

Bis(amido)titanium complexes having chelating diaryloxo ligands bridged by sulfur or methylene and their catalytic behaviors for ring-opening polymerization of cyclic esters

Yoshinori Takashima ^a, Yuushou Nakayama ^b, Toshikazu Hirao ^a,
Hajime Yasuda ^b, Akira Harada ^{c,*}

^a Department of Materials Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

^b Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

^c Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Received 29 August 2003; accepted 27 October 2003

Abstract

A series of bis(dialkylamido) titanium complexes coordinated by O–E–O (E = S, CH₂) chelating bis(aryloxo) ligands, Ti[E(4-Me-6-^tBuC₆H₂O)₂](NR₂)₂ (**1**: E = S, R = Me; **2**: E = S, R = Et; **3**: E = CH₂, R = Me; **4**: E = CH₂, R = Et), were synthesized by the reaction of Ti(NR₂)₄ (R = Me, Et) with 2,2'-E(4-Me-6-^tBuC₆H₂OH)₂ (E = S, CH₂). The crystal structures of complexes **2** and **4** were determined by X-ray diffraction study. Complex **2** has a trigonal bipyramidal structure with the sulfur and nitrogen atom in *trans* positions and complex **4** has a tetrahedral structure. The complex **2** was found to initiate the controlled polymerization of ϵ -caprolactone in toluene at 100 °C affording poly(ϵ -caprolactone) and poly(L-lactide) with relatively narrow molecular weight distributions. The complex **4** showed higher activity for the polymerization of ϵ -caprolactone to give a polymer with a broader molecular weight distribution in comparison with complex **2**.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Titanium complexes; Sulfur- or methylene-bridged bis(aryloxo) ligands; Dialkylamido ligand; Cyclic esters; Ring-opening polymerization

1. Introduction

Early transition metal complexes with various chelating bis(aryloxo) ligands have recently been noticed as catalyst precursors for the polymerization of ethylene [1,2], α -olefins [1,2] and cyclic esters [3,4], and for ring-opening metathesis polymerization [5,6]. Kakugo and Miyatake reported that a titanium complex having a sulfur-bridged bis(aryloxo) ligand, Ti(^tBu₂tbp)Cl₂ (^tBu₂tbp = 2,2'-thiobis(4-methyl-6-*tert*-butylphenoxo)) and Ti(^tBu₂tbp)(OⁱPr)₂, which had shown distinctively high activity for the polymerization of ethylene, propylene, styrene and dienes, as well as for copolymerization of ethylene with styrene, upon activation with methylalu-

minoxane [7]. These dianionic ligand contribute not only to stabilization of the active species but also to raising the activity of the catalyst system, and the coordination of the bridging sulfur atom to the metal is the key feature for the high activity of the bis(aryloxo) titanium complexes [8]. Titanium complexes bearing a methylene-bridged bis(aryloxo) ligand, [Ti(mbp)X₂]₂ (mbp = 2,2'-CH₂(4-Me-6-^tBuC₆H₂O)₂, X = Cl and OⁱPr), have been known to initiate controlled polymerization of ϵ -CL in the presence of some cocatalysts such as propylene oxide and oxetane [9], in sharp contrast to the uncontrolled polymerization of cyclic esters with Ti(OⁿBu)₄ [10]. Our group has reported the syntheses and structures of titanium complexes having a tellurium-bridged chelating diaryloxo ligand, (TeBP)TiX₂ (X = Cl and OⁱPr, TeBP = 2,2'-tellurobis(4-methyl-6-*tert*-butylphenoxo)) and (C₅R₅)TiCl(TeBP) (R = H and Me), and their catalytic behaviors for polymerization of ethylene and cyclic esters [11]. However, these complexes were hardly soluble in toluene

* Corresponding author. Fax: +81-6-6850-5446.

E-mail address: harada@chem.sci.osaka-u.ac.jp (A. Harada).

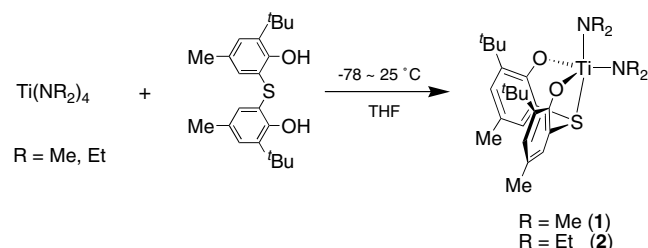
and gave poly(ϵ -caprolactone) with rather broad molecular weight distribution in toluene. In order to improve the solubility of these complexes, we studied about their bis(dialkylamido) derivatives. To the best of our knowledge, no group 4 bis(dialkylamido) complex having sulfur- or methylene-bridged bis(aryloxo) ligand has been known, while a series of their dichloro and diisopropoxo derivatives has been reported [12–15]. Here we report the synthesis and structures of the bis(dialkylamido)titanium complexes with sulfur- or methylene-bridged chelating bis(aryloxo) ligands and the catalytic behavior of these bis(amido)titanium complexes for ring-opening polymerization of ϵ -caprolactone and L-lactide.

