7538 *Macromolecules* **2002,** *35,* 7538−7544

Articles

Polymerizations of Cyclic Esters Catalyzed by Titanium Complexes Having Chalcogen-Bridged Chelating Diaryloxo Ligands

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Received March 25, 2002; Revised Manuscript Received June 27, 2002

ABSTRACT: A series of titanium complexes having tellurium-bridged chelating bis(aryloxo) ligands, [TiX$_2$-{2,2′-Te(4-Me-6-^{t}Bu-C$_6$H$_2$O)$_2$}]$_2$ (**5**: X = Cl; **6**: X = O^{i}Pr), catalyzed the ring-opening polymerization of cyclic esters such as ϵ-caprolactone, δ-valerolactone, and L-lactide. The strong dependence of polymerizations on the solvent was observed in this catalytic system. When the polymerizations of ϵ-caprolactone and L-lactide were carried out in toluene at 100 °C, tellurium-bridged bis(aryloxo)titanium complex **5** was found to give polymers with rather broad molecular weight distribution due to back-biting. When the polymerizations of ϵ-caprolactone and L-lactide was carried out in anisole or in dioxane at 100 °C, complex **5** was found to initiate the controlled polymerization, to result in quantitative polymer yields and narrow molecular weight distributions (living nature). The diblock copolymers of L-lactide and ϵ-caprolactone were also obtained with the catalyst system **5** in anisole. The diblock copolymers showed two melting endothermic at 44.7−53.5 °C derived from the ploy(ϵ-caprolactone) block and at 155.2−156.8 °C derived from the ploy(L-lactide) block.

Introduction

Recently, increasing attention has been paid to high molecular weight aliphatic polyesters due to their biodegradable and biocompatible ability which is rapidly emerging as a potential environmentally friendly replacement for bioresistant polymers such as poly(α-olefin).[1] ϵ-Caprolactone (ϵ-CL) and L-lactide (L-LA) can be polymerized with initiators containing alkali metal,[2] tin octoate,[3] tris(acetylacetonato)aluminum,[4] (porphinato)aluminum,[5] and alkoxides of aluminum,[6] zinc,[4,7] and the rare earth metals.[8] In early transition metal complexes, metallocene complexes of titanium[9] and zirconium[10] also initiate the ring-opening polymerization of cyclic esters. Aida and co-workers reported that titanium complexes bearing a methylene-bridged bis(aryloxo) ligand, {2,2′-CH$_2$(4-Me-6-^{t}BuC$_6$H$_2$O)$_2$}TiX$_2$ (**1**: X = Cl, **2**: X = O^{i}Pr), initiated controlled polymerization of ϵ-CL in the presence of some cocatalysts such as propylene oxide and oxetane.[11]

On the other hand, nonmetallocene-type group 4 complexes are of great interest as a new kind of highly active homogeneous catalyst precursors for olefin polymerization. Miyatake and Kakugo reported that titanium complexes having a sulfur-bridged bis(aryloxo) ligand, (TBP)TiX$_2$ (**3**: X = Cl, **4**: X = O^{i}Pr, TBP = 2,2′-thiobis(4-methyl-6-*tert*-butylphenoxo)), showed distinctively high activity for the polymerization of ethylene and propylene upon activation with methylaluminoxane (MAO).[12] The **3**/MAO system is an order of magnitude more active than the systems based on the corresponding methylene-bridged bis(aryloxo) complex **1** and similar 2,2′-biphenolate complexes.[13] Thus, the coordination of sulfur to the metal is the key feature for the high activity of **3**. The TBP ligand was found to coordinate to the metal in *fac* fashion.[14] A theoretical study by Morokuma and co-workers indicated that the coordination of the sulfur atom was essential to reduce the activation energy for olefin insertion to a metal−carbon bond.[15] To evaluate the effect of the bridging moiety, we studied the synthesis, structure, and catalytic behavior for ethylene polymerization of the titanium complexes having a tellurium-bridged chelating diaryloxo ligand, (TeBP)TiX$_2$ (**5**: X = Cl, **6**: X = O^{i}Pr, TeBP = 2,2′-tellurobis(4-methyl-6-*tert*-butylphenoxo)) and (C$_5$R$_5$)TiCl(TeBP) (**7**: R = H, **8**: R = Me).[16] These complexes showed 20−50 times higher activities than the methylene-bridged bis(aryloxo) complex **1**; thus, the coordination of tellurium also enhanced the catalytic activity of the catalyst systems.

