Macromolecules **2000,** *33,* 725−729

Bulky Titanium Bis(phenolate) Complexes as Novel Initiators for Living Anionic Polymerization of ϵ-Caprolactone

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Received August 24, 1999; Revised Manuscript Received December 13, 1999

ABSTRACT: Bulky bis(phenolate) complexes of titanium alcoholates were found to initiate living polymerization of ϵ-caprolactone, affording a polyester with a narrow molecular weight distribution. By changing the initial monomer-to-initiator mole ratio, the molecular weight of the polymer was controlled over a wide range. ^{1}H NMR studies on the produced polymer showed the presence of an alkoxy group originating from the initiator at the polymer terminal, indicating that the polymerization takes place at the titanium alcoholate bond of the initiator. Use of titanium complexes prepared with nonbridged hindered phenols or a less bulky bisphenol resulted in a poorly controlled chain growth or no polymerization.

Introduction

The chemistry of metallocene complexes of transition metals has greatly expanded because of its successful application to controlled polymerization of olefins[1] and polar vinylic monomers[2] and more recently to ring-opening polymerization of some heterocyclic monomers such as cyclic esters (lactones)[3a,b] and carbonates.[3c] On the other hand, structurally well-defined non-metallocene-type complexes have attracted increasing attention as initiators for controlled olefin polymerizations.[4] For example, some diamide and diimide complexes of transition metals such as Ti, Zr, and Ni have been reported to bring about living polymerization of α-olefins. Bis(phenolate) complexes of group 4 metals are also highly active initiators for the polymerization of α-olefins and styrene.[5] On the other hand, application of such transition metal complexes to the polymerization of polar vinylic monomers is only very limited, and no successful examples have been reported for controlled ring-opening polymerization of heterocyclic monomers with non-metallocene complexes of transition metals.

In the present paper, we report results of ring-opening polymerization of heterocyclic monomers using titanium phenolate complexes as initiators and wish to highlight the living polymerization of ϵ-caprolactone initiated with titanium alcoholate complexes of bulky bis(phenolate)s having *tert*-butyl or phenyl substituents. Polylactones have attracted attention in view of their possible application as biodegradable polymers. For the controlled synthesis of polylactones, there have been reported some excellent initiators or catalysts that include alkylaluminum alcoholates,[6] aluminum porphyrins,[7] lanthanide complexes,[8] tin octanoate,[9] and mesoporous zeolite.[10] On the other hand, as for early transition metal complexes, only metallocene complexes of titanium[3a] and zirconium[3b,c] have been investigated as initiators for the polymerization of lactones.

Results and Discussion

Synthesis and Characterization of Titanium Bis(phenolate)s. Titanium complexes of bulky bis(phenolate)s were prepared from titanium compounds and phenolic ligands: **1a** was obtained by the reaction of $TiCl_4$ with 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) in hexane at 25 °C, followed by recrystallization from hexane.[11] ^{1}H NMR spectroscopy of **1a** in $CDCl_3$ at 25 °C showed two doublet signals at δ 3.74 and 4.08 ppm assignable to the bridging CH_2 group of the bis(phenolate) ligand. This is consistent with the boat conformation of the dioxatitanacycle, as reported by Floriani et al. on the basis of the crystal structure analysis of **1a**.[11] Likewise **1b** was obtained from $Ti(OCHMe_2)_4$ and 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) in ether.[12] We also prepared **2a** by the reaction of $TiCl_4$ with 2,2′-methylenebis(6-phenylphenol) in toluene. ^{1}H NMR spectroscopy of **2a** in $CDCl_3$ at 25 °C again showed two doublet signals at δ 3.52 and 4.33 ppm due to the bridging CH_2 group. However, these signals were broader than those of **1a**, indicating a higher conformational flexibility of the dioxatitanacycle in **2a**. Recrystallization of **2a** from THF/hexane gave a THF complex of **2a** (THF/**2a** = 2/1) as dark-red cubic crystals. X-ray crystal structure analysis showed that two THF molecules are coordinated to the octahedral titanium center of **2a** at a distance of 2.16 and 2.20 Å.[13] Okuda et al. have reported that recrystallization of **1a** from THF/ether also affords a THF complex of **1a** (**1a**·(thf)), in which, however, only one THF molecule is coordinated to the trigonal-bipyramidal titanium center of **1a** at a distance of 2.16 Å. The reaction of $Ti(OCHMe_2)_4$ with 2,2′-methylenebis(6-phenylphenol) in toluene gave **2b**, which also showed two broad CH_2 signals at δ 3.45 and 4.40 ppm, indicating that the bis(phenolate) ligand in the complex forms a dioxatitanacycle.