2. Results and discussion

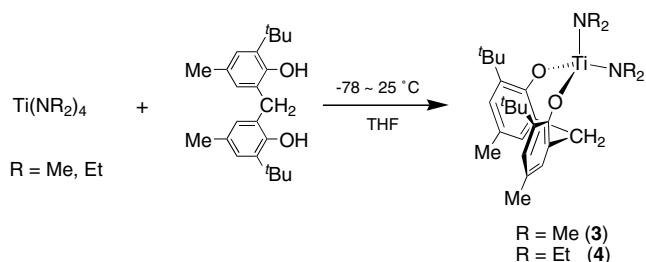
2.1. Preparation and characterization of bis(dialkylamido)titanium complexes 1–4

The reaction of $\text{Ti}(\text{NMe}_2)_4$ with 1 equivalent of 2,2'- $\text{CH}_2(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{OH})_2$ was reported by Chisholm et al. [16] to give an amide-free bis(mbp) complex, $\text{Ti}(\text{mbp})_2$, at 0 °C in toluene. In order to obtain bis(dialkylamido)titanium complexes, we investigated similar reactions at lower temperature in THF. $\text{Ti}(\text{NR}_2)_4$ (R = Me, Et) were reacted with 1 equivalent of 2,2'- $\text{S}(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{OH})_2$ in THF at –78 °C to afford bis(dialkylamido)titanium complexes, $\text{Ti}(^t\text{Bu}_2\text{tp})(\text{NR}_2)_2$ (**1**: R = Me, **2**: R = Et) (Scheme 1). The corresponding mbp complexes, $\text{Ti}(\text{mbp})(\text{NR}_2)_2$ (**3**: R = Me, **4**: R = Et), were also synthesized in a similar manner (Scheme 2). Slow addition of the solution of the bis(aryloxo) ligand to $\text{Ti}(\text{NR}_2)_4$ solution at low temperature (–78 °C) is very important to obtain the bis(dialkylamido)titanium complexes. In fact, the quick addition of the ligand solution to the $\text{Ti}(\text{NMe}_2)_4$ solution at 25 °C only gave $\text{Ti}[\text{E}(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2]_2$ in low yield instead of **1** and **3**. All of these bis(dialkylamido)titanium complexes were highly air-sensitive.

The ^1H NMR spectra of the complexes **1–4** showed one singlet for the protons of the two *tert*-butyl substituents and one singlet for the protons of the two



Scheme 1.



Scheme 2.

methyl substituents, while the aromatic protons at 3- and 5-positions appeared as two doublets. The signals for the methylene protons of the methylene-bridged bis(aryloxo) ligand in **3** and **4** appeared as two doublets (**3**: $^2J_{\text{HH}} = 13.7$ Hz, **4**: $^2J_{\text{HH}} = 14.1$ Hz). The protons at dialkyl amido ligands appeared as two singlet for the protons of dimethyl amido substituents in **1** and **3** and two quartet and two triplets for the protons of diethyl amido substituents in **2** and **4** (Fig. 1). The two amido groups are inequivalent even in the mbp complexes **3** and **4**, suggesting that the flipping of the mbp ligand is restricted.

2.2. Molecular structures of bis(diethylamido)titanium complexes 2 and 4 by X-ray analyses

The single crystals of the bis(diethylamido)titanium complexes **2** and **4** were grown by slow crystallization from *n*-pentane. Figs. 2 and 3 demonstrate the molecular structures of **2** and **4** elucidated by X-ray crystallographic analyses and Table 1 summarizes the selected

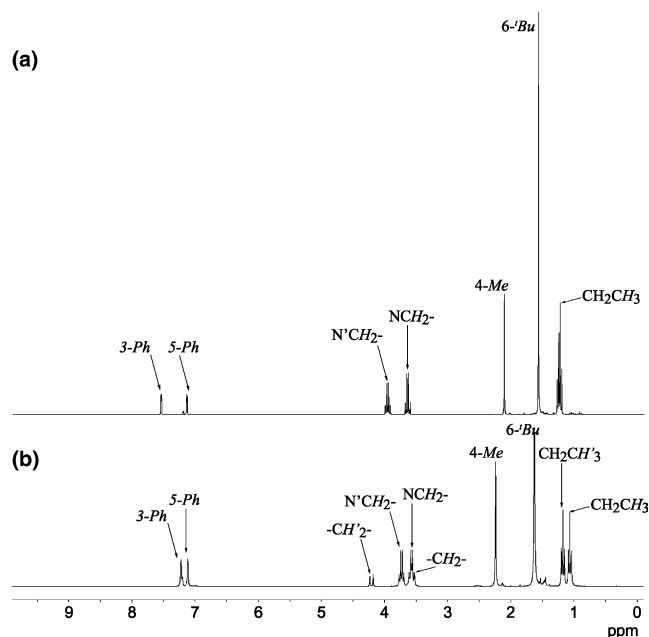


Fig. 1. ^1H NMR spectra of (a) $\text{Ti}(^t\text{Bu}_2\text{tp})(\text{NEt}_2)_2$ (**2**) and (b) $\text{Ti}(\text{mbp})(\text{NEt}_2)_2$ (**4**).

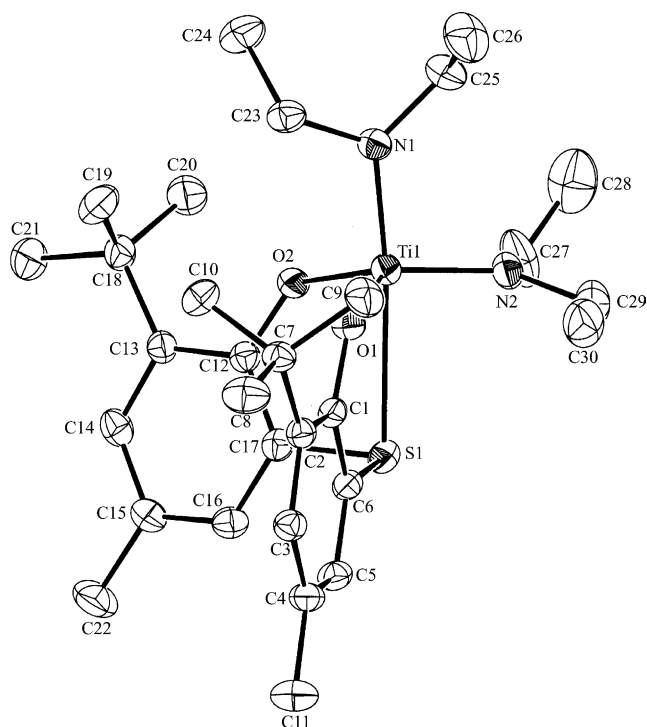


Fig. 2. ORTEP drawing of $\text{Ti}(\text{tBu}_2\text{tbp})(\text{NEt}_2)_2$ (**2**) with numbering scheme. All hydrogen atoms are omitted for clarity.

