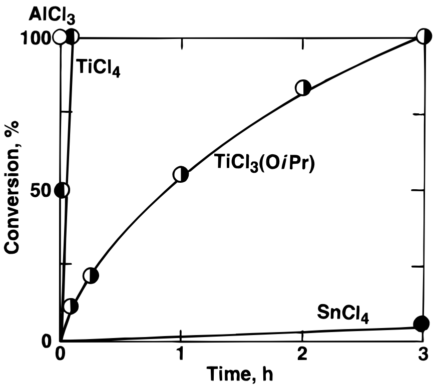


Figure 1. Polymerization of β-pinene with **1a**/MX_n/nBu$_4$NCl in CH_2Cl_2 at −40 °C: $[M]_0 = 1.0$ M; $[\mathbf{1a}]_0 = 20$ mM; $[MX_n]_0 = 100$ mM; $[n\mathrm{Bu}_4\mathrm{NCl}]_0 = 10$ mM. MX_n: $AlCl_3$ (○); $TiCl_4$ (◐); $TiCl_3(OiPr)$ (◑); $SnCl_4$ (●).

Results and Discussion

1. Search of Lewis Acid Activators. One of the most important keys to living cationic polymerizations of vinyl monomers is the use of a Lewis acid (activator) suited for the reactivity of a particular monomer.[9] We thus examined the polymerizations of β-pinene with the HCl−2-chloroethyl vinyl ether adduct (**1a**, HCl−CEVE) and a series of Lewis acids [MX_n: $AlCl_3$, $SnCl_4$, $TiCl_4$, and $TiCl_3(OiPr)$], where the acidity was varied by their metals and substituents. The reactions were carried out in the presence of nBu$_4$NCl in CH_2Cl_2 at −40 °C ($[M]_0/[\mathbf{1a}]_0/[MX_n]_0/[n\mathrm{Bu}_4\mathrm{NCl}]_0 = 1000/20/100/10$ mM).

The overall rates of the polymerizations (Figure 1) depended strongly on the Lewis acid activators: $AlCl_3 > TiCl_4 > TiCl_3(OiPr) \gg SnCl_4$. $AlCl_3$ and $TiCl_4$ induced almost instantaneous and extremely rapid polymerizations, whereas the reaction by $SnCl_4$ was very slow (6% conversion in 3 h). In contrast, $TiCl_3(OiPr)$, a weaker Lewis acid than $TiCl_4$,[13,16] led to smooth and quantitative polymerization at a moderate rate.

Figure 2 shows the number-average molecular weights $\bar{M}_n$ and molecular weight distributions (MWD) of the polymers thus obtained. The MWDs with $TiCl_3(OiPr)$ were narrow ($\bar{M}_w/\bar{M}_n \sim 1.3$), and the $\bar{M}_n$ increased with monomer conversion. The $\bar{M}_n$ of the polymers with $TiCl_4$ also increased as the polymerization proceeded, but the MWD was broader than that with $TiCl_3(OiPr)$ ($\bar{M}_w/\bar{M}_n \sim 2$). These results indicate that the titanium-based initiating systems gave polymers with controlled molecular weights and their distributions, and that a weaker Lewis acid, $TiCl_3(OiPr)$, was suited for the control of the rates, molecular weights, and MWDs.

In sharp contrast, the $AlCl_3$ system resulted in less controlled polymers with very broad MWDs ($\bar{M}_w/\bar{M}_n = 3.4$) and relatively high molecular weights. On the other hand, $SnCl_4$ gave low molecular weight oligomers, mostly dimers, although the Lewis acid is strong enough to lead to living cationic polymerizations of styrene.[14,15] The high activity of $AlCl_3$ and low activity of $SnCl_4$ for cationic polymerizations of β-pinene are consistent with the reported results of conventional polymerizations of β-pinene with Lewis acids in toluene.[5]

From these results, $TiCl_3(OiPr)$, a modified titanium chloride with an alkoxy group, is the most suitable activator among the employed Lewis acids for living cationic polymerization of β-pinene. This titanium compound is also useful for living cationic polymerizations of styrene,[16] which suggests the reactivity of β-pinene to be comparable to that of styrene.