Ring-Opening Polymerization with Titanium Bis(phenolate) Complexes. For the ring-opening polymerization with titanium bis(phenolate) complexes **1** and **2**, ϵ-caprolactone (CL), 1,2-epoxypropane (propylene oxide; PO), and oxetane (oxacyclobutane; OX)[14] were chosen as potential monomers. When 100 equiv of CL was added at 25 °C to a CH_2Cl_2 solution of **1b**, the polymerization of CL took place to attain 23, 66, and 100% monomer conversion in 1, 2, and 5 h, respectively. The produced polymer had a narrow molecular weight distribution (MWD) with M_n and M_w/M_n of 6500 and 1.15, respectively. The degree of polymerization (D_p) of

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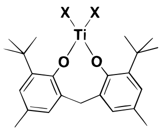
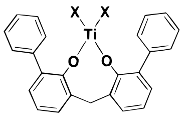
10.1021/ma991441+ CCC: $19.00



1a: X = Cl
1b: X = OCHMe$_2$



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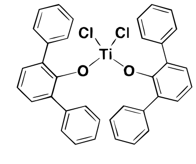

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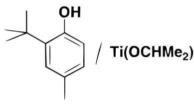

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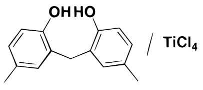
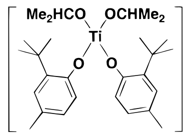
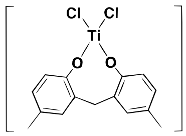


5 (1/1)





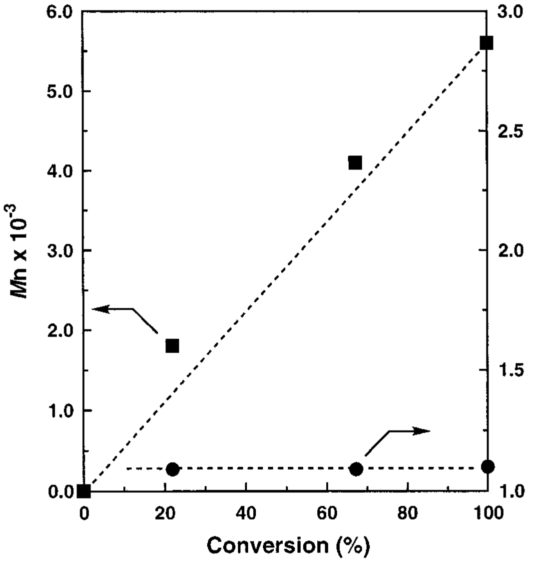


Figure 1. Polymerization of ϵ-caprolactone (CL) initiated with **2b** ([**2b**]$_0$ = 33 mM, [CL]$_0$/[**2b**]$_0$ = 100) in CH_2Cl_2 at 25 °C. Relationship between M_n of the polymer and monomer conversion.

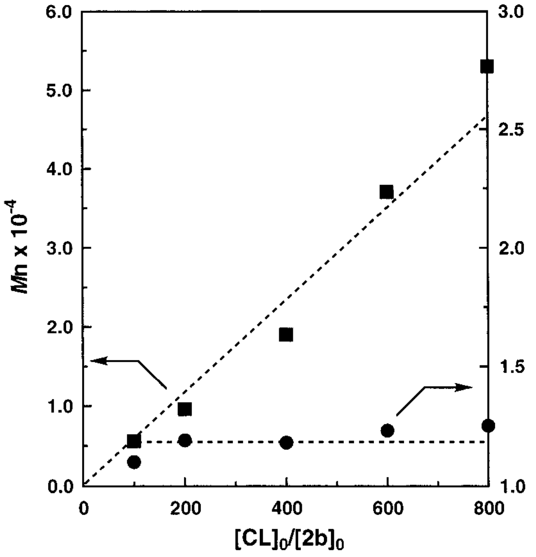


Figure 2. Polymerization of ϵ-caprolactone (CL) initiated with **2b** in CH_2Cl_2 at 25 °C. Relationship between M_n of the polymer at 100% monomer conversion and initial monomer-to-initiator mole ratio [CL]$_0$/[**2b**]$_0$.