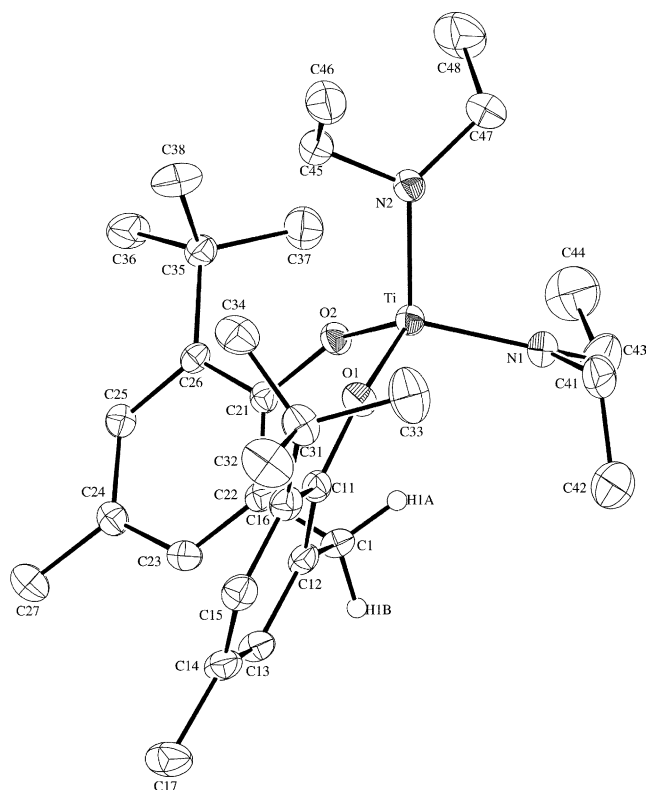


Fig. 3. ORTEP drawing of $\text{Ti}(\text{mbp})(\text{NEt}_2)_2$ (**4**) with numbering scheme. All hydrogen atoms except for H1A and H1B are omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for **2** and **4**

	Complex 2	Complex 4
<i>Bond distances</i>		
Ti–N1	1.892(3)	1.895(2)
Ti–N2	1.863(3)	1.869(2)
Ti–S	2.783(1)	–
Ti–O1	1.886(2)	1.8341(19)
Ti–O2	1.887(2)	1.826(2)
Ti···C1	–	3.267(3)
Ti···H1A	–	2.564
<i>Bond angles</i>		
O–Ti–O	110.20(10)	107.74(9)
C–E–C (E = S, CH ₂)	103.3(1)	114.2(2)
N1–Ti–N2	100.6(1)	105.10(11)
Ti–O–C	135.1(2) (O1)	148.73(18) (O1)
	131.9(2) (O2)	142.57(17) (O2)
Ti···H1A–C1	127.87	

bond distances and angles. Both **2** and **4** were obtained as mononuclear complexes, in sharp contrast to the dinuclear structures of the corresponding chloro and alkoxo complexes having tBu_2tbp ligand, $\{\text{Ti}(\text{tBu}_2\text{tbp})\text{Cl}_2\}_2$ (**5**) [11a] and $\{\text{Ti}(\text{tBu}_2\text{tbp})(\text{O}^i\text{Pr})_2\}_2$ (**6**) [17]. The coordination geometry around the titanium center in **2** can be described as pseudo C_s symmetric trigonal bipyramidal in which one of the two diethylamido ligands and the sulfur atom of the tBu_2tbp ligand occupy the apical positions. The complex **4** has a pseudo C_s symmetric tetrahedral structure. The Ti–S bond length in **2** (2.783(1) Å) is longer than those in the corresponding dichloro complex **5** (2.664(2) Å) [11a], diisopropoxo complex **6** (2.719(1) Å) [17], and aryl complex $\text{Ti}(\text{tBu}_2\text{tbp})(o\text{-CH}_2\text{NMe}_2\text{C}_6\text{H}_4)\text{Cl}$ (**7**: 2.704(1) Å) [17], and shorter than that in a cyclopentadienyl (Cp) complex, $\text{Ti}(\text{tBu}_2\text{tbp})\text{CpCl}$ (**8**: 2.907(1) Å) [18]. The Ti–O distances in the sulfur-bridged complex **2** (av. 1.887 Å) is longer than that in methylene-bridged complex **4** (av. 1.830 Å), due to the decreased π -donation from oxygen atoms by coordination of the sulfur-bridging atom to titanium metal center. The Ti–O distances in **2** are comparable to the diisopropoxo complex **6** (1.892 Å) [17], and longer than those in the corresponding chloride complex **5** (1.846 Å) [17], aryl complex **7** (1.855 Å) [9a] and Cp complex (**8**: 1.827 Å) **8** in the titanium complex with the tbp ligand. The Ti–O distances in the methylene-bridged complex **4** are longer than that of a series of titanium complexes with methylene-bridged bis(aryloxo) ligand (1.751–1.788 Å) [19–21] and the other titanium complex with monodentate aryloxo or alkoxo ligands [22–27], due to the π -donation from the nitrogen atoms to the metal center [28]. The axial Ti–N bond distance in the sulfur-bridged complex **2** is 0.03 Å longer than the equatorial one in **2**. The Ti–N1 distance farther from the bridging methylene group in **4** was also longer by 0.03 Å than that closer to the methylene

group. Although the Ti···C1 distance (3.267(3) Å) in **4** is much longer than those of agostic Ti···H–C interaction, the Ti···H1A (one of the two hydrogen atoms on C1) distance (2.58 Å) in **4** is only slightly longer than typical Ti···H distances of agostic Ti···H–C interaction (2.06–2.45 Å) [29]. Thus, the complex **4** could have a weak Ti···H–C interaction. This could be the reason for the restricted flipping of the mbp ligand in **3** and **4** (vide supra).