2. Effects of Salt (nBu$_4$NCl) Concentration. It has been shown that ammonium salt (nBu$_4$NCl) is necessary for the living cationic polymerization of styrene with $SnCl_4$ and $TiCl_3(OiPr)$,[14,16] and the above-described results suggest that the same will be true for β-pinene polymerization. The effects of the salt concentration were then investigated in the polymerizations with **1a**/$TiCl_3(OiPr)$ (20/100 mM).

As seen in Figure 3, the reaction rate at the early stage decreased with increasing nBu$_4$NCl concentration. However, the polymerization in the absence of nBu$_4$NCl apparently stopped at ~70% conversion, and as it proceeded, the reaction mixture became heterogeneous due to the precipitation of the Lewis acid, which may retard the polymerizations significantly. In contrast, the reaction mixtures with nBu$_4$NCl remained homogeneous throughout the reaction, which occurred efficiently up to quantitative conversion.

Figure 4 shows the $\bar{M}_n$ and MWDs of the polymers obtained at varying concentrations of nBu$_4$NCl. In both the absence and presence of nBu$_4$NCl, the $\bar{M}_n$ increased in direct proportion to monomer conversion up to relatively high molecular weights ($\bar{M}_n \sim 4000$), and the MWDs were narrow, although they became slightly broader as the polymerization proceeded. Therefore, though the living nature of the polymerizations is essentially unaffected by nBu$_4$NCl concentration, it is worth noting that the MWDs were narrower in the presence of nBu$_4$NCl (10 mM) than in the absence. In addition, the salt is necessary for quantitative, better controlled, and homogeneous polymerizations of β-pinene. Thus, nBu$_4$NCl made the MWDs narrower probably by enhancing the relative rate of interconversion between the dormant and the activated species to propagation via trapping the cationic species.

3. Monomer-Addition Experiments. To examine the living nature of the polymerization with **1a**/$TiCl_3(OiPr)$/nBu$_4$NCl at −40 °C, a fresh feed of β-pinene was added to the reaction mixture just before the initial charge of the monomer had been consumed almost completely (conversion ~98%). The added β-pinene was smoothly polymerized at nearly the same rate as in the first stage. Even after the monomer addition, the molecular weights further increased in direct proportion to monomer conversion (Figure 5). The MWDs broadened only slightly even after the addition. Thus, it was demonstrated that the HCl−vinyl ether adduct leads to living cationic polymerizations of β-pinene in conjunction with $TiCl_3(OiPr)$ as a Lewis acid activator in the presence of nBu$_4$NCl.

4. Polymerization with HCl−Styrene Adduct (1b). The choice of initiator components is also one of the most important keys to the living cationic polymerizations of vinyl monomers.[9,16] We also employed the HCl−styrene adduct (**1b**; 1-phenylethyl chloride) as an alternative initiator for the living cationic polymerizations of β-pinene with $TiCl_3(OiPr)$ in place of HCl−vinyl ether adduct (**1a**). As shown in Figure 6A, the reaction with **1b** was faster than that with **1a** otherwise under the same conditions. This is probably due to the absence of a basic oxygen atom in the initiator unit, which may reduce the effective concentrations of the Lewis acid activator by complexing.