the polymer was almost a half of the monomer-to-initiator mole ratio, suggesting the formation of two polymer molecules from every molecule of **1b**. Use of **2b** in place of **1b** for the polymerization of CL resulted in the formation of a polyester with a much narrower MWD, although the rate of polymerization was smaller than that with **1b** as the initiator. For example, at the monomer-to-initiator (**2b**) mole ratio of 100, the polymerization in CH_2Cl_2 at 25 °C proceeded to 23 and 67% monomer conversion in 6 and 24 h, respectively, and was completed in 75 h, affording a polymer with M_n and M_w/M_n of 5600 and 1.10, respectively. The M_n value of the polymer was observed to increase proportionally to monomer conversion, while the M_w/M_n ratio remained almost constant at 1.1 (Figure 1). As shown in Figure 2, the M_n value was successfully controlled over a wide range by changing the initial mole ratio of CL to **2b**. In each case, the M_n value was again close to the calculated value for the formation of two polymer molecules from every molecule of **2b**. For example, at the mole ratio [CL]$_0$/[**2b**]$_0$ of 800, a narrow MWD polyester with M_n and M_w/M_n respectively of 53 000 ($M_{n,calc}$ = 44 000) and 1.25 was obtained at 100% monomer conversion.

For the end group analysis, a polymerization mixture of CL with **2b** ([CL]$_0$/[**2b**]$_0$ = 100, 100% monomer conversion) was poured into methanol, and white precipitates formed were collected, dried, and subjected to ^{1}H NMR spectroscopy. As shown in Figure 3, the isolated polymer showed signals a–e due to repeating $-C(O)(CH_2)_5O-$ units and relatively weak signals f (δ 1.23), g (δ 5.02), and h (δ 3.65) assignable to the terminal $(CH_3)_2CH$, $(CH_3)_2CH$, and $HOCH_2$, respectively.[6c] The degree of polymerization (D_p) of the polymer, as evaluated from the intensity ratio of the signals a to h, was 53, which agrees well with a half of the initial mole ratio of CL to **2b**. Gel permeation chromatography (GPC) of this polymer was silent at 254 nm when monitored with an UV detector, indicating the absence of bis(phenolate) groups originating from **2b** in the polymer chain. Therefore, the polymerization is concluded to proceed by the reaction of CL with the two alcoholate groups bound to the titanium center of **2b** (Scheme 1). In contrast to the above, the titanium alcoholate complexes (**1b**, **2b**), under similar conditions, were inert for the ring-opening polymerization of other heterocyclic monomers such as 1,2-epoxypropane (PO) and oxetane (OX). For example, when 50 equiv of OX was added at 25 °C to a CH_2Cl_2 solution of **1b**, no ring-opening reaction took place throughout an observation over a period of 48 h, where the titanium alcoholate species in **1b** remained unreacted, as observed by ^{1}H NMR (δ 1.38 ppm; $(CH_3)_2CHO-Ti$).

When compared with the titanium alcoholate complexes (**1b**, **2b**), the corresponding dichloride complexes (**1a**, **2a**) are of much higher Lewis acidity. When 100 equiv of CL was added at 25 °C to a CH_2Cl_2 solution of **1a**, the solution immediately turned from dark red to bright red. However, in the ^{1}H NMR spectrum of the reaction mixture, no signals assignable to ring-opened products were detected even after 24 h. In contrast, an attempted reaction of PO with **1a** resulted in the formation of a ring-opened product. Thus, 50 equiv of PO was added to a CH_2Cl_2 solution of **1a**, and after stirred for 3 h at 25 °C, an aliquot of the reaction mixture was taken out and subjected to ^{1}H NMR spectroscopy. In $CDCl_3$, the spectrum showed a set of relatively small two double-doublet signals at δ 3.38 and 3.51 ppm and a multiplet signal at δ 3.92 ppm, which