2.3. Polymerization of ϵ -caprolactone and L-lactide by **2** and **4**

Recently, Aida and coworkers reported that a diisopropoxo analogue of **4**, Ti(mbp)(OⁱPr)₂, initiated living polymerization of lactones [9c]. The dichloro complex Ti(mbp)Cl₂ was inactive without addition of propylene oxide [9c], while the corresponding dichloride complex having the sulfur-bridged ligands Ti(tbp)Cl₂ catalyzed the polymerization of ϵ -caprolactone (ϵ -CL) without any cocatalysts at 100 °C to give the polymers in good yield, although the resulting poly(ϵ -CL) had a relatively broad molecular weight distribution [11b]. In contrast, the corresponding bis(diethylamido) complexes having the sulfur- or methylene-bridged ligands **2** and **4** polymerized ϵ -CL in toluene at 100 °C without any cocatalyst to give poly(ϵ -CL) with relatively narrow molecular weight distribution (Table 2). The complex **2** catalyzed polymerization of ϵ -CL in 90.3% yield within 32 h to afford poly(ϵ -CL) with M_n of 18,800 and M_w/M_n of 1.31. The molecular weight distribution of the polymer obtained with the amido complex **2** was narrower than that obtained with the corresponding chloro complex **5** in toluene, though the activity of **2** is lower than that of **5** [11b]. The basicity of the amido group of **2** should suppress the side reactions such as back-biting. The polymerization of ϵ -CL with complex **4** proceeded to reach to 91.0% yield within 8 h to afford a polymer with higher molecular weight ($M_n = 56,200$) and relatively

broader molecular weight distribution ($M_w/M_n = 1.60$). The molecular weight of the polymers obtained by **2** and **4** systems were higher than that calculated from the initial molar ratio of ϵ -CL to catalysts. In comparison between the sulfur-bridged complex **2** system and the methylene-bridged complex **4** system, the reaction rate at the initial stage in sulfur-bridged complex **2** system is faster than that in methylene-bridged complex **4** system at the polymerization time of 4 h, while the polymer yield of the methylene-bridged complex **4** grew higher than that in the sulfur-bridged complex **2** at the polymerization time of 8 h. At this stage, the polymer obtained with **2** had lower molecular weight and narrower molecular weight distribution than those obtained with **4**. This suggests that the sulfur-bridged complex **2** system would be more effective for the initiation than the methylene-bridged complex **4** system, while the propagation in the complex **2** system would be slower than that in the complex **4** system.

In the ¹H NMR spectrum of the poly(ϵ -CL) obtained by **2** (run 4 in Table 2), resonances for –CH₂OH, –NCH₂CH₃ and –NCH₂CH₃ end-groups appeared at 3.63, 3.35 and 1.17 ppm, respectively (Fig. 4). Thus, the

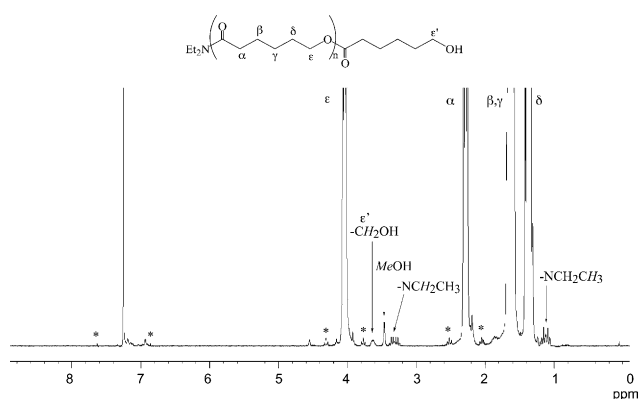


Fig. 4. ¹H NMR spectrum (400 MHz, CDCl₃, 30 °C) of the poly(ϵ -caprolactone) obtained by **2**. *: side band.

Table 2
Polymerization of ϵ -caprolactone by **2** and **4**

Run	Complex	Time (h)	Yield (%)	$\overline{M}_n/10^3$ ^a		$\overline{M}_w/\overline{M}_n$ ^a
				Calculated ^a	Observed ^b	
1	2	4	56.9	13.0	8.2	1.09
2	2	8	80.2	18.3	13.1	1.13
3	2	16	89.3	20.4	14.8	1.14
4	2	32	90.3	20.6	18.8	1.31
5	4	2	23.5	5.4	15.3	1.16
6	4	4	52.9	12.1	21.8	1.17
7	4	5	83.5	19.1	39.2	1.47
8	4	8	91.0	20.8	56.2	1.60

In toluene, at 100 °C, [ϵ -CL]₀/[Ti] = 200.

^a \overline{M}_n (calcd) = (MW of ϵ -CL) × [ϵ -CL]₀/[Ti] × (polymer yield).

^b Determined by GPC analysis in THF calibrated with standard poly(styrene).

Table 3
Polymerization of L-lactide by **2**

Run	Time (h)	Yield (%)	$\overline{M}_n/10^{3a}$		$\overline{M}_w/\overline{M}_n^a$
			Calculated ^b	Observed ^b	
1	36	24.4	7.0	7.6	1.08
2	48	54.2	15.6	13.6	1.13
3	86	82.1	23.7	18.1	1.19
4	120	90.3	26.0	20.4	1.23

In toluene, at 100 °C, $[L-LA]_0/[Ti] = 200$.

^a $\overline{M}_n(\text{calcd}) = (\text{MW of L-LA}) \times [L-LA]_0/[Ti] \times (\text{polymer yield})$.

^b Determined by GPC analysis in THF calibrated with standard poly(styrene).

initiation in these systems would be formal migratory insertion of the monomer into Ti–NEt₂ bond to generate titanium alkoxide species, and repeated monomer insertion and quenching with MeOH would give polymers with hydroxy and amide end groups. The M_n of this polymer can be calculated to be 1.8×10^4 based on the ¹H NMR spectrum, which is almost equal to that estimated by GPC calibrated with standard poly(styrene).

