Efficient Bimodal Ring-opening Polymerization of ε-Caprolactone Catalyzed by Titanium Complexes with *N*-Alkoxy-β-ketoiminate Ligands

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A series of titanium complexes containing terdentate β-ketoiminate ligands were found to be efficient for the ring-opening polymerization of ε-caprolactone (ε-CL), producing poly(ε-caprolactone) (PCL) with bimodal distribution. Steric factors imposed by methyl substituents on the back bone of the alkoxy group affected significantly the polymerization rate and physical properties of the resulting PCL. Intra- and intermolecular transesterifications rather than disproportional rearrangements were responsible for the bimodal behavior and for the change in the molecular weight (M_w). Dilution with toluene reduced yield, and lowered polydispersity (PDI) and M_w of PCL, while the catalytic activities of the dimeric complex, [Ti(O*i*-Pr)$_2$(*N*-alkoxy-β-ketoiminate)]$_2$ and Ti(O*i*-Pr)$_4$ were not sensitive to the added solvent. The dimeric complex showed living character, while other catalysts suffered from chain termination reactions.

Key Words : *N*-Alkoxy-β-ketoiminate, Titanium complexes, ε-Caprolactone, Ring-opening polymerization, Transesterification

Introduction

Recently, increasing attention has been paid to biodegradable aliphatic polyesters with high molecular weight because they can be used potentially as environmentally benign materials to replace the polymers recalcitrant against degradation such as poly(α-olefin).[1] It has been reported that ε-caprolactone (ε-CL) and L-lactide (L-LA) can be polymerized with a variety of catalysts such as organometallics based on alkali[2] and alkaline earth metal,[3] tin,[4] aluminum,[5] titanium,[6] zinc,[5(a),7] zirconium,[8] and rare earth metals.[9] Even though most of recent researches have been focused on the biocompatible catalysts such as Ca, Mg, and Fe-based catalysts/initiators due to the difficulty in the removal of catalyst residues, research on the development for new active catalysts for ring-opening polymerization of cyclic esters, especially for well-defined PLA still in progress. Copolymerization with poly(ethylene glycol) (PEG),[10] and other cyclic monomers or cyclic esters with functional groups[5(f),11] have been also intensively studied due to the favorable properties of the resulting copolymers. In this regard, titanium complexes have attracted much attention due to their well-known high activities in olefin polymerization and similarity to tin complexes. Various monomeric and tetrameric titanium alkoxides have been employed for the ring-opening polymerization of cyclic esters. Recently, we reported the preparation of [Ti(O*i*-Pr)$_2$(*N*-alkoxy-β-ketoiminate)]$_2$ and [Ti(*N*-alkoxy-β-ketoiminate)$_2$].[12] Here we report that [Ti(*N*-alkoxy-β-ketoiminate)$_2$] containing only terdentate ligands are highly efficient for the ring-opening polymerization (ROP) of ε-CL. Also, interesting bimodal molecular weight distribution of the polymer obtained with these titanium complexes has been observed and a plausible mechanism for these behaviors is presented.

Experimental Section

General procedures. All manipulations involving air- and moisture-sensitive compounds were carried out using a standard Schlenk techniques under a nitrogen atmosphere. The complexes were prepared according to the literature procedures.[12] Ti(O*i*-Pr)$_4$ was purchased from Strem Co. Toluene and methanol were freshly distilled under a nitrogen atmosphere prior to use according to the literature procedures. Lactones were distilled over CaH_2 under nitrogen and stored over molecular sieves (4A) before using.

^{1}H and ^{13}C NMR spectra were recorded by using 5 mm tube on a Varian Unity Inova 400 (400.265 and 100.657 MHz, respectively) or Varian Gemini 2000 (199.976 and 50.289 MHz, respectively) spectrometer and were referenced to tetramethylsilane (TMS). Molecular weight and molecular weight distribution were measured using GPC (Waters 150C plus with a differential refractometer detector and a column composed of Styragel HT6E, HT5 and HT3) with THF (1.0 mL/min) as an eluent using polystyrene (Showadenko SL-105).