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10.1021/ma0204711 CCC: $22.00

Chart 1

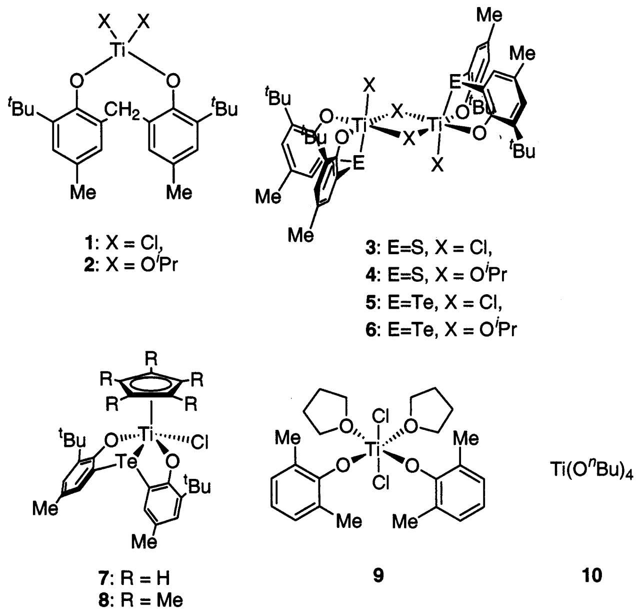


Table 1. Polymerization of ϵ-Caprolactone with Various Catalyst Systems in Toluene or without Solvent[a]

run	complex	solvent	temp (°C)	time (h)	yield (%)	$\bar{M}_n/10^3$ [b]	$\bar{M}_w/\bar{M}_n$[b]
1	**3**	none	100	6	93	62.2	2.07
2		toluene	100	6	100	72.3	2.28
3	**5**	none	100	12	55	45.1	1.65
4		toluene	50	6	<1		
5		toluene	100	6	88	26.0	1.20
6	**6**	none	100	12	85	37.9	1.43
7		toluene	100	6	<1		
8	**7**	toluene	100	6	<1		
9	**8**	toluene	100	6	<1		
10	**9**	toluene	100	6	<1		
11	**10**	toluene	100	6	<1		

[a] $[\epsilon\text{-CL}]_0/[\text{Ti}]_0 = 100$. [b] Determined by GPC analysis in THF calibrated with standard poly(styrene).

We expected that such activation effects of the chalcogen-bridged chelating bis(aryloxo) ligands could be observed in polymerizations of polar monomers. We chose cyclic esters as monomers to elucidate the function of the bridging group in the chelating bis(aryloxo) complex. Here we report the catalytic behavior of titanium dichloro complexes with various chalcogen-bridged chelating bis(aryloxo) ligands for ring-opening polymerizations of cyclic esters and investigated the effect of various solvents on the polymerization reaction.

Results and Discussion

Polymerization of Cyclic Esters in Toluene. Chart 1 shows a series of aryloxo and alkoxo titanium complexes used in this study. We used toluene, anisole, and dioxane as polymerization solvents because of their high boiling point and appropriate polarizability. Table 1 shows the results of the polymerization of ϵ-CL by the titanium complexes in toluene or without solvent. Titanium complexes having chelating diaryloxo ligands bridged by sulfur (**3**) or tellurium (**5** and **6**) catalyzed the polymerization of ϵ-CL at 100 °C to give the polymers in good yield. Recently, Aida and co-workers reported that the methylene-bridged analogue, $\{2,2'\text{-CH}_2(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2\}\text{Ti(O}^i\text{Pr)}_2$ (**2**), initiated living polymerization of lactones.[11] These results are in sharp contrast to the fact that a monodentate bis(aryloxo) complex, $(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{O})_2\text{TiCl}_2(\text{thf})_2$ (**9**),[17] and a tetrakis(alkoxo) compound, $\text{Ti(O}^n\text{Bu)}_4$ (**10**),[18] were inactive under the same conditions, indicating that the chelating coordination of the bis(aryloxo) ligands in **2**, **3**, **5**, and **6** significantly enhances the catalytic activities of the complexes. The dichloride complex **1** having the methylene-bridged bis(aryloxo) ligand was not active without addition of propylene oxide, while the corresponding dichloride complexes having the sulfur- or tellurium-bridged ligands **3** and **5** permit the polymerization of ϵ-CL without any cocatalyst. Thus, not only the chelating coordination of the diaryloxo ligands but also the coordination of sulfur or tellurium in **3** and **5** is essential for the initiation of the polymerization. Cyclopentadienyl complexes (**7** and **8**) having the tellurium-bridged ligand were also inactive.

Table 2. Polymerization of δ-Valerolactone, γ-Butylolactone, and β-Propiolactone with Complexes 5 and 6[a]

run	monomer	complex	solvent	time (h)	yield (%)	$\bar{M}_n/10^3$ [b]	$\bar{M}_w/\bar{M}_n$[b]
1	δ-valerolactone	**5**	none	6	51	38.4	1.52
2			toluene	6	49	24.5	1.29
3		**6**	none	6	82	62.4	1.64
4			toluene	6	<1		
5	β-propiolactone	**5**	toluene	6	<1		

[a] $[\text{Monomer}]_0/[\text{Ti}]_0 = 100$, temperature = 100 °C. [b] Determined by GPC analysis in THF calibrated with standard poly(styrene).