As with the vinyl ether adduct **1a**, the $\bar{M}_n$ of the polymers with the styrene adduct **1b** increased in direct proportion to monomer conversion, and the MWDs were similarly narrow ($\bar{M}_w/\bar{M}_n \sim 1.3$) (Figure 6). These results indicate that living cationic polymerizations of

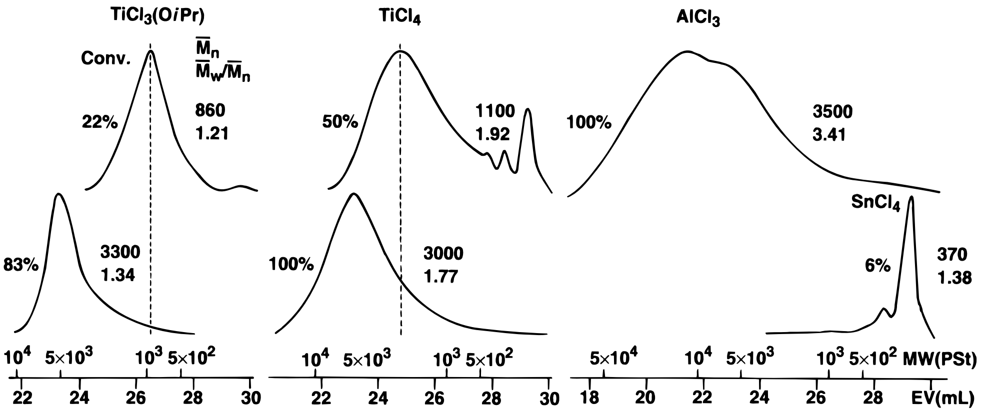


Figure 2. MWD curves of poly(β-pinene) obtained with **1a**/MX_n/$n$$Bu_4NCl$ in CH_2Cl_2 at −40 °C: $[M]_0$ = 1.0 M; $[\mathbf{1a}]_0$ = 20 mM; $[MX_n]_0$ = 100 mM; $[nBu_4NCl]_0$ = 10 mM.

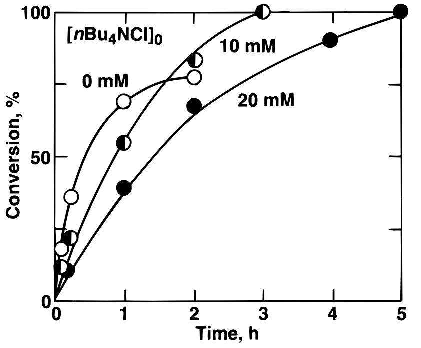


Figure 3. Effects of added $n$$Bu_4NCl$ concentration on the polymerization with **1a**/$TiCl_3(OiPr)$ in CH_2Cl_2 at −40 °C: $[M]_0$ = 1.0 M; $[\mathbf{1a}]_0$ = 20 mM; $[TiCl_3(OiPr)]_0$ = 100 mM; $[nBu_4NCl]_0$ = 0 (○); 10 (◐); 20 (●) mM.

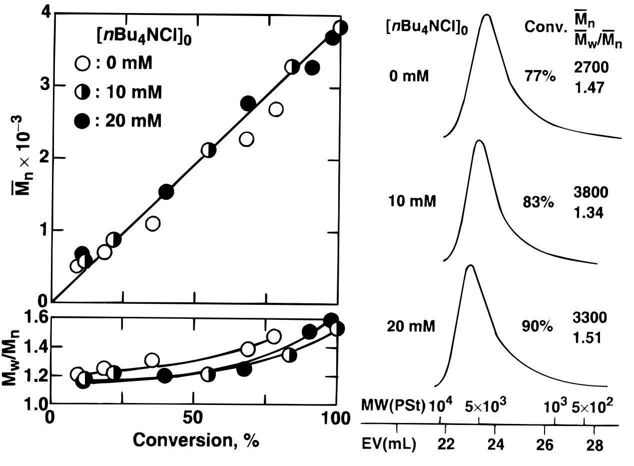


Figure 4. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(β-pinene) obtained with varying $n$$Bu_4NCl$ concentration in CH_2Cl_2 at −40 °C: $[M]_0$ = 1.0 M; $[\mathbf{1a}]_0$ = 20 mM; $[TiCl_3(OiPr)]_0$ = 100 mM; $[nBu_4NCl]_0$ = 0 (○); 10 (◑); 20 (●) mM.