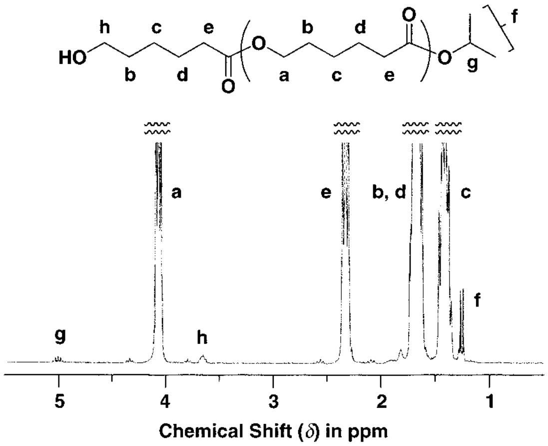
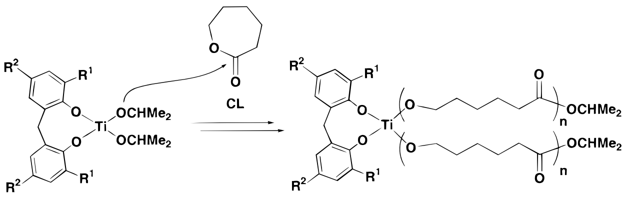


Figure 3. Polymerization of ϵ-caprolactone (CL) initiated with **2b** ($[\mathbf{2b}]_0 = 33$ mM, $[\mathrm{CL}]_0/[\mathbf{2b}]_0 = 100$) in CH_2Cl_2 at 25 °C. ^1H NMR spectrum in $CDCl_3$ at 25 °C of a polymer isolated by precipitation from CH_2Cl_2/methanol.

Scheme 1



1b: R^1 = *tert*-Bu, R^2 = Me
2b: R^1 = Ph, R^2 = H

are assignable respectively to CH_2 and CH of 1-chloro-2-propanol, the ring-opened adduct.[15] The relative intensities of these signals to those of the bis(phenolate) ligand of **1a** indicated a one-to-one stoichiometry of the ring-opening reaction. Thus, it is likely that the epoxide is inserted into only one of the two Cl−Ti bonds of **1a** to form a chlorotitanium monoalcoholate species (**1c**). It should be also noted, however, that no signals assignable to polymeric products were detected. Therefore, similarly to the titanium bis(alcoholate) complexes (**1b**, **2b**), the alcoholate, formed by the reaction of **1a** with PO, possesses only a very low activity toward further addition of PO, possibly due to a low Lewis acidity and therefore a low monomer activation power of the alcoholate.

A similar result was obtained for the reaction of **1a** with oxetane (OX). The formation of 1-chloro-3-propanol, a ring-opened adduct, was confirmed by ^1H NMR spectroscopy of the reaction mixture between **1a** and OX (1:50), where signals due to $ClCH_2$ (δ 3.71), CH_2 (δ 2.04), and CH_2OH (δ 3.85) were observed in addition to those due to unreacted OX (δ 4.84 [OCH_2], δ 2.72 [CH_2]). Investigation of the relative signal intensities again indicated the formation of a chlorotitanium monoalcoholate species (**1d**). Since no signals due to polymeric products were observed, this alcoholate also has a very low reactivity toward OX.

