



## Characteristics of heterogeneous titanium alkoxide catalysts for ring-opening polymerization of lactide to produce polylactide

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### ABSTRACT

TiCl(O-*i*-Pr)<sub>3</sub>/SiO<sub>2</sub> and Ti(O-*i*-Pr)<sub>4</sub>/SiO<sub>2</sub> were prepared by immobilizing titanium(IV) chloride triisopropoxide (TiCl(O-*i*-Pr)<sub>3</sub>) and titanium(IV) tetraisopropoxide (Ti(O-*i*-Pr)<sub>4</sub>), respectively, over pretreated silica. A series of solution polymerizations of L-lactide were conducted with homogeneous alkoxide catalysts and silica-supported titanium alkoxide catalysts to compare their catalytic activity and the characteristics of the polylactide (PLA) produced. The conversion of L-lactide with the silica-supported alkoxide catalysts was higher than that with homogeneous catalysts even though the catalyst activity was low. In addition, the PLA produced using silica-supported alkoxide catalysts had a higher molecular weight and *T<sub>m</sub>* than those produced with the homogeneous catalyst.

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## 1. Introduction

Poly lactide (PLA) is biodegradable aliphatic polyester which is synthesized from lactic acid derived from renewable sources such as starch and molasses [1,2]. PLA has excellent mechanical properties comparable to conventional polymers such as PS and PE and has been used for medical devices and industrial packaging materials [3–5]. Over the last two decades, many types of metal alkoxide catalysts such as tin, aluminum, zinc, and magnesium alkoxides have been studied for the ring-opening polymerization of lactide to produce PLA [6–9]. Recently, titanium alkoxides have been investigated as potential catalysts for the ring-opening polymerization of lactide [10–12,15]. Homogeneous titanium alkoxide catalysts for lactide polymerization have been the focus to date. However, from a practical point of view, it would be desirable for these catalysts to be heterogeneous for better control of the polymerization process and easier separation of the catalysts from the polymer product [13,14]. In this work, silica-supported catalysts were prepared by reacting TiCl(O-*i*-Pr)<sub>3</sub> and Ti(O-*i*-Pr)<sub>4</sub> with pretreated silica. A series of solution polymerizations of L-lactide were performed with both the homogeneous and heterogeneous catalysts to compare the catalyst activities and polymer characteristics.

## 2. Experimental

### 2.1. Materials

L-Lactide (PURASORB L, PURAC) was recrystallized with toluene three times prior to use. Toluene was purified by distillation over sodium metal in a pure nitrogen atmosphere to remove residual traces of moisture and oxygen and was stored over a 4 Å molecular sieve. Silica (sylopol 948, Grace Davison) was used as a support to immobilize the catalysts. Titanium tetraisopropoxide (Ti(O-*i*-Pr)<sub>4</sub>, Sigma, 97%) and titanium chloride triisopropoxide (TiCl(O-*i*-Pr)<sub>3</sub>, Sigma, 95%) were used as received without further purification. All processes for monomer purification and catalyst preparation were performed under a dry nitrogen atmosphere.

### 2.2. Characterization

Inductively coupled plasma spectroscopy was used to determine the titanium content of the supported catalysts using ICP-AES (JY Horiva, JY Activa). Specific surface area measurements were performed using the BET method (Micromeritics, ASAP 2020) at 78 K using nitrogen as the adsorption gas. Before the measurement, the samples were outgassed at 423 K for 4 h to reach a final pressure of 10<sup>-4</sup> Torr. A scanning electron microscope (JEOL, JSM-6500F) was used to observe the morphologies of the supported catalysts and energy dispersive spectroscopy (EDS) was used to measure the titanium content on the surface of the supported catalysts. The number-average and weight-average molecular weights (*M<sub>n</sub>* and

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**Table 1**  
Characteristics of PLA produced with homogeneous titanium alkoxide catalysts.