β-pinene can also be initiated from the styryl cation generated from **1b** as well as from the vinyl ether cation from **1a**. This suggests the comparable reactivity of β-pinene to that of styrene and therefore the possibility of its block copolymerizations with styrene and its derivatives.[18]

5. Initiation Mechanism. To understand the initiation mechanism of the polymerization, the terminal structure of the polymers was analyzed by ^1H NMR spectroscopy. Figure 7A shows the spectrum of a typical poly(β-pinene) sample obtained with **1a**/$TiCl_3(OiPr)$/$n$$Bu_4NCl$.

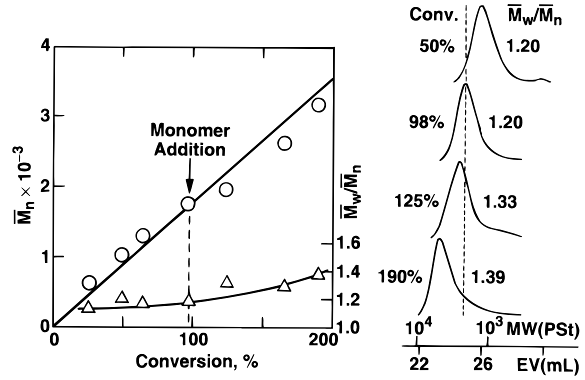


Figure 5. Monomer-addition experiments in the polymerization of β-pinene with **1a**/$TiCl_3(OiPr)$/$n$$Bu_4NCl$ in CH_2Cl_2 at −40 °C: $[M]_0 = [M]_{add}$ = 0.50 M; $[\mathbf{1a}]_0$ = 20 mM; $[TiCl_3(OiPr)]_0$ = 100 mM; $[nBu_4NCl]_0$ = 10 mM.

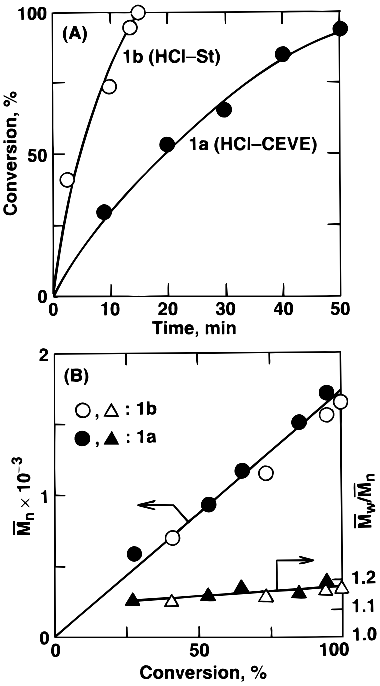


Figure 6. Polymerization of β-pinene with **1**/$TiCl_3(OiPr)$/$n$$Bu_4NCl$ in CH_2Cl_2 at −40 °C: $[M]_0$ = 0.50 M; $[\mathbf{1}]_0$ = 20 mM; $[TiCl_3(OiPr)]_0$ = 100 mM; $[nBu_4NCl]_0$ = 10 mM. Initiator (**1**): **1a** (●, ▲); **1b** (○, △).

As with the samples prepared by conventional cationic or inifer initiating systems,[7,8] the poly(β-pinene) from **1a** gave typical absorptions of the *endo*-olefin in the cyclohexene unit (*f*) at 5.2−5.5 ppm, in addition to the