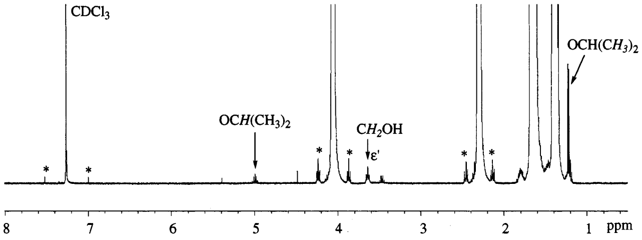


Figure 1. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 30 °C) of the poly(ϵ-caprolactone) obtained by **6**.

The tellurium-bridged complexes **5** and **6** were also active for the polymerization of δ-valerolactone (Table 2). Despite a larger strain energy of β-propiolactone (β-PL) than that of ϵ-CL, β-PL was not polymerized by these titanium complexes under the same conditions. This might result from the formation of the stable six-membered chelating ring compounds as an intermediate as reported for mono-Cp titanium and lanthanoid complexes.[9a,19] The complex **5** also catalyzed the polymerization of L-LA to give poly(L-LA) with relatively narrow molecular weight distribution.

In the ^{1}H NMR spectrum of the poly(ϵ-CL) obtained by **6**, a resonance for the $-\text{C}H_2\text{OH}$ end group appeared at 3.63 ppm together with the signals of terminal isopropyl ester, indicating that the growing end group is the titanium−alkoxide species (Figure 1). Therefore, the ring cleavage of a lactone occurs between the acyl−oxygen bond. The molecular weight of the polymer can be calculated from the intensity of the terminal group and that of the main chain to be $M_n = 1.4 \times 10^4$, which is about half of that estimated by GPC calibrated with standard poly(styrene).

In comparison between the sulfur- and tellurium-bridged systems, the latter system is better controlled, although $\bar{M}_w/\bar{M}_n$ values of the obtained polymers are still not lower than 1.2. This can be caused by a backbiting process or by slow initiation in the tellurium-

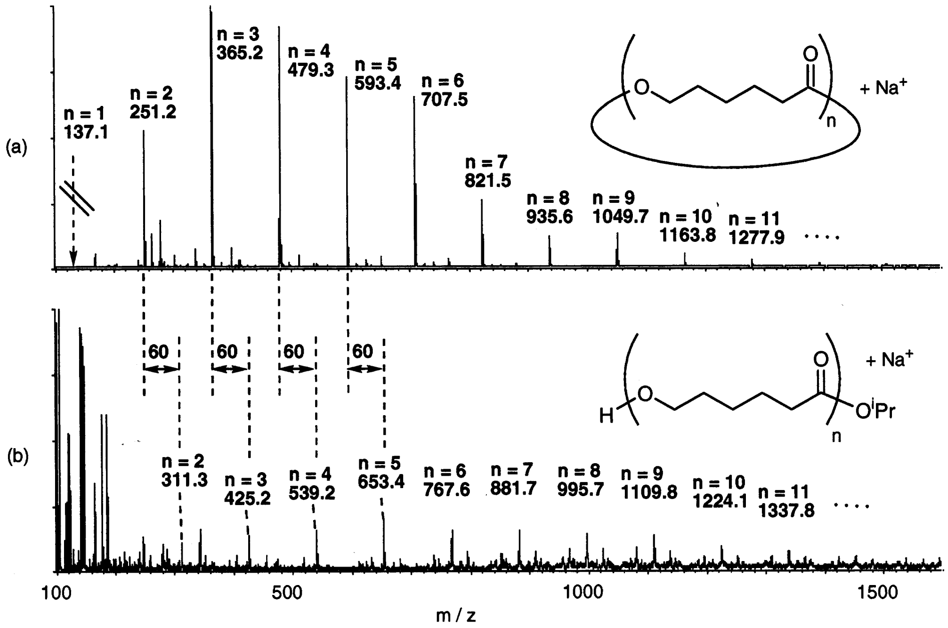


Figure 2. ESI-MS spectra of oligo(ϵ-caprolactone)s. (a) MeOH-soluble fraction generated from degradation of poly(ϵ-caprolactone) by $[(TeBP)TiCl_2]_2$ (**5**). (b) Oligomerization of ϵ-caprolactone by **6** ($[M]_0/[Ti]_0 = 10$).

bridged system. To determine which is the reason, we performed the reaction of the tellurium-bridged catalyst **5** with poly(ϵ-CL). The methanol-insoluble poly(ϵ-CL) with M_n of 37 000, which exhibits isopropyl ester and hydroxyl end groups, was treated with the tellurium-bridged complex **5** in toluene at 100 °C for 3 days. The MeOH insoluble part was reduced to 43 wt %, which consisted of poly(ϵ-CL) with lower M_n value (8000) than that of the starting polymer. Since the ^1H NMR spectrum of the methanol-soluble fraction showed no signals of the end group, thus the MeOH-soluble fraction of the product was composed of cyclic oligomers and of nominal linear oligomers, which indicated that the ratio of cyclic oligomers to linear oligomers increased with reaction time. This is also supported by the ESI-MS analysis (Figure 2). The signals in the ESI-MS spectrum of the methanol-soluble fraction can clearly be assigned as sodium cation adducts of cyclic dimer and higher cyclic oligomers (~11-mer). Each signal appears at 60 amu smaller mass number than that of the linear oligomer having isopropyl ester and hydroxyl end groups. The number-average molecular weight of the methanol-soluble part was only 1300. These results indicate that the broadening molecular weight degradation in the tellurium-bridged system was caused by backbiting process.