As already described, the titanium bis(alcoholate) complexes (**1b**, **2b**) are not capable of causing ring-opening reaction of PO and OX, but they can effectively initiate the controlled polymerization of ϵ-caprolactone (CL). Thus, we were motivated to investigate the polymerization of CL with the alcoholate formed by the reaction of **1a** with 1,2-epoxypropane (PO) [**1c**] or oxetane (OX) [**1d**]: PO was added to a CH_2Cl_2 solution of **1a** at a mole ratio $[\mathrm{PO}]_0/[\mathbf{1a}]_0$ of 5 ($[\mathbf{1a}]_0 = 0.10$ mM) under Ar, and after 24 h stirring at 25 °C, 100 equiv of CL with respect to **1a** was added to the reaction mixture, whereupon the polymerization of CL took place to attain 39, 63, and 100% monomer conversion in 1, 2, and 6 h, respectively. The M_n value of the polymer was observed to increase linearly with monomer conversion, retaining the narrow MWD, and finally reached 9200 with M_w/M_n of 1.21. The M_n value, thus observed, is close to the calculated one (11 000) from the assumption that every molecule of the titanium complex produces one polymer molecule. This stoichiometry is consistent with the monoalcoholate structure (**1c**), as suggested for the reaction product between **1a** and PO. As shown in Figure 4, the M_n value of the polymer was controlled over a wide range from 0.5 to 5 × 10^4 by changing the initial monomer-to-initiator mole ratio from 50 to 400. To confirm the living character of the polymerization, a sequential two-stage polymerization of CL was investigated with the **1a**/PO (1/5) system. Thus, the first-stage polymerization of CL ($[\mathrm{CL}]_0/[\mathrm{Ti}]_0 = 50$) was allowed to proceed up to 100% monomer conversion [Figure 5 (I); $M_n = 5900$, $M_w/M_n = 1.11$], and then 100 equiv of CL was newly added to the system, whereupon the second-stage polymerization ensued to give, at 100% monomer conversion, a higher molecular weight polymer with M_n and M_w/M_n of 18 000 and 1.28, respectively [Figure 5 (II)]. The ^1H NMR spectrum of the polymerization mixture showed characteristic signals due to PO even after the second-stage polymerization, again indicating that the growing alcoholate species are virtually inert for the ring-opening reaction of PO. Likewise, when oxetane (OX; 50 equiv) and CL (100 equiv) were added subsequently to a CH_2Cl_2 solution of **1a** at 25 °C, only CL was polymerized to give a polyester with M_w/M_n of 1.26. The M_n value of the polymer (9400) was again close to the calculated one (11 000) from the assumption that every molecule of the titanium complex (**1d**) produces one polymer molecule. Therefore, OX here simply served to convert **1a** into the monoalcoholate complex (**1d**), an initiating species for the polymerization of CL.

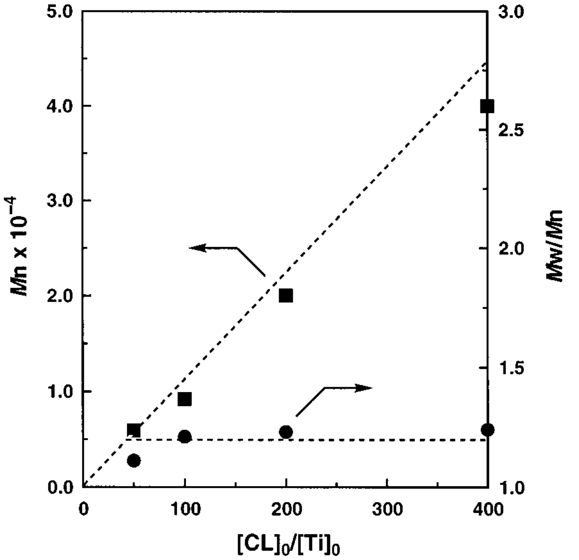


Figure 4. Polymerization of ϵ-caprolactone (CL) initiated with a reaction mixture of **1a** and PO ($[\mathrm{PO}]_0/[\mathbf{1a}]_0 = 5$) in CH_2Cl_2 at 25 °C. Relationship between M_n of the polymer at 100% monomer conversion and initial monomer-to-initiator ratio $[\mathrm{CL}]_0/[\mathrm{Ti}]_0$.

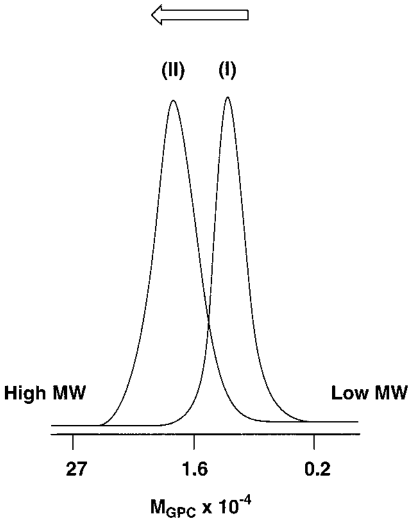


Figure 5. Two-stage polymerization of ϵ-caprolactone (CL) initiated with a reaction mixture of **1a** and PO ($[\mathrm{PO}]_0/[\mathbf{1a}]_0 = 5$) in CH_2Cl_2 at 25 °C. GPC profiles of the polymers formed at (I) the first stage ($[\mathrm{CL}]_0/[\mathrm{Ti}]_0 = 50$, 100% monomer conversion, $M_n = 5900$, $M_w/M_n = 1.11$) and (II) the second stage ($[\mathrm{CL}]_0/[\mathrm{Ti}]_0 = 150$, 100% monomer conversion, $M_n = 18\,000$, $M_w/M_n = 1.28$).