Run <sup>a</sup>	Catalyst	Time (h)	Conversion (%)	Activity (g PLA/mol Ti–h)	T <sub>m</sub> (°C)
1	TiCl(O- <i>i</i> -Pr) <sub>3</sub>	2	54	3897	158.2
2		6	72	1729	162.0
3		12	72	860	161.5
4		24	73	439	163.1
5	Ti(O- <i>i</i> -Pr) <sub>4</sub>	2	34	2466	154.3
6		6	52	1237	156.1
7		12	66	792	154.3
8		24	70	418	154.8

<sup>a</sup> Polymerization conditions: L-lactide/Ti = 100, 20 ml toluene, temperature = 70 °C.

*M<sub>w</sub>*, respectively) and the polydispersity index (PDI, *M<sub>w</sub>*/*M<sub>n</sub>*) of the produced PLA were determined by gel permeation chromatography (Polymer Laboratory, PL-GPC 120) using CHCl<sub>3</sub> as a solvent. The melting temperature of the PLA was determined using differential scanning calorimetry (TA instrument, Q20) from the second heating cycle at a heating rate of 10 °C/min.

### 2.3. Preparation of the supported catalysts

A silica support was calcined at 400 °C under a 100 cc/min stream of N<sub>2</sub> for 10 h before reacting with catalysts to remove residual traces of moisture and hydroxyl groups on the silica surface. Four grams of calcined silica was suspended in 100 ml of dry toluene and the predetermined amount of titanium alkoxide was added. The mixture was stirred for 3 h at 50 °C and the resulting catalyst was filtered and washed three times with 100 ml of toluene. Finally, the slurry was dried for 12 h under vacuum and stored in a glove box.

### 2.4. L-Lactide polymerization

Solution polymerization of L-lactide was carried out using a flask equipped with a magnetic stirrer. Predetermined amounts of purified L-lactide, dried toluene, and homogeneous or supported catalyst were charged, in that order, into a flask under an argon atmosphere. The polymerization was carried out at 70 °C for 2, 6, 12, and 24 h. The reaction was terminated by addition of 5 ml of methanol and the polymer was precipitated in an excess amount of methanol. The obtained polymer was washed with methanol and dried at 50 °C under vacuum for 12 h.

## 3. Results and discussion

### 3.1. Solution polymerization of L-lactide with homogeneous catalysts

Solution polymerization of L-lactide was carried out at 70 °C with TiCl(O-*i*-Pr)<sub>3</sub> or Ti(O-*i*-Pr)<sub>4</sub> catalyst at a L-lactide/catalyst molar ratio of 100. A white and thin plat-shaped polymer was obtained after vacuum drying.

The results of lactide polymerization with homogeneous titanium alkoxide catalysts are summarized in Table 1. The conversion of both TiCl(O-*i*-Pr)<sub>3</sub> and Ti(O-*i*-Pr)<sub>4</sub> catalyst increased with increasing reaction time reaching saturation at around 70% after

6 h with TiCl(O-*i*-Pr)<sub>3</sub> catalyst and after 12 h with Ti(O-*i*-Pr)<sub>4</sub>. Both the homogeneous catalysts showed similar activity profiles, as the catalytic activity was high in the initial stage and then steadily decreased with time on stream. The maximum catalytic activity of TiCl(O-*i*-Pr)<sub>3</sub> was 3897 g PLA/(mol Ti–h), which was 1.5 times higher than that of Ti(O-*i*-Pr)<sub>4</sub>.

The molecular weights and molecular weight distributions of the PLAs were measured by GPC for the 12 h reaction time polymer samples. From the GPC results, the *M<sub>n</sub>* and *M<sub>w</sub>* of the PLA produced by TiCl(O-*i*-Pr)<sub>3</sub> catalyst were 9590 and 15,100 g/mol, respectively and the PDI was 1.41 (Run 3), while the *M<sub>n</sub>* and *M<sub>w</sub>* of the PLA produced by Ti(O-*i*-Pr)<sub>4</sub> catalyst were 9650 and 13,600 g/mol, respectively, and the PDI was 1.57 (Run 4). The *T<sub>m</sub>* of the polymer produced with TiCl(O-*i*-Pr)<sub>3</sub> was observed to be around 160 °C, which was 5 °C higher than that of the polymer produced with Ti(O-*i*-Pr)<sub>4</sub>. Based on the fact that the molecular weights were similar to each other, the difference of the *T<sub>m</sub>* between the two homogeneous catalysts was not related to the molecular weight.