Table 3. Polymerization of ϵ-Caprolactone by 3 and 5 in Anisole[a]

				$\bar{M}_n/10^3$		
run	complex	time (h)	yield (%)	calcd[b]	obsd[c]	$\bar{M}_w/\bar{M}_n$[c]
1	**3**	1	23	5.3	8.0	1.05
2	**3**	1.5	38	8.7	9.8	1.03
3	**3**	2	50	11.4	10.9	1.05
4	**3**	3	71	16.2	11.3	1.04
5	**3**	4	82	18.7	21.9	1.08
6	**3**	5	91	20.8	28.2	1.17
7	**3**	6	94	21.5	28.1	1.14
8	**3**	8	97	22.1	16.8	1.07
9	**5**	1.0	5.1	1.2	3.3	1.04
10	**5**	1.5	23	5.3	5.4	1.04
11	**5**	2.5	44	10.0	8.8	1.04
12	**5**	3	61	13.9	9.9	1.05
13	**5**	4	77	17.6	10.9	1.05
14	**5**	6	87	19.9	11.0	1.09
15	**5**	8	93	21.2	12.5	1.08
16	**5**	18	96	21.9	11.8	1.17

[a] $[\epsilon\text{-CL}]_0/[Ti]_0 = 200$. [b] M_n(calcd) = (M_w of ϵ-CL) × $[\epsilon\text{-CL}]_0/[Ti]$ × (polymer yield). [c] Determined by GPC analysis in THF calibrated with standard poly(styrene).

Polymerization of Cyclic Esters in Anisole and Dioxane. We investigated the catalytic behavior of **3** and **5** for the polymerization of cyclic esters using anisole and dioxane as polymerization solvents. The molecular weight of the poly(ϵ-CL) obtained by the tellurium-bridged complex **5** increased in the first order to the monomer conversion, and the molecular weight distributions remained very narrow (M_w/M_n = 1.04−1.17) during the polymerization process (Table 3, Figure 3). We also found that the M_n value of the polymer increased proportionally to the monomer conversion, while the M_w/M_n ratio remained almost constant at 1.1 during the polymerization of ϵ-CL by the tellurium-bridged complex **5** in dioxane (Table 4, Figure 4). These catalyst systems were then applied to the polymerization of L-LA. Similarly, the ring-opening polymerization of L-LA by **5** in anisole gave poly(L-LA) with narrow molecular weight distribution (Table 5, Figure 5). No backbiting reaction took place throughout the polymerization over a period of 112 h, since the M_n value of the polymer increased proportionally to the monomer conversion and the M_w/M_n ratio remained almost constant at 1.1. These results indicated that the present polymerizations of ϵ-CL and L-LA by the tellurium-bridged complex **5** proceeded in a living fashion in anisole and in dioxane. In contrast, the linearity between the molecular weight and the conversion in the sulfur-bridged **3** system was lower than that in the tellurium-bridged **5** system, and the molecular weight drastically increased after the polymer yield went over 80% (Table 3). The ^1H NMR spectrum of the poly(L-LA) obtained by **5** showed a resonance for the $-CH(CH_3)$-OH end group at 4.36 ppm.

To confirm the living nature of the polymerization in anisole, a sequential two-stage polymerization of L-LA was carried out using **5**. Thus, the first stage polymer-

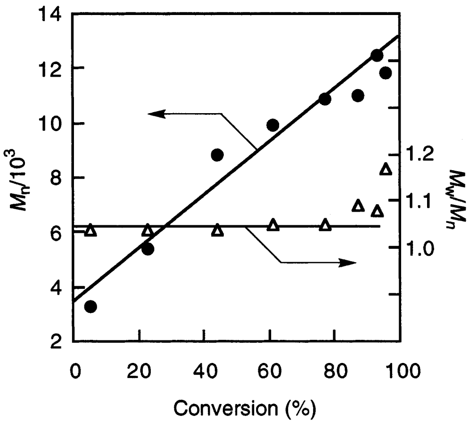


Figure 3. Dependence of molecular weights and polydispersities on conversions for the polymerization of ϵ-caprolactone catalyzed by $[(TeBP)TiCl_2]_2$ (**5**) in anisole at 100 °C.