For comparison with the titanium bis(phenolate) complexes having bulky *tert*-butyl or phenyl substituents (**1**, **2**), titanium complexes prepared with nonbridged hindered phenols or a less bulky bis(phenol) were used for the polymerization of CL: According to the literature method,[16] crystallographically defined **3** (deep-red crystals) was prepared from $TiCl_4$ and 2 equiv of 2,6-diphenylphenol in toluene at 25 °C, followed by recrystallization from toluene. Then, PO was added to a CH_2Cl_2 solution of **3** at a mole ratio $[\mathrm{PO}]_0/[\mathbf{3}]_0$ of 5 ($[\mathbf{3}]_0 = 33$ mM) under Ar, and after 24 h stirring at 25 °C, 100 equiv of CL with respect to **3** was added to the reaction mixture. Here, the polymerization took place to attain 100% monomer conversion in 24 h, but the produced polymer had a broader MWD, as indicated by the ratio M_w/M_n of 1.57 ($M_n = 6900$). Although the polymers prepared with **1** and **2** as initiators are silent at 254 nm (vide supra), the GPC chromatogram of the polymer obtained with **3** showed an elution peak when monitored with a UV detector at 254 nm. This result indicates an unfavorable incorporation of the phenolate ligand of **3** into the polymer terminal. A similar result was obtained for the polymerization of CL with a titanium alcoholate complex prepared with $Ti(OCHMe_2)_4$ and a nonbridged hindered phenol such as 2-*tert*-butyl-4-methylphenol ($[\mathrm{CL}]_0/[\mathrm{Ti}]_0 = 100$): The polymerization at 25 °C reached 100% monomer conversion in 7 h, but the produced polymer had a broader MWD ($M_n = 6300$, $M_w/M_n = 1.47$) with an absorption band at 254 nm. Along the line of this study, we were interested in utilization of a titanium complex having a less hindered bis(phenolate) ligand for the polymerization of CL. Thus, 2,2′-methylenebis(4-methylphenol) was allowed to react with $TiCl_4$ under conditions similar to those for the preparation of **1a** and **2a**, and then the reaction mixture was subjected to recrystallization from hexane, affording dark-red powder. In contrast with the case of the sterically hindered bis(phenolate) complexes, the ^{1}H NMR spectrum of the product in $CDCl_3$ at 25 °C was rather complicated, where only broad signals were observed at δ 2.31 and 3.2−4.4 ppm for the CH_3 and CH_2 resonances, respectively. This is most likely due to aggregation of some titanium phenolate species. When the product in CH_2Cl_2 was stirred with PO at 25 °C for 24 h, the solution turned from deep red to light orange, characteristic of bis(phenolate)titanium alcoholate species. However, addition of 100 equiv of CL to the reaction mixture resulted in no polymerization, as observed by ^{1}H NMR over a period of 48 h. Thus, these three control experiments clearly indicate the importance of the bulky dioxatitanacycle structures of **1** and **2** for the "living" chain growth in the polymerization of CL.

Conclusion

We have demonstrated that titanium alcoholates complexes of methylene-bridged hindered phenolates (**1**, **2**) serve as new transition metal initiators for the living polymerization of a cyclic ester such as ϵ-caprolactone, in which the bulky dioxatitanacycle structure plays an important role. Ring-opening polymerization of lactones often suffers an essential problem associated with the competitive transesterification, leading to broadening of MWD. Although alcoholates complexes of half titanocenes are also excellent initiators for the controlled polymerization of six- and seven-membered lactones, a signature of concomitant transesterification has been clearly observed at the latter stage of the polymerization.[3a] On the other hand, in the polymerization with non-metallocene initiator **2**, the growing species has a much lower activity for such side reactions. Fine-tuning of the ligands and further application to the polymerization of other monomers are subjects worthy of further investigation.