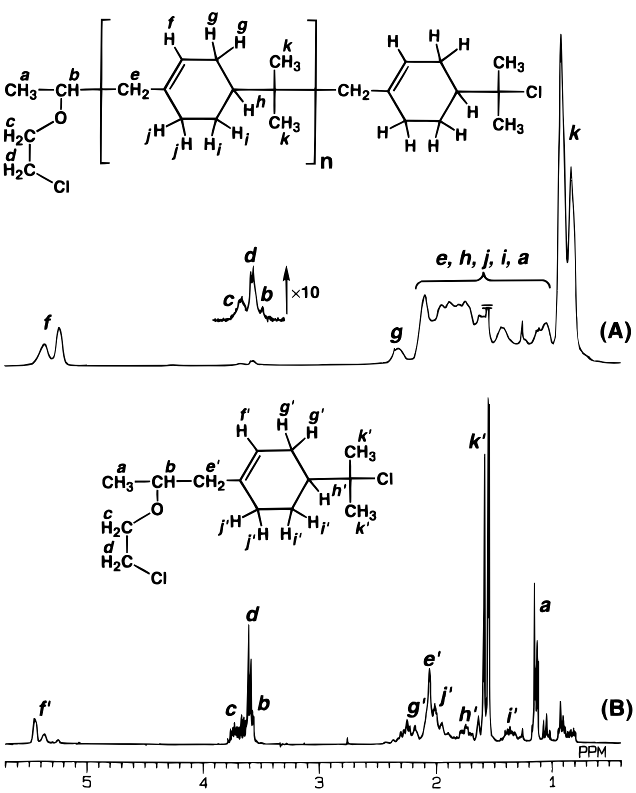
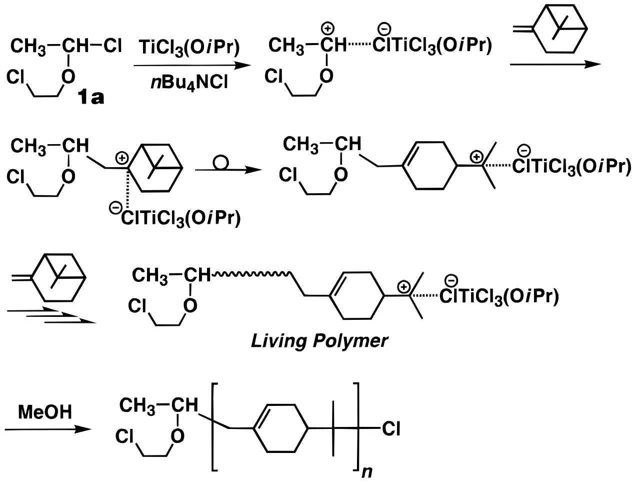


Figure 7. ^1H NMR spectra of poly(β-pinene) (A) and adduct of **1a** with β-pinene (B) obtained with **1a**/$TiCl_3(OiPr)$/$n$$Bu_4NCl$ in CH_2Cl_2 at −40 °C: $[M]_0 = 1.0$ M; $[\mathbf{1}]_0 = 20$ mM; $[TiCl_3(OiPr)]_0 = 100$ mM; $[nBu_4NCl]_0 = 10$ mM. Conversion of β-pinene: 100% (A), ~5% (B).

Scheme 1



aliphatic protons at 0.8−2.4 ppm, and thus the main chain consists of the repeat unit generated from the addition to the *exo*-methylene double bond followed by the ring opening of the cyclobutane unit in β-pinene (cf. Scheme 1).

Besides these signals (*e*−*k*), there appeared characteristic absorptions (*b*−*d*; 3.5−3.9 ppm) assignable to the initiator fragment. Furthermore, the number-average degree of polymerization [DP_n(NMR)], determined from the peak area ratio of the main-chain repeat units (*f*) to the initiator moiety (*b*−*d*), was close to the calculated value [DP_n(calcd)] from the initial feed ratio of the monomer to the initiator [DP_n(NMR)/DP_n(calcd) = 47/50]. These results indicate that **1a** generates one living polymer chain in the presence of $TiCl_3(OiPr)$ and $n$$Bu_4NCl$.

The ω-end of the polymers seems to be a chloride from the HCl−adduct initiator, as with the polymers of styrene, *p*-methylstyrene, and α-methylstyrene prepared by similar living polymerizations.[14−17] There were no terminal vinyl protons [$C(CH_3)=CH_2$] that would be seen at 4.6 ppm.[8] These can be generated from β-proton elimination during polymerizations or dehydrochlorination of the ω-end during the workup of the products. This also suggests that the living β-pinene polymerization is free of undesirable chain transfer.