Table 4. Polymerization of ϵ-Caprolactone by 5 in Dioxane[a]

			$\bar{M}_n/10^3$		
run	time (h)	yield (%)	calcd[b]	obsd[c]	$\bar{M}_w/\bar{M}_n$[c]
1	1	8.1	1.8	4.5	1.04
2	2	29	6.6	8.5	1.04
3	3	51	11.6	12.3	1.04
4	4	66	15.1	14.9	1.04
5	6	90	20.5	17.6	1.06
6	8	92	21.0	20.2	1.08
7	24	95	21.7	19.2	1.09

[a] $[\epsilon\text{-CL}]_0/[Ti] = 200$. [b] $\bar{M}_n(\text{calcd}) = (M_w \text{ of } \epsilon\text{-CL}) \times [\epsilon\text{-CL}]_0/[Ti] \times (\text{polymer yield})$. [c] Determined by GPC analysis in THF calibrated with standard poly(styrene).

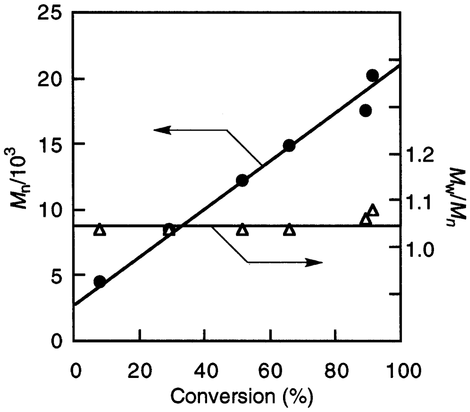


Figure 4. Dependence of molecular weights and polydispersities on conversions for the polymerization of ϵ-caprolactone catalyzed by $[(TeBP)TiCl_2]_2$ (**5**) in dioxane at 100 °C.

Table 5. Polymerization of L-Lactide by Complex 5 in Anisole[a,b]

			$\bar{M}_n/10^3$ [b]		
run	time (h)	yield (%)	calcd[b]	obsd[c]	$\bar{M}_w/\bar{M}_n$[c]
1	8	18	5.2	4.9	1.07
2	16	56	16.1	13.7	1.08
3	24	74	21.3	14.5	1.04
4	32	84	24.2	18.7	1.08
5	40	96	27.7	19.2	1.06
6	48	98	28.2	20.9	1.08
7	112	97	28.0	21.8	1.13

[a] $[\text{L-LA}]_0 / [Ti] = 200$. [b] $\bar{M}_n(\text{calcd}) = (M_w \text{ of L-LA}) \times [\text{L-LA}]_0/[Ti] \times (\text{polymer yield})$. [c] Determined by GPC analysis in THF calibrated with standard poly(styrene).

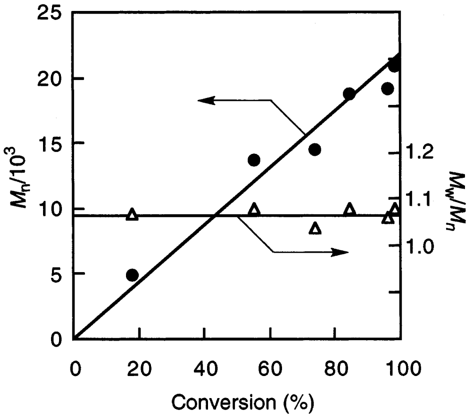


Figure 5. Dependence of molecular weights and polydispersities on conversion for the polymerization of L-lactide catalyzed by $[(TeBP)TiCl_2]_2$ (**5**) in anisole at 100 °C.

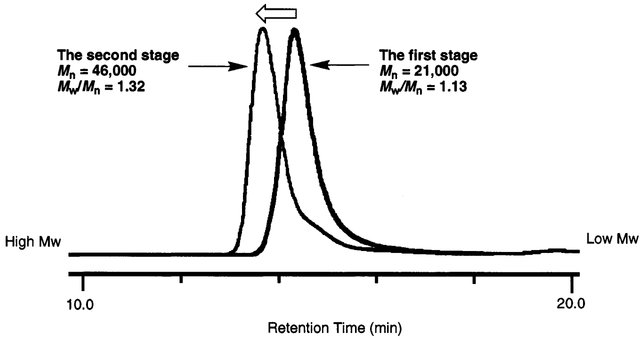


Figure 6. Two-stage polymerization of L-lactide initiated by $[(TeBP)TiCl_2]_2$ (**5**) in anisole at 100 °C.

ization of L-LA ($[M]_0/[Ti] = 200$) proceeded to reach to 98% monomer conversion at 100 °C within 48 h ($M_n = 21\,000$, $M_w/M_n = 1.13$). Then 200 equiv of L-LA was newly added to the system, whereupon the second-stage polymerization occurred to attain 194% monomer conversion in 48 h to afford a higher molecular weight polymer with M_n of 46 000 and with M_w/M_n of 1.32 (Figure 6). This indicated that the polymerization of L-LA by **5** proceeded in a living fashion without any significant side reactions.