Polymerization of ε-caprolactone. ε-Caprolactone or a toluene solution containing 2 g of ε-caprolactone was added a toluene solution of the appropriate catalyst with the amount of the catalyst for [ε-caprolactone]/[Ti] = 100. Polymerization was carried out while maintaining the desired temperature. After the prescribed reaction time, the polymerization was terminated by adding a large amount of methanol. The resulting polymer was collected by filtration and dried in vacuo.

Results and Discussion

Polymerization results of ε-CL by the new titanium

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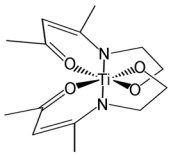
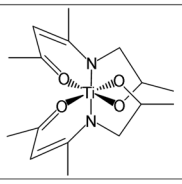
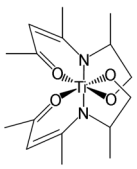
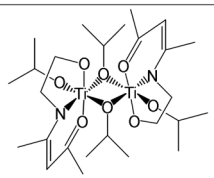
			

Table 1. Polymerization Results of ε-caprolactone

Entry	Catalysts	Solvent	T (°C)	Time (h)	Yield (%)	TON	MP/10^3		Mn/10^3	PDI
1	**1**	none	40	24	69	2.9	29.6	–	23.1	1.53
2			70	3	99	33	41.2	–	26.2	1.79
3			100	1.5	74.5	50				
4					76*	51				
5		1 mL	70	5.3	70	13	28.4[1](4.2)[+]	0.8[2]	18.9	1.50
6			100	3	81	27	–	–	9.7	1.64
7					61*	20	–	–	11.1	1.44
8	**2**	none	70	11	70	6.4	13.0	–	12.2	1.71
9		none	100	0.5	1	2.0	–	–	–	–
10				1	53.1	53	12.8(1.2)	0.8	11.1	1.70
11				1.5	72	48	29.1(5.0)	0.8	17.6	1.77
12				2	81.5	41	24.5	–	17.7	1.88
13		1 mL	70	19	55	2.9	13.4(7.6)	0.9	11.8	1.62
14		2 mL	70	19	49	2.6	12.7(9.8)	0.8	11.2	1.58
15		3 mL	70	19	20	1.1	5.7(17.6)	0.8	5.9	1.52
16	**3**	none	70	11	98	8.9	52.5(22.7)	0.8	28.1	1.78
17		1 mL	70	15.5	95	6.1	38.2(8.9)	0.8	24.2	1.69
18	**4**	none	70	0.17	76	460	9.6(6.4)	0.8	7.3	1.48
19				1	87	87	10.4	–	7.5	1.73
20		1 mL	70	0.5	77	150	9.7(2.1)	0.8	7.2	1.46
21					156*	160	21.0(6.4)	0.7	12.5	1.53
22				1	80.9	81	9.4	–	7.0	1.65
23		2 mL	70	1	75	75	9.0(1.6)	0.8	7.2	1.42
24	**Ti(O*i*-Pr)$_4$**	none	70	0.17	88	530	7.0(55.4)	0.6	6.1	1.47
25		1 mL	70	0.17	83.5	500	6.1(76.9)	0.6	5.6	1.49
26		2 mL	70	0.17	86.5	520	10.0(7.3)	0.6	7.7	1.53

Solvent: toluene; MP: medium molecular weight; TON, turnover number (hr^{-1}). 1. medium molecular weight in higher molecular weight portion. 2. medium molecular weight in lower molecular weight portion. *2nd polymerization result. +ratio of (higher molecular weight portion/lower molecular weight portion)

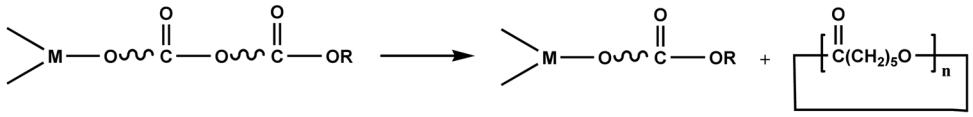
complexes containing *N*-alkoxy-β-ketoiminate ligands are summarized in Table 1. Ti(O*i*-Pr)$_4$ was used as a reference.