The sulfur-bridged complex **2** system was also applied to the polymerization of L-lactide (L-LA) and the results are summarized in Table 3. The polymer yield reached to 96.2% within 120 h to afford poly(L-LA) with M_n of 20,400 and M_w/M_n of 1.23. The molecular weight of the polymer increased linearly to the polymer yield, indicating living nature of this polymerization system, although, the molecular weight distribution was also increasing with the polymer yield. Some side reaction such as back-biting could be accompanying the polymerization.

3. Conclusion

A series of bis(dialkylamido)titanium complexes containing sulfur- or methylene-bridged chelating bis(aryloxo) ligands, $Ti[E(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2](NR_2)_2$ (**1**: E = S, R = Me; **2**: E = S, R = Et; **3**: E = CH₂, R = Me; **4**: E = CH₂, R = Et), was prepared and the complexes **2** and **4** were determined to have mononuclear pseudo C_s symmetric structures by X-ray diffraction study. In their catalytic behavior for ring-opening polymerization of ϵ -caprolactone and L-lactide, the sulfur-bridged complex **2** produced poly(ϵ -CL) with controlled molecular weight and relatively narrow molecular weight distribution in toluene without any cocatalyst. The ring-opening polymerization of ϵ -CL by **4** gave poly(ϵ -CL) with higher molecular weight and broader molecular weight distribution for those for complex **2**, while the corresponding dichloride complex, $Ti[CH_2(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2]Cl_2$, was inactive for the polymerization of ϵ -caprolactone without cocatalyst.

4. Experimental

4.1. General considerations

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by the use of standard Schlenk techniques under an argon atmosphere. THF, toluene and *n*-pentane were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. C₆D₆ was dried over Na/K alloy and thoroughly degassed by trap-to-trap distillation before use. 2,2'-Thiobis(4-methyl-6-*tert*-butylphenol) was supplied by Ciba-Geigy AG. ϵ -Caprolactone and 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol) purchased from Nacarai Tesque Co. Ti(NMe₂)₄ and Ti(NEt₂)₄ were prepared according to the literature [30].

The ¹H (500 and 400 MHz), and ¹³C (125 and 100 MHz) NMR spectra in C₆D₆ was measured on JEOL JNM-LA500 and JEOL JNM-GSX400 spectrometers. Assignments for ¹H and ¹³C NMR peaks for some complexes were aided by 2D ¹H–¹H NOESY, 2D 1H–1H COSY, 2D, 2D HMQC and 2D HMBC spectra. Mass spectra were recorded on a JEOL SX-102 spectrometer. All melting points of the complexes were measured in sealed tubes under an argon atmosphere and were not corrected.

4.2. Preparation of $Ti[S(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2](NMe_2)_2$ (**1**)

A solution of 2,2'-S(4-Me-6-*t*-BuC₆H₂O)₂ (0.35 g, 0.97 mmol) in THF (5 ml) was slowly added to a solution of Ti(NMe₂)₄ (0.33 g, 0.97 mmol) in THF (35 ml) at –78 °C. The reaction mixture was stirred for 10 min and then allowed to warm to ambient temperature followed by stirring for 2 h. The color of the solution changed from yellow to orange. All volatiles were removed under reduced pressure to give microcrystals. Recrystallization from *n*-pentane gave $Ti[S(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2](NMe_2)_2$ (**1**) (0.32 g, 59%) as orange crystals, m.p. 98–102 °C (dec.). ¹H NMR (C₆D₆, 30 °C, 400 MHz): δ 7.52 (d, ⁴J_{HH} = 2.1 Hz, 2H, 3-C₆H₂O), 7.15 (d, ⁴J_{HH} = 2.1 Hz, 2H, 5-C₆H₂O), 3.45 (s, 6H, –NMe₂), 3.32 (s, 6H,

–N'Me₂), 2.11 (s, 6H, 4-Me), 1.58 (s, 18H, 6-^tBu). ¹³C NMR (C₆D₆, 30 °C, 100 MHz): δ 165.2 (1-C₆H₂O), 137.9 (6-C₆H₂O), 132.2 (4-C₆H₂O), 129.7 (5-C₆H₂O), 128.8 (3-C₆H₂O), 124.6 (2-C₆H₂O), 35.6 (6-CMe₃), 29.7 (6-CMe₃), 29.7 (–N'CH₃), 26.1 (–NCH₃), 20.9 (4-Me). HRMS (EI): Calc. for C₂₆H₄₀O₂N₂Ti₁S₁ 492.2293. Found 492.2277.

4.3. Preparation of Ti[S(4-Me-6-^tBuC₆H₂O)₂](NEt₂)₂ (**2**)

The complex **2** was synthesized and isolated as orange crystals in 64% yield in a similar manner to **1**, m.p.; 123–128 °C. ¹H NMR (C₆D₆, 30 °C, 500 MHz): δ 7.55 (d, ⁴J_{HH} = 1.6 Hz, 2H, 3-C₆H₂O), 7.14 (d, ⁴J_{HH} = 1.6 Hz, 2H, 5-C₆H₂O), 3.96 (q, 4H, ³J_{HH} = 6.9 Hz, –N(CH₂Me)₂), 3.64 (q, 4H, ³J_{HH} = 7.1 Hz, –N'(CH₂Me)₂), 2.12 (s, 6H, 4-Me), 1.57 (s, 18H, 6-^tBu), 1.26 (t, ³J_{HH} = 6.9 Hz, 6H, –CH₂Me), 1.23 (t, ³J_{HH} = 7.1 Hz, 6H, –CH₂Me'). ¹³C NMR (C₆D₆, 30 °C, 125 MHz): δ 166.0 (1-C₆H₂O), 137.9 (6-C₆H₂O), 133.0 (4-C₆H₂O), 130.0 (5-C₆H₂O), 128.8 (3-C₆H₂O), 125.7 (2-C₆H₂O), 48.8 (–NCH₂–), 47.7 (–N'CH₂–), 35.5 (6-CMe₃), 30.0 (6-CMe₃), 20.7 (4-Me), 15.5 (–NCH₂CH₃), 15.1 (–N'CH₂CH₃). HRMS (EI): Calc. for C₃₀H₄₈O₂N₂Ti₁S₁ 548.2919. Found 548.2932.