Experimental Part

Materials. Dichloromethane (CH_2Cl_2), washed successively with concentrated H_2SO_4, water, and aqueous $NaHCO_3$, was dried over $CaCl_2$ and fractionally distilled in an Ar atmosphere after refluxing over CaH_2. Ether and hexane were refluxed over sodium benzophenone ketyl and fractionally distilled in an Ar atmosphere. Deuterated chloroform ($CDCl_3$) was used as received. ϵ-Caprolactone (CL) was refluxed over CaH_2 and fractionally distilled under Ar. 1,2-Epoxypropane (PO) was refluxed over a mixture of KOH pellets and CaH_2 and fractionally distilled under Ar. Oxetane (OX) was distilled from Na under Ar. 2,2′-Methylenebis(6-*tert*-butyl-4-methylphenol), 2,2′-methylenebis(4-methylphenol), 2-*tert*-butyl-4-methylphenol, and 2,6-diphenylphenol were recrystallized from hexane. Titanium tetrachloride ($TiCl_4$) was distilled in the presence of Cu powder under reduced pressure in an Ar atmosphere. Titanium tetrakis(2-propanolate) ($Ti(OCHMe_2)_4$) was fractionally distilled under reduced pressure under Ar.

Procedures. (a) Preparation of 2,2′-Methylenebis(6-phenylphenol).[17] 2-Phenylphenol (8.51 g, 50 mmol), paraformaldehyde (0.75 g, 25 mmol), and xylene (12 mL) were added to a 100 mL stainless steel autoclave containing a magnetic stirring bar, and the mixture was stirred at 180 °C for 24 h. Then, volatile fractions were removed from the reaction mixture under reduced pressure to leave an orange oil, which was chromatographed on silica gel using $CHCl_3$/hexane (7/1) as eluent. The second band was collected and evaporated to dryness, and the residue was subjected to recrystallization from benzene, affording 2,2′-methylenebis(6-phenylphenol) as white plates (3.36 g, 9.5 mmol) in 38% yield. ^{1}H NMR ($CDCl_3$): δ 4.12 (2H, s, CH_2), 6.35 (2H, s, OH), and 6.9−7.7 (16H, m, Ar).

(b) Preparation of Dichlorotitanium Bis(phenolate) Complexes (1a, 2a, 3, and 5).[11,12] To a 50 mL round-bottomed flask equipped with a three-way stopcock, containing 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) (1.0 mmol, 0.34 g) and a magnetic stirring bar under Ar, were successively added hexane (25 mL) and $TiCl_4$ (1.0 mmol, 0.11 mL) at 25 °C, and the mixture was stirred for 1 h, whereupon deep-red precipitates formed. The reaction mixture was once heated at 60 °C, and the resulting clear solution was allowed to cool to 25 °C, affording deep-red crystals. Then, the supernatant liquid phase was removed by a syringe from the flask in an Ar stream, and the residue was washed several times with dry hexane (2 mL) and then dried under reduced pressure at 25 °C, to leave **1a** as deep-red crystals in 71% yield. ^1H NMR ($CDCl_3$): δ 1.47 (18H, s, $C(CH_3)_3$), 2.36 (6H, s, CH_3), 3.73 (1H, d, CH_2), 4.21 (1H, d, CH_2), 7.00 (2H, s, C_6H_2), and 7.19 (2H, s, C_6H_2). Likewise, **2a** and **5** were prepared from $TiCl_4$ and the corresponding bis(phenol)s. ^1H NMR ($CDCl_3$) **2a**: δ 3.89 (1H, br, CH_2), 4.39 (1H, br, CH_2), and 6.87−7.54 (16H, m, Ar). **5**: δ 2.31 (6H, s, CH_3), 3.2−4.4 (2H, br, CH_2), and 6.90−7.45 (6H, m, C_6H_3). **3** was prepared from $TiCl_4$ and 2 equiv of 2,6-diphenylphenol, according to the reported procedure.[16]