Figure 7B shows the spectrum of oligomers with MW ~ 300 obtained at a very low conversion of β-pinene. This compound (see the inset) is the adduct of **1a** and β-pinene to be generated from the addition of the vinyl ether cation to the double bond of β-pinene followed by the opening of the cyclobutane ring.

From these results, the polymerization of β-pinene with **1a**/$TiCl_3(OiPr)$ is concluded to be living "isomerization" polymerization (Scheme 1). Thus, the C−Cl bond in the HCl−vinyl ether adduct is activated by $TiCl_3(OiPr)$ to generate a vinyl ether cation that subsequently adds to the *exo*-methylene double bond in β-pinene, to give the strained and sterically hindered cation. The unstable cation isomerizes via ring opening of the cyclobutane unit to give a stable tertiary cation, which is structurally very similar to that derived from isobutene. The isomerization process may broaden MWDs a little, because they depend on the rate of the isomerization relative to the interconversion between the dormant and the growing end, along with the propagation of the latter.

Experimental Section

Materials. (−)-β-Pinene (Wako Chemicals; purity > 97%) was distilled twice under reduced pressure over calcium hydride before use. 2-Chloroethyl vinyl ether (CEVE) (Nisso Maruzen Chemical; > 99%) was washed with 10% aqueous sodium hydroxide and then water, dried overnight with anhydrous sodium sulfate, and distilled twice under reduced pressure over calcium hydride before use. 1-Phenylethyl chloride (**1b**; Wako Chemicals; purity > 97%) was distilled twice under reduced pressure. $AlCl_3$ (Aldrich; purity > 99.99%), $SnCl_4$, $TiCl_4$ (both Aldrich; 1.0 M solutions in methylene chloride), and $n$$Bu_4NCl$ (Tokyo Kasei; purity > 98%) were used as received. CH_2Cl_2 was doubly distilled over phosphorus pentoxide and then over calcium hydride before use. *n*-Hexane (the solvent for **1a**) and chlorobenzene (an internal standard for gas chromatography) were doubly distilled over calcium hydride before use.

Isopropoxytitanium chloride [$TiCl_3(OiPr)$][13,16] and adduct **1a**[15,17] were prepared and purified as already reported.

Polymerization Procedures. Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example is given below. The reaction was initiated by adding, via dry syringes, a solution of **1a** (in *n*-hexane; 0.50 mL) and a mixture (in CH_2Cl_2; 1.0 mL) of $TiCl_3(OiPr)$ and $n$$Bu_4NCl$ sequentially in this order into a solution (3.5 mL) of β-pinene (0.78 mL) and chlorobenzene (0.22 mL) in CH_2Cl_2 at −40 °C. The reaction was quenched with prechilled methanol (2 mL) after predetermined intervals.

The quenched reaction mixture was diluted with *n*-hexane (25 mL) and washed sequentially with 2% hydrochloric acid, aqueous 1% sodium hydroxide solution, and water to remove Ti-containing residues. The organic layer was evaporated to dryness under reduced pressure and dried in vacuo at 40 °C for 5 h to give the product polymers. In most cases, the gas-chromatographic conversion of the monomer is higher than the polymer yield by gravimetry, because isomerization of the residual β-pinene monomer occurred in the GC columns. Thus, the gravimetric conversion was used throughout this work.

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, and K-804) 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 ($\bar{M}_n$ = 800−300000; $\bar{M}_w/\bar{M}_n$ = 1.03−1.10) as well as styrene oligomers (tetramer, trimer, and dimer). ^{1}H NMR spectra of the polymers were recorded in $CDCl_3$ at room temperature on a JEOL JNM-GSX270 spectrometer (270.7 MHz). Polymers and lower molecular weight oligomers for ^{1}H NMR analysis were fractionated by preparative SEC (columns: Shodex K-2002 and H-2001, respectively).

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