4.4. Preparation of Ti[CH₂(4-Me-6-^tBuC₆H₂O)₂](NMe₂)₂ (**3**)

The complex **3** was synthesized and isolated as yellow crystals in 56% yield in a similar manner to **1**, m.p. 124–128 °C (dec.). ¹H NMR (CD₂Cl₂, 30 °C, 400 MHz): δ 7.05 (s, 2H, 5-C₆H₂O), 6.87 (s, 2H, 3-C₆H₂O), 3.82 (d, ²J_{H²H¹} = 13.7 Hz, 1H, CH²H¹), 3.45 (s, 6H, –N'Me₂), 3.31 (d, ²J_{H¹H²} = 13.7 Hz, 1H, CH¹H²), 2.87 (s, 6H, –NMe₂), 2.20 (s, 6H, 4-Me), 1.37 (s, 18H, 6-^tBu). ¹³C NMR (CD₂Cl₂, 30 °C, 100 MHz): δ 158.5 (1-C₆H₂O), 137.2 (6-C₆H₂O), 131.5 (4-C₆H₂O), 129.4 (5-C₆H₂O), 128.9 (3-C₆H₂O), 125.8 (2-C₆H₂O), 45.0 (–CH₂–), 33.1 (6-CMe₃), 33.1 (–N'CH₃), 30.6 (–NCH₃), 30.3 (6-CMe₃), 21.2 (4-Me). HRMS (EI): Calc. for C₂₇H₄₂O₂N₂Ti₁ 474.2729. Found 474.2748.

4.5. Preparation of Ti[CH₂(4-Me-6-^tBuC₆H₂O)₂](NEt₂)₂ (**4**)

The complex **4** was synthesized and isolated as yellow crystals in 74% yield in a similar manner to **1**, m.p. 143–148 °C (dec.). ¹H NMR (C₆D₆, 30 °C, 500 MHz): δ 7.22 (d, ⁴J_{HH} = 2.1 Hz, 2H, 3-C₆H₂O), 7.11 (d, ⁴J_{HH} = 2.1 Hz, 2H, 5-C₆H₂O), 4.21 (d, ²J_{H¹H²} = 14.1 Hz, 1H, CH²H¹), 3.73 (q, 4H, ³J_{HH} = 7.1 Hz, –N'CH₂–), 3.57 (q, 4H, ³J_{HH} = 6.9 Hz, –NCH₂–), 3.55 (d, ²J_{H²H¹} = 14.1 Hz, 1H, –CH²H¹–), 2.24 (s, 6H, 4-Me), 1.62 (s, 18H, 6-^tBu), 1.18 (t, ³J_{HH} = 6.9 Hz, 6H, –CH₂Me), 1.07

(t, ³J_{HH} = 7.1 Hz, 6H, –CH₂Me'). ¹³C NMR (C₆D₆, 30 °C, 125 MHz): δ 159.9 (1-C₆H₂O), 136.6 (6-C₆H₂O), 133.3 (4-C₆H₂O), 129.4 (3-C₆H₂O), 128.3 (2-C₆H₂O), 125.9 (5-C₆H₂O), 47.6 (–N'CH₂–), 47.4 (–NCH₂–), 35.3 (–CH₂–), 34.2 (6-CMe₃), 30.6 (6-CMe₃), 21.1 (4-Me), 15.5 (–N'CH₂CH₃), 15.2 (–NCH₂CH₃). HRMS (EI): Calc. for C₃₁H₅₀O₂N₂Ti₁ 530.3355. Found 530.3336.

4.6. Polymerization of cyclic esters

To a solution of monomer (1 mmol) in toluene (0.90 ml) was added a toluene solution (0.10 ml) of complex **2** or **4** (5 μmol). The reaction mixture became a orange-clear solution. 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.

4.7. GPC analysis of the polymers

Gel permeation chromatographic (GPC) analyses were carried out at 40 °C using a Tosoh TSKgel G2000HXL and G3000HXL columns connected to a Tosoh RI-8012 detector. THF was used as a eluent at a flow rate of 0.8 ml/min. Samples were prepared in THF (0.5 mg/ml) and were filtered through a Advantec DIS-MIC-25JP filter in order to remove particulates before injection. The GPC column was calibrated versus poly(styrene) standards (Aldrich).

4.8. Crystallographic data collections and structure determination of **2** and **4**

A crystal of **2** was sealed in a glass capillary under argon. The measurement of **2** was made on a Rigaku AFC-5R four-circle diffractometer for data collection using Mo Kα radiation. Relevant crystal and data statistics are summarized in Table 4. Three standard reflections were chosen and monitored every 150 reflections. Empirical absorption correction was carried out on the basis of an azimuthal scan. The unit cell parameters at 23 °C were determined by a least-squares fit to 2θ values of 25 strong higher reflections for complex **2**. Complex **2** showed no significant intensity decay during the data collection. The structures of complex **2** was solved by direct methods (SHELXS-86) [31] and expanded using Fourier techniques (DIRDIF 94) [32] and refined by the full-matrix least square method. Measured non-equivalent reflections with $I > 2.0\sigma(I)$ were used for the structure determination. In the subsequent refinement the function $\sum \omega(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors amplitudes, respectively. The