(c) Preparation of Bis(alcoholate) Complexes of Titanium Bis(phenolate)s (1b, 2b, and 4).[12] Typically, to a 50 mL round-bottomed flask equipped with a three-way stopcock, containing 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) (2.1 mmol, 0.70 g) and a magnetic stirring bar in an Ar atmosphere, were successively added ether (8 mL) and $Ti(OCHMe_2)_4$ (2.0 mmol, 0.6 mL), and the mixture was stirred for 1 h at 25 °C. The resulting clear reddish-orange solution was cooled to −78 °C, affording orange microcrystals. Then, the supernatant liquid phase was removed by a syringe from the flask in an Ar stream, and the residue was washed several times with hexane (2 mL) and then dried under reduced pressure at 25 °C, to leave **1b** as orange crystals in 56% yield. ^1H NMR ($CDCl_3$): δ 1.38 (12H, d, $CH(C\mathit{H}_3)_2$), 1.44 (18H, s, $C(CH_3)_3$), 2.30 (6H, s, $ArCH_3$), 3.52 (1H, d, CH_2), 4.33 (1H, d, CH_2), 4.78 (2H, m, $C\mathit{H}(CH_3)_2$), 6.93 (2H, s, C_6H_2), and 7.11(2H, s, C_6H_2). Likewise, **2b** was prepared from $Ti(OCHMe_2)_4$ and an equivalent of 2,2′-methylenebis(6-phenylphenol). ^1H NMR ($CDCl_3$): δ 1.15 (12H, d, CH_3), 3.45 (1H, br, CH_2), 3.98 (2H, m, CH), 4.40 (1H, br, CH_2), and 6.50−7.72 (16H, m, Ar). **4** was prepared from $Ti(OCHMe_2)_4$ and 2 equiv of 2-*tert*-butyl-4-methylphenol. ^1H NMR ($CDCl_3$): δ 1.11−1.29 (12H, m, $CH(C\mathit{H}_3)_2$), 1.36 (18H, s, $C(CH_3)_3$), 2.34 (6H, s, $ArCH_3$), 3.9−4.8 (2H, m, CH), and 6.8−7.1 (4H, m, C_6H_2).

Polymerization. Typically, to a 50 mL round-bottomed flask attached to a three-way stopcock, containing a CH_2Cl_2 solution (3 mL) of **1c** (0.1 mmol) and a magnetic stirring bar under Ar, was added ϵ-caprolactone (CL) (10 mmol, 1.11 mL) by a syringe, and the mixture was stirred at 25 °C. An aliquot of the polymerization mixture was periodically taken out from the flask and subjected to ^1H NMR spectroscopy ($CDCl_3$) and gel permeation chromatography (GPC) to determine monomer conversion and average molecular weights (M_n, M_w) of the produced polymer, respectively. Monomer conversion was calculated from the relative intensity of the signals at δ 2.58 and 2.33 ppm due to $-C(O)CH_2-$ in CL and poly(CL), respectively. For isolation of the polymer, the polymerization mixture was poured into methanol, and white precipitates formed were collected and dried in vacuo at 25 °C.

Measurements. Gel permeation chromatography (GPC) was performed at 40 °C on a TOSO model 8020 high-speed liquid chromatograph equipped with a differential refractometer detector and a variable-wavelength UV−vis detector, using tetrahydrofuran as eluent at a flow rate of 1.0 mL min^{-1}. The molecular weight calibration curve was obtained by using standard polystyrenes; M_n (M_w/M_n): 2 890 000 (1.09), 422 000 (1.04), 107 000 (1.07), 43 900 (1.01), 16 700 (1.02), 9000 (1.06), 6200 (1.04), 4000 (1.10), and 2800 (1.05). Molecular weights (M_n and M_w), as estimated by GPC, were multiplied by a factor of 0.6.[6c] ^1H and ^{13}C NMR measurements were performed using $CDCl_3$ as a solvent on a JEOL type GSX-270 spectrometer, where the chemical shifts were determined with respect to $CHCl_3$ (δ 7.28) for ^1H and $CDCl_3$ (δ 77.2) for ^{13}C as internal standards.

Acknowledgment. The present work was partly supported by a Grant-in-Aid No. 10132211 for Scientific Research on Priority Area, the Ministry of Education, Science, Sports and Culture, Japan, and by a grant for “Precision Catalytic Polymerization” from the New Energy and Industrial Technology Development Organization (NEDO) under the Ministry of International Trade and Industry, Japan. We thank Dr. Y. Ishii of the University of Tokyo for technical guidance for X-ray crystal structure analysis of **2a**·(thf)$_2$.

Supporting Information Available: X-ray crystal structure data of **2a**·(thf)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA991441+