Among the titanium complexes with *N*-alkoxy-β-ketoiminate ligands, dimeric complex, **4** exhibited the highest activity, but its activity is still lower than Ti(O*i*-Pr)$_4$. The order of the activity was found to decrease in the order of Ti(O*i*-Pr)$_4$ > **4** > **1** > **3** > **2**, clearly demonstrating that the catalytic activity is significantly affected by the presence of the methyl substituent. The presence of a monodentate alkoxy group or groups in the complex seems to make the catalyst more active. The more the alkoxy groups, the higher the activity of the catalyst.

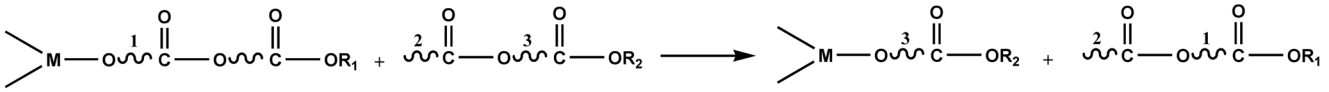
Activity of the catalyst **2**, with a methyl group located α to the alkoxy end group was lower than that of the catalyst **3**, bearing a methyl group located β to the alkoxy group. This indicates that the active site or the initiating site of the complex may be the alkoxy end group of the β-ketoiminate ligand as was expected. Shen proved by the NMR analysis that the initiation involves the participation of the alkoxy group and not of the β-diketonate ligand in [Ln(EA)$_2$(Oi-Pr)] (EA: EtOC(O)CHC(O)Me).[9(g)] However, the initiation at the chelating ketoiminate ligand[5(m)] or diamide ligand[5(o)] was also proposed.

PDIs of the resulting PCL were nearly constant (1.42-

Intramolecular Transesterification



Intermolecular Transesterification



Scheme 1. Intra- and Intermolecular Transesterification.

1.88) regardless of the catalysts employed. At 70 °C, M_w of PCL decreased in the order of **3** > **1** > **2** > **4** > Ti(O*i*-Pr)$_4$. (entry 2, 8, 16, 19, 24) This is likely due to presence of the methyl substituent on the backbone in **3**, which might prevent the active species from aggregation. The production of PCL with higher M_w by the catalyst with a longer alkyl group in the aluminum ketoiminate complex were explained similarly.[5(m)] The steric hindrance due to the methyl group in the catalyst **2** seems to limit the substrate to approach to the active site, thereby resulting in the decrease of both catalytic activity and M_w of PCL. Both Ti(O*i*-Pr)$_4$ and the catalyst **4** having alkoxy active sites produced PCL with much lower M_w. This may be due to the intra- and intermolecular transesterifications, which is frequently observed in the alkoxide complexes as shown in Scheme 1.

PCL with bimodal molecular weight distribution was produced in some cases. At first, the disproportionation reation in the catalyst **4** was suggested to explain the bimodal molecular weight distribution of PCL due to the possible presence of two different complexes (Ti(O*i*-Pr)$_4$ and complex **1**).[12] However, the fact that PCL with bimodal molecular weight distribution was also produced sometimes by the catalysts **1**, **2**, and **3** excluded this possibility, because disproportional rearrangements are not possible in these cases.