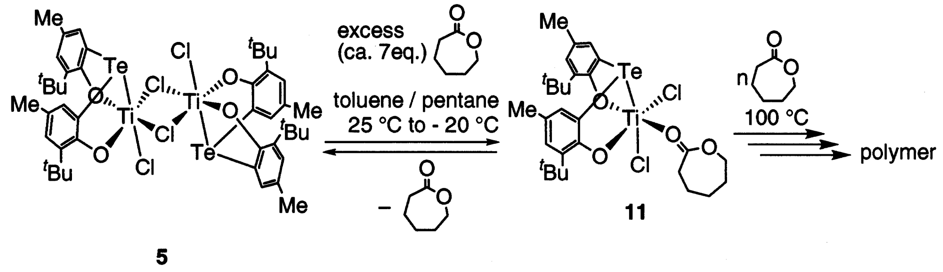
The important features of the living polymerization are not only to synthesize precisely sized polymers but also to afford block copolymers of defined structures. In other words, block copolymerization should be achieved if the present polymerization proceeded in living fashion. The diblock copolymerization of L-LA with ϵ-CL was studied by using the complex **5** system. Prepolymerization of L-LA was performed in a similar manner. After the first monomer was consumed, ϵ-CL was successively added, and the diblock copolymerization was completed in 24 h followed by usual work-up. Results are presented in Table 6. GPC results showed that the molecular weight of the copolymers were linear to the amount of the added ϵ-CL and that the polydispersity of the copolymers were around 1.25. Thus, the composition and the molecular weight of the block copolymers were controlled over a wide range by changing the molar ratio of ϵ-CL and L-LA. No low molecular weight fractions were detected, indicating that all of the active end groups of poly(L-LA)s were effective in initiating the polymerization of ϵ-CL. The thermal properties of the synthesized diblock copolymers were determined by DSC. The block copolymers showed two melting endotherms, where the lower melting endotherms of poly-

Table 6. Diblock Copolymerizations of L-Lactide and ε-Caprolactone in Anisole by 5[a]

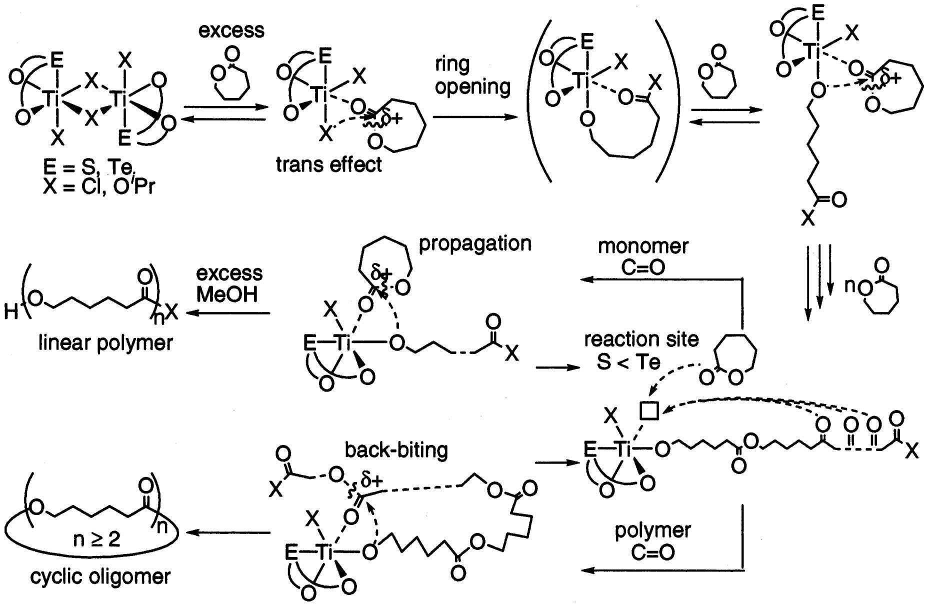
	prepolymer				copolymer				
run	yield (%)	$\bar{M}_n/10^3$ [b]	$\bar{M}_w/\bar{M}_n$ [b]	mp	ε-CL block [ε-CL]/[I]	yield (%)	$\bar{M}_n/10^3$ [b]	$\bar{M}_w/\bar{M}_n$ [b]	mp
1	93	11.6	1.10	163.8	200	99	32.1	1.29	53.5, 156.5
2	100	12.5	1.12	160.1	100	92	19.5	1.26	48.5, 155.1
3	94	10.8	1.10	163.6	50	95	14.9	1.24	44.7, 156.8

[a] $[\text{L-LA}]_0/[\text{Ti}]_0 = 100$. [b] Determined by GPC analysis in THF calibrated with standard poly(styrene).