Table 4
Crystal data and collection parameters

	Complex 2	Complex 4
Formula	C ₃₀ H ₄₈ N ₂ O ₂ S ₁ Ti ₁	C ₃₁ H ₅₀ N ₂ O ₂ Ti ₁
Formula weight	548.68	530.63
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (#14)	<i>P</i> 2 ₁ / <i>c</i> (#14)
<i>a</i> (Å)	15.498(4)	16.355(3)
<i>b</i> (Å)	21.770(8)	12.160(3)
<i>c</i> (Å)	9.396(4)	16.725(5)
α (°)	–	–
β (°)	93.35(3)	111.541(12)
γ (°)	–	–
<i>V</i> (Å ³)	3164(1)	3093.7(13)
<i>Z</i>	4	4
Number of reflections for cell determination (<i>2</i> θ range)	25 (25.0–29.0)	13074 (2.7–54.8)
<i>D</i> _{calcd} (g/cm ³)	1.151	1.139
<i>F</i> (000)	744.00	1152
μ [Mo K α] (cm ⁻¹)	3.63	3.04
Diffractometer	AFC-5R	R-AXIS-RAPID
Temperature (K)	296(2)	193(2)
Scan speed (deg/min)	16.0	–
Scan width (°)	0.74 + 0.3 tan θ	–
Total oscillation angles (°)	–	222.0
Exposure time (min per deg)	–	5.0
<i>2</i> θ _{max} (°)	55.0	54.8
Number of reflections measured (total)	8928	27135
Number of reflections measured (unique) (<i>R</i> _{int})	7257 (0.109)	7011 (0.1090)
Number of variables	325	337
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.113, 0.1430	0.1254, 0.1495
<i>R</i> (<i>I</i> > 2.0 σ (<i>I</i>))	0.0494	0.0632
GOF on <i>F</i> ²	1.246	0.983
Δ (e Å ⁻³)	0.55, -1.27	0.614, -0.362

agreement indices are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum \omega(|F_o| - |F_c|)^2 / \sum \omega(|F_o|)^2]^{1/2}$ where $\omega^{-1} = \sigma^2(F_o) = [\sigma_c^2(F_o) + p^2/4(F_o^2)]$. The positions of all non-hydrogen atoms for complex **2** were found from a difference Fourier electron density map and refined anisotropically. All hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and constrained to ride on their respective carbon atoms.

A crystal of **4** suitable for X-ray diffraction study was mounted on a cryoloop. The measurement of **4** was made on a Rigaku R-AXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71069$). Relevant crystal and data statistics are summarized in Table 4. Indexing was performed from one oscillation, which was exposed for 5.0 min. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. The data was corrected for Lorentz and polarization effects. The structures of complex **4** was solved by direct methods (SIR-92) [33] and expanded using Fourier techniques (DIRDIF 94) [32] and refined by full-matrix least squares refinement (SHELXL-97) [34]. In the subsequent refinement the function $\sum \omega(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors amplitudes, respectively. The agreement indices are defined as $R = \sum ||F_o| - |F_c|| /$

$\sum |F_o|$ and $R_w = [\sum \omega(F_o^2 - F_c^2)^2 / \sum \omega(F_o^2)^2]^{1/2}$. The positions of all non-hydrogen atoms for complex were found from a difference Fourier electron density maps and refined anisotropically. All hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and kept fixed.

All calculations were performed using the TEXSAN crystallographic software package, and illustrations were drawn with ORTEP.

Crystallographic data for the structural analysis of **2** and **4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 218168 and 218167, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Acknowledgements

We are indebted to a Grant-in-Aid for Scientific Research (Grant no. 14044072 and 14350488) from the Ministry of Education, Culture, Sports, Science and Technology. 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.