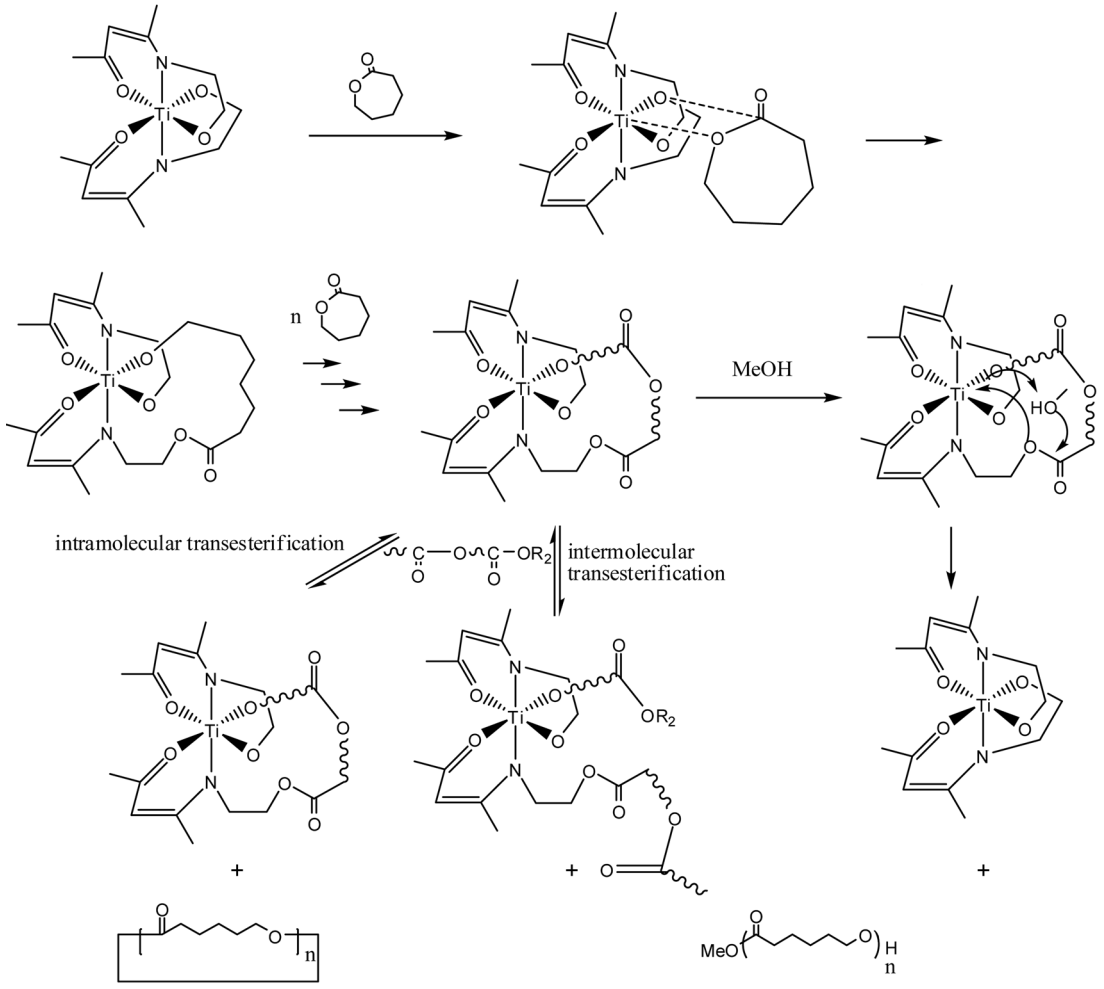
M_w of PCL produced by Ti(O*i*-Pr)$_4$ was also different significantly from that of PCL produced by the catalyst **4**. In the absence of solvent, amount of PCL with lower M_w of 600-800 was also dependent upon the nature of the catalyst. That is to say, the polymerization with catalysts **1** and **2** did not produce PCL with lower M_w (entry 1, 2, 8). The ratio of higher M_w portion to lower M_w one was the lowest in the catalyst **4** (entry 18) and the ratio was the highest in the catalyst Ti(O*i*-Pr)$_4$ (entry 24). Almost identical M_w of the portion of PCL with lower M_w indicates that PCL with lower M_w was formed through a similar pathway such as transesterification.