Scheme 1



Scheme 2



(ε-CL) block were raising from $T_m = 44.7$ °C to $T_m = 53.5$ °C with the increase in the ε-CL unit. The other endotherms from the poly(L-LA) block appeared at around 155 °C. These data of the copolymers are similar to those of the reported poly(L-LA-*b*−ε-CL)s having similar compositions.[22]

Mechanism for the Lactone and Lactide Polymerization. To gain some insights into the initiation mechanism, we tried to isolate intermediates. The reaction of the tellurium-bridged complex **5** with about 7 equiv of ε-CL monomer below room temperature gave a titanium:ε-CL = 1:1 complex, TiCl_2(TeBP)(ε-CL) (**11**) (Scheme 1). An ESI-MS spectrum of the complex **11** revealed it to be monomeric. The weakly coordinating ε-CL ligand should be placed at the trans position to aryloxo oxygen in **11**.[20] Addition of 1 equiv of ε-CL to the complex **5** resulted in the recovery of the starting dinuclear complex **5**. At 100 °C, complex **11** exhibited essentially the same catalytic behavior with that of the dinuclear complex **5** for the polymerization of ε-CL.

From these results, we speculate on the mechanism for these polymerization systems (Scheme 2). The first step is coordination of the monomer to the dimeric complex to generate the monomeric adduct, in which the weakly donating monomer may prefer the trans position to the strong donor, aryloxo oxygen.[17] The monodentate anionic ligands (Cl in **5** and **3**, O^{i}Pr in **4** and **6**) activated by the trans effect of the bridging atom should attack the carbonyl carbon of the coordinated monomer to cleave the acyl−oxygen bond to forming the Ti−alkoxo polymer end. Continuous coordination and insertion of the monomer yields linear polymers. In the polymerization of ε-CL by the tellurium-bridged complex **5**, the backbiting process also proceeds with decreasing monomer concentration to give cyclic oligomers in toluene, while the living polymerization proceeds in anisole and in dioxane. These solvent effects can be rationalized by the higher polarity of anisole and dioxane. The solvation of the complex **5** would reduce the Lewis acidity on the titanium center and stabilize active species not to react with the ester groups of the polymer so as to achieve the living polymerization in polar solvent. The sulfur-bridged complex **3** also initiated polymerization of ε-CL, in which the M_n value of the polymer monotonically increased with monomer conversion. However, the M_n value increased explosively at the monomer conversion of over 80% both in toluene and in anisole. This might be attributed to the narrower reaction site in **3** than that in **5** as indicated by the X-ray analysis.[16] The distortion of the O1−Ti−O2 angle from the octahedral geometry in **3** (100.6(2)°) is significantly larger than that in **5** (97.7(2)°), and the C1−E−C2 angle in **3** (102.9(3)°) is wider than that in **5** (96.0(2)°). The narrower reaction site in **3** would hinder the solvation to result in smaller effect of the solvent in **3** system. Although the Ti−Te bond distance of **5** (2.933(1) Å) is longer than the Ti−S bond distance of **3** (2.664(2) Å), the Ti−terminal Cl bond distances trans to tellurium in **5** (2.262(2) Å) is substantially longer than that trans to sulfur in **3** (2.236(2) Å). This suggests that the bridging tellurium atom in **5** coordinated to the titanium center more strongly than the bridging sulfur atom in **3**. Stronger coordination of tellurium in **5** would make the Ti center less Lewis acidic than that in **3**. Thus, complex **5** is sterically more susceptible to backbiting but electronically less susceptible to it in comparison with **3**. In anisole or in dioxane, solvation of **5** would make it less susceptible to backbiting both sterically and electronically to enable the living polymerization.

Conclusion

A series of titanium dichloride complexes **3** and **5** having sulfur- or tellurium-bridged chelating bis(aryloxo) ligands were found to catalyze the polymerization of cyclic esters without any cocatalyst. The activities of these titanium complexes were comparable to the most common tin-based catalyst systems,[3] although still lower than those of the rare earth metals[8] and alkali metals.[2] The polymerizations of ϵ-CL with these complexes in toluene gave polymers with rather broad molecular weight distributions due to back-biting. The resulting polymer can be degraded by backbiting to give cyclic oligomers catalyzed by **5** in toluene. In contrast, the tellurium-bridged complex **5** conducted the living polymerizations of ϵ-caprolactone and L-lactide in anisole and dioxane. The tellurium-bridged **5** system was superior to the sulfur-bridged **3** system in the point of the linearity between the molecular weight and the conversion.

Experimental Section

General Procedures. All manipulations involving air- and moisture-sensitive compounds were carried out by the use of standard Schlenk techniques under an argon atmosphere. The complexes **3**,[1,2] **5**,[8] **6**,[8] **7**,[8] **8**,[8] and **9**[17,21] were prepared according to the literature. $\mathrm{Ti(O^{n}Bu)_4}$ (**10**) was purchased from Tokyo-Kasei Co. THF, toluene, anisole, and dioxane were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. Methanol was dried and deoxygenated by distillation over magnesium methoxide under argon. Lactones were distilled over $\mathrm{CaH_2}$ under argon atmosphere and dried over molecular sieves (4A). L-LA was recrystallized from THF. $\mathrm{CDCl_3}$ was dried over $\mathrm{P_2O_5}$ and degassed by trap-to-trap distillation.