References

- [1] (a) A review for polymerization olefins: H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1143;
(b) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 428.
- [2] (a) C.J. Schaverien, A.J. van der Linden, A.G. Orpen, *Polym. Prepr. (Am. Chem. Soc., Polym. Div.)* 35 (1994) 672;
(b) A.J. van der Linden, C.J. Schaverien, N. Meijboom, C. Ganter, A.G. Orpen, *J. Am. Chem. Soc.* 117 (1995) 3008.
- [3] (a) M. Hayakawa, M. Mitani, T. Yamada, T. Mukaiyama, *Macromol. Chem., Rapid Commun.* 17 (1996) 865;
(b) M. Hayakawa, M. Mitani, T. Yamada, T. Mukaiyama, *Macromol. Chem. Phys.* 198 (1997) 1305.
- [4] (a) J. Okuda, I.L. Rushkin, *Macromolecules* 26 (1993) 5530;
(b) J. Okuda, T. Kleinhann, P. König, I. Taden, S. Ngo, I.L. Rushkin, *Macromol. Symp.* 95 (1995) 195.
- [5] A review for ring-opening metathesis polymerization: R.R. Schrock, *Acc. Chem. Res.* 23 (1990) 158.
- [6] (a) Y. Nakayama, H. Saito, N. Ueyama, A. Nakamura, *Organometallics* 18 (1999) 3149;
(b) Y. Takashima, Y. Nakayama, A. Harada, *Chem. Lett.* (2001) 488;
(c) Y. Takashima, Y. Nakayama, H. Yasuda, A. Harada, *J. Organomet. Chem.* 651 (2002) 114;
(d) Y. Takashima, Y. Nakayama, H. Yasuda, A. Nakamura, A. Harada, *J. Organomet. Chem.* 654 (2002) 74.
- [7] (a) M. Kakugo, T. Miyatake, K. Mizunuma, *Chem. Express* 2 (1987) 445;
(b) T. Miyatake, K. Mizunuma, Y. Seki, M. Kakugo, *Macromol. Chem., Rapid Commun.* 10 (1989) 349;
(c) T. Miyatake, K. Mizunuma, M. Kakugo, *Makromol. Chem., Macromol. Symp.* 66 (1993) 203.
- [8] (a) F.G. Sernetz, R. Mülhaupt, S. Fokken, J. Okuda, *Macromolecules* 30 (1997) 1562;
(b) R.D.J. Froese, D.G. Musaev, T. Matsubara, K. Morokuma, *J. Am. Chem. Soc.* 119 (1997) 7190;
(c) R.D.J. Froese, D.G. Musaev, K. Morokuma, *Organometallics* 18 (1999) 373.
- [9] (a) D. Takeuchi, Y. Watanabe, T. Aida, S. Inoue, *Macromolecules* 28 (1995) 651;
(b) D. Takeuchi, T. Aida, *Macromolecules* 29 (1996) 8096;
(c) D. Takeuchi, T. Nakamura, T. Aida, *Macromolecules* 33 (2000) 725;
(d) D. Takeuchi, T. Aida, *Macromolecules* 33 (2000) 4607.
- [10] H.R. Kricheldorf, M. Berl, N. Scharnagl, *Macromolecules* 21 (1988) 286.
- [11] (a) Y. Nakayama, K. Watanabe, N. Ueyama, A. Nakamura, A. Harada, J. Okuda, *Organometallics* 19 (2000) 2498;
(b) Y. Takashima, Y. Nakayama, K. Watanabe, T. Itono, N. Ueyama, A. Nakamura, A. Harada, J. Okuda, *Macromolecules* 35 (2002) 7535.
- [12] (a) J. Okuda, S. Fokken, H.-C. Kang, W. Massa, *Chem. Ber.* 128 (1995) 221;
(b) S. Fokken, T.P. Spaniol, J. Okuda, F.G. Sernetz, R. Mülhaupt, *Organometallics* 16 (1997) 4240;
(c) J. Okuda, S. Fokken, T. Kleinhenn, T.P. Spaniol, *Eur. J. Inorg. Chem.* (2000) 1321.
- [13] (a) P.J. Toscano, E.J. Schermerhorn, C. Dettelbacher, D. Macherone, J. Zubieta, *J. Chem. Soc., Chem. Commun.* (1991) 933;
(b) J. Okuda, S. Fokken, H.-C. Kang, W. Massa, *Polyhedron* 17 (1998) 943;
(c) D.R. Mulford, P.E. Fanwick, I.P. Rothwell, *Polyhedron* 19 (2000) 35.
- [14] L. Porri, A. Ripa, P. Colombo, E. Miano, S. Capelli, S.V. Meille, *J. Organomet. Chem.* 514 (1996) 213.
- [15] L. Higham, M. Thornton-Pett, M. Bochmann, *Polyhedron* 17 (1998) 3047.
- [16] M.H. Chisholm, J.-H. Huang, J.C. Huffman, W.E. Streib, D. Tiedtke, *Polyhedron* 16 (1997) 2941.
- [17] S. Fokken, T.P. Spaniol, H.-C. Kang, W. Massa, J. Okuda, *Organometallics* 15 (1996) 5069.
- [18] F. Amor, S. Fokken, T. Kleinhenn, T.P. Spaniol, J. Okuda, *J. Organomet. Chem.* 621 (2001) 3.
- [19] C. Floriani, F. Corazza, W. Lesueur, A. Chiesi-Villa, C. Guastini, *Angew. Chem.* 101 (1989) 93;
Angew. Chem. Int. Ed. Engl. 28 (1989) 66.
- [20] F. Corazza, C. Floriani, A. Chiesi-Villa, C. Guastini, *Inorg. Chem.* 30 (1991) 145.
- [21] E.E.C.G. Gielens, T.W. Dijkstra, P. Berno, A. Meetsma, B. Hessen, J.H. Teuben, *J. Organomet. Chem.* 591 (1999) 88.
- [22] M. Mazzanti, C. Floriani, A. Chiesi-Villa, C. Guastini, *J. Chem. Soc., Dalton Trans.* (1989) 1793.
- [23] K. Watenpaugh, C.N. Caughlan, *Inorg. Chem.* 5 (1966) 1782.
- [24] J.R. Dilworth, J. Hanich, M. Krestel, J. Beck, J. Strahle, *J. Organomet. Chem.* 315 (1986) C9.
- [25] J.E. Hill, J.M. Nash, P.E. Fanwick, I.P. Rothwell, *Polyhedron* 9 (1990) 1617.
- [26] N. Kane-hisa, Y. Kai, N. Kasai, H. Yasuda, Y. Nakayama, K. Takei, A. Nakamura, *Chem. Lett.* (1990) 2167.
- [27] A.V. Firth, D.W. Stephan, *Organometallics* 16 (1997) 2183.
- [28] P.T. Wolczanski, *Polyhedron* 14 (1995) 3335.
- [29] (a) Z. Dawoodi, M.L.H. Green, V.S.B. Mtetwa, K. Prout, A.J. Schultz, J.M. Williams, T.F. Koetzle, *J. Chem. Soc., Dalton Trans.* 8 (1986) 1629;
(b) H. Weiss, F. Haase, R. Ahlrichs, *Chem. Phys. Lett.* 194 (1992) 492;
(c) W. Scherer, T. Priermeier, A. Haaland, H.V. Volden, G.S. McGrady, A.J. Downs, R. Boese, D. Blaeser, *Organometallics* 17 (1998) 4406;
(d) A.H. Cowley, G.S. Hair, B.G. McBurnett, R.A. Jones, *Chem. Commun.* 5 (1999) 437.
- [30] (a) D.C. Bradley, I.M. Thomas, *Proc. Chem. Soc.* (1959) 225;
J. Chem. Soc. (1960) 3857;
(b) M.H. Chisholm, C.E. Hammond, J.C. Huffman, *Polyhedron* 7 (1988) 2515.
- [31] G.M. Sheldrick, in: G.M. Sheldrick, C. Krüger, R. Goddard (Eds.), *Crystallographic Computing*, vol. 3, Oxford University Press, Oxford, 1985.
- [32] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, *The DIRDIF-94 program system*, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.
- [33] A. Altomare, M.C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Cryst.* 27 (1994) 435.
- [34] G.M. Sheldrick, *Program for the solution of Crystal structures*, Universität Göttingen, Germany, 1997.