Higher reaction temperature favored the formation of the lower M_w portion even with the catalyst **2** (entry 8, 10, 11). The amount of the lower M_w portion decreased with the reaction time (entry 10-12). The ratio of the macrocylic PCL oligomer to linear PCL polymer should increase with decreasing concentration of ε-CL and the initially formed macrocylic PCL oligomer would react with catalysts again to produce polymers with higher M_w.

Effect of dilution with solvent on the ratio of higher M_w portion to lower M_w one depended upon the nature of the catalyst; the ratio increased with the catalysts **1** (entry 5) and **2** (entry 13-15), while it decreased with **4** (entry 20, 21, 23) and Ti(O*i*-Pr)$_4$ (entry 25, 26). Such dilution effect was not clear with **3** possibly due to limited data. These results can be rationalized as follows; with **1** and **2** (possibly **3** also), chelating ε-ketoiminate ligands should effectively block the intramolecular transesterification which occurred more easily than the intermolecular one. Dilution clearly reduces the chance of the intermolecular collision and the formation of PCL with lower M_w. With **4** and Ti(O*i*-Pr)$_4$, dilution reduced the viscosity of the solution and increased the intramolecular motions, which in turn raised the chance of the intramolecular transesterification. It is also worth to note that the dilution did not affect the yield significantly in these complexes.

Dilution with toluene reduced the yield and M_w of PCL because effective concentration of the substrate around the active site decreased. PDI also decreased as a result of the dilution. However, the yields with catalysts **4** and Ti(O*i*-Pr)$_4$ were not sensitive to the solvent addition. In the bulk polymerization with the catalyst **2**, PDI became broad and both yield and M_w increased as the reaction time increased. However, induction period was observed as seen in entry 9-12 and both yield and M_w increased rapidly after the induction period and reached asymptotic values in the final stage. For the TON, this reached maximum after 1 hr and decreased thereafter.

For the comparison experiment with entry 2, polymerization under the identical conditions except the addition of methanol (0.5 mL) at the beginning of the polymerization were carried out but reveal lower yield (99%:88%), M_w (47.1×10^3 : 25.6×10^3), and M_n (26.2×10^3 : 14.7×10^3) even though PDI (1.79:1.75) was almost identical. Bimodal M_w distribution was observed after the addition of methanol, while unimodal M_w distribution was obtained in the absence of methanol. The reason for this behavior is not clear at the moment but it is likely that a faster termination of the polymerization with methanol may cause these results as indicated by the NMR experiment with complex **1** (no



Scheme 2. Proposed polymerization mechanism of monomeric titanium complexes containing β-ketoiminate ligands.

change was observed after addition of methanol).

More substrate was added again after the initial polymerization in order to check the possible living character of the catalyst. The dimeric complex **4** showed living character, because the yield and M_w increased from 77% to 159% and from 10.5×10^3 to 19.2×10^3, respectively, while keeping PDI almost constant (1.46 → 1.53) (entry 20, 21). The amount of the lower M_w portion was reduced after the additional incorporation of the substrate, possibly due to the increase in reaction time. However, the new complexes with a chelating β-ketoiminate ligand did not exhibit living character, because the yields did not change even after the additional incorporation of the substrate.