^{1}H (400 and 270 MHz) NMR spectra were measured on a JEOL JNM-GSX400 or a JEOL JNM-EX270 spectrometer. When $\mathrm{CDCl_3}$ was used as solvent, the ^{1}H NMR and ^{13}C NMR spectra were referenced to the residual solvent protons at δ 7.26 and 77.0 ppm, respectively. Elemental analyses were performed at Elemental Analysis Center, Faculty of Science, Osaka University. All melting points of the compounds were measured in sealed tubes under an argon atmosphere and were not corrected. ESI-MS measurements were performed on a Perkin-Elmer/Sciex API III plus spectrometer.

Polymerizations of Lactones. To a solution (0.90 mL) of a lactone (1 mmol) in an appropriate solvent was added a THF solution (0.10 mL) of complex **5** (5 μmol). The reaction mixture become an orange-clear solution by the reacting the mixture at −78 °C. Then, the reaction tube was sealed under an argon atmosphere and kept at 100 °C with stirring. After the prescribed reaction time, the polymerization was terminated by adding a large amount of methanol. The resulting white polymer was collected by centrifugation and dried in vacuo.

Degradation of Poly(ϵ-caprolactone). The poly(ϵ-CL) was obtained as described above by using **6** as a catalyst. A mixture of the polymer (158.9 mg, 1.39 mmol as monomer unit) and **5** (12.1 mg, 10.6 μmol) in toluene (3 mL) was stirred for 3 days at 100 °C. Then the product was extracted with MeOH. The extract was revealed to include pure cyclic oligomers by ESI-MS and ^{1}H NMR spectroscopy. The MeOH-insoluble residue was dried in vacuo, producing the polymer in 43% yield.

Block Copolymerizations of L-Lactide with ϵ-Caprolactone. To the anisole solution (0.90 mL) of L-LA (1 mmol) was added a THF solution (0.10 mL) of complex **5** (0.01 mmol). The reaction mixture become an orange-clear solution at −78 °C. The reaction tube was the sealed under an argon atmosphere and kept at 100 °C with stirring. After 48 h, a 0.50 mL portion of the reaction mixture was separated by using syringe for GPC analysis of the prepolymer. Then, to the residual polymerization solution was added the prescribed amount of ϵ-caprolactone. After the mixture was stirred for 24 h at 100 °C, the resultant polymer solution was poured into excess methanol to precipitate the polymer, and the precipitated solid was dried in vacuo. The polymer yield was 92−99%.

Preparation of $\{\mathrm{TeBP}\}\mathrm{TiCl_2}$($\epsilon$-caprolactone) (11). To the dark red microcrystalline solid of $[\mathrm{(TeBP)TiCl_2}]_2$ (**5**) (152 mg, 0.13 mmol) was added ϵ-caprolactone (0.03 mL, 2.26 mmol). The reaction mixture was dissolved in toluene (5 mL). The reaction mixture immediately turned to a dark red suspension. After stirring for 5 min, it was allowed to warm to room temperature and stirred here for 1 h. The precipitated dark red microcrystalline solid was separated and dried under vacuum to afford 266 mg of **11** (74%); mp >300 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 30 °C): δ 7.46 (s, 2H, *ph-3- or 5-H*), 7.08 (s, 2H, *ph-3- or 5-H*), 4.24 (t, 2H, $\mathrm{CH_2}$), 2.68 (m, 2H, $\mathrm{CH_2}$), 2.26 (s, 6H, Me), 1.85 (m, 2H, $\mathrm{CH_2}$), 1.77 (m, 4H, $\mathrm{CH_2}$), 1.38 (s, 18H, ^{t}Bu). Anal. Calcd for $\mathrm{C_{28}H_{38}Cl_2O_4TeTi}$: C, 49.10; H, 5.59. Found: C, 49.15; H, 5.66. ESI-MS (in MeCN) *m/z*, 686 [M$^-$].

GPC Analyses. Gel permeation chromatographic (GPC) analyses were carried out at 40 °C using a Shimadzu LC-10A liquid chromatograph system, equipped with a RID-10A differential refractometer and SPD-10A absorbance detector, connected to a Shodex KF-806L column in Tables 1 and 2. Other GPC analyses were carried out using Tosoh TSKgel G2000HXL and G3000HXL columns connected to a Tosoh RI-8012 detector. THF was used as an eluent at a flow rate of 0.8 mL/min. Samples were prepared in THF (0.5 mg/mL) and were filtered through an Advantec DISMIC-25JP filter in order to remove particulates before injection. The GPC column was calibrated vs poly(styrene) standards (Aldrich).

Acknowledgment. This work was carried out financed by the NEDO International Joint Research Grant Program (Biodegradable Copolymers). Y.T. is a research fellow of the Japan Society for the Promotion of Science, 2000−2002.

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MA0204711