### 3.2. Characteristics of silica-supported catalysts

Silica-supported catalysts were prepared by reacting TiCl(O-*i*-Pr)<sub>3</sub> or Ti(O-*i*-Pr)<sub>4</sub> with silica which was calcined at 400 °C for 10 h. Table 2 shows the Ti contents and BET surface areas of the silica-supported titanium catalysts. The silica support has a specific surface area of 260 m<sup>2</sup>/g, while the specific surface areas of TiCl(O-*i*-Pr)<sub>3</sub>/SiO<sub>2</sub> and Ti(O-*i*-Pr)<sub>4</sub>/SiO<sub>2</sub> were 246.1 and 229.6 m<sup>2</sup>/g, respectively. It was found that the specific surface areas of the catalysts were slightly decreased by immobilizing the titanium alkoxide on the silica surface.

ICP-AES was used to determine the titanium content of the catalyst. When we prepared the supported catalysts, we added an excess amount of catalyst equivalent to 5 wt.% titanium based on the support material. As shown in Table 2, the amount of titanium remaining in the catalyst was analyzed. It was found that 60–65% of the titanium was immobilized based on the total titanium added and as a result, the titanium contents of both catalysts were ca. 3 wt.%. In addition, EDS analysis was performed to examine the distribution of titanium on the silica surface. The total Ti/Si molar ratio of the TiCl(O-*i*-Pr)<sub>3</sub>/SiO<sub>2</sub> catalyst was 0.202 as determined by ICP, whereas the Ti/Si molar ratio of the TiCl(O-*i*-Pr)<sub>3</sub>/SiO<sub>2</sub> catalyst surface was 0.0302 as determined by EDS. Therefore, it is likely that most of the catalyst components existed in the silica pores.

The morphologies of silica, TiCl(O-*i*-Pr)<sub>3</sub>/SiO<sub>2</sub>, and Ti(O-*i*-Pr)<sub>4</sub>/SiO<sub>2</sub> are shown in Fig. 1. Although the smooth surface of silica

**Table 2**  
Ti contents and BET surface areas of the silica-supported catalysts.

Support/catalyst	Titanium alkoxide (g)	Silica (g)	Ti content (wt.%)	Specific surface area (m <sup>2</sup> /g)
Silica	–	–	–	263.4
TiCl(O- <i>i</i> -Pr) <sub>3</sub> /SiO <sub>2</sub>	1.0887	4	3.02	246.1
Ti(O- <i>i</i> -Pr) <sub>4</sub> /SiO <sub>2</sub>	1.7518	4	3.22	229.6

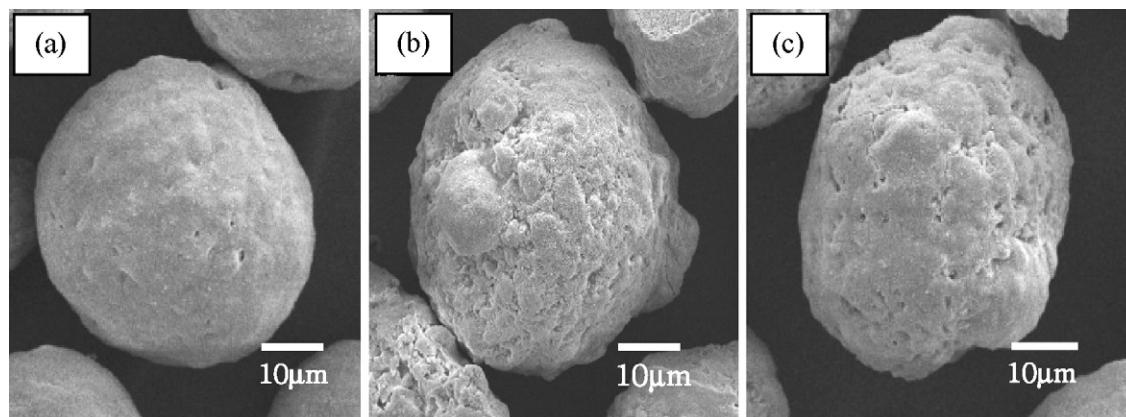


Fig. 1. SEM photographs of (a) calcinated silica, (b)  $\text{TiCl(O