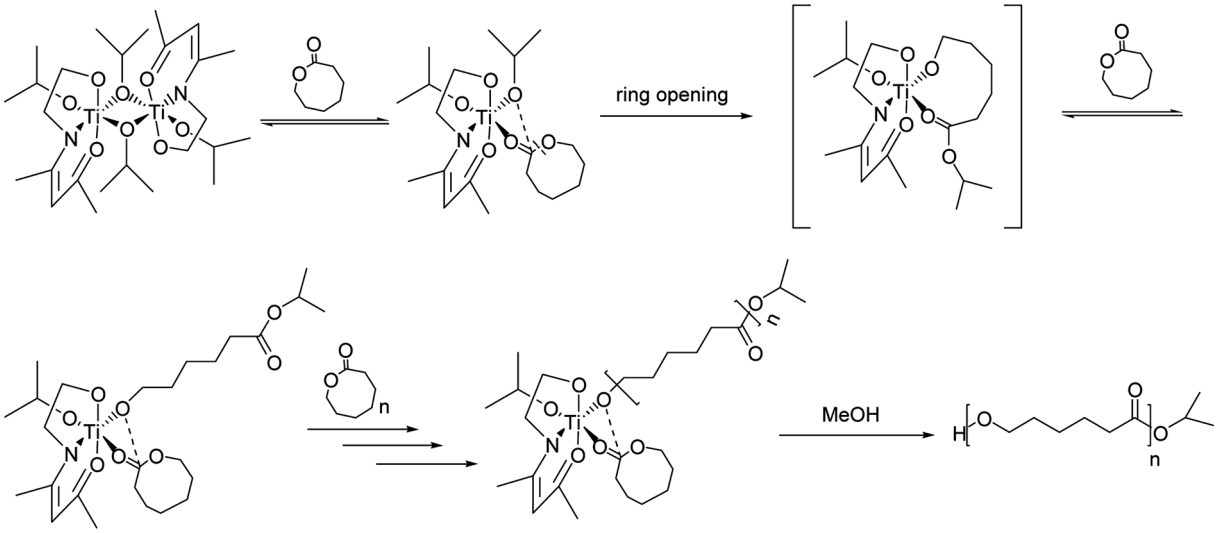
The polymerization in toluene solution with additional substrate in the presence of catalyst **1** at 100 °C resulted in the reduced yield (81% compared to 61%) (entry 6, 7), whereas almost same polymerization yield (81% compared to 85%) was obtained when the additional polymerization was conducted with pure substrate. In these cases, unimodal M_w distributions were observed. Moreover, M_w did not change notably.

End group analysis by NMR proved that MeO and OH groups were present in the PCL produced with complexes **1**, **2**, and **3**, while *i*-PrO and OH were found in the PCL produced with complexes **4** and Ti(O*i*-Pr)$_4$. However, peaks for the cyclic polyesters could not be identified due to overlapping with the peaks for aliphatic polyesters.

From these observations, plausible mechanisms for these complexes can be proposed as depicted in Scheme 2 and 3. In the Scheme 2, it is expected that intermolecular transesterification producing PCL with a β-ketoiminate ligand as an end group does not occur effectively and end group analysis supports this expectation. Intramolecular transesterification may be favorable if the ring size becomes sufficiently larger and this may be blocked in the early stage. In this regard, these may be the reasons why catalysts **1-3** with chelating β-ketoiminate ligands show less activity but higher Mw.

Conclusion

A series of titanium complexes containing chelating β-ketoiminate ligands were found to be efficient for the ring-opening polymerization of ε-CL. These complexes produced PCL with bimodal M_w distribution. The methyl substituent on the back bone of the alkoxy group affected significantly



Scheme 3. Proposed polymerization mechanism of dimeric titanium complexes containing β-ketoiminate and alkoxy ligands.

the polymerization rate and characteristics of the resulting PCL. The catalyst activity decreased in the order of Ti(O*i*-Pr)$_4$ > **4** > **1** > **3** > **2**, while M_w of PCL produced at 70 °C decreased in the order of **3** > **1** > **2** > **4** > Ti(O*i*-Pr)$_4$. Intra- and intermolecular transesterifications rather than disproportional rearrangements may be the main reason for the bimodal behavior and for the change of M_w. Dilution with toluene reduced the yield, narrowed PDI, and decreased M_w of PCL. In contrast, the catalytic behavior of the catalyst **4** and Ti(O*i*-Pr)$_4$ were not sensitive to the solvent addition. Dimeric complex (catalyst **4**) showed living character, while other catalysts were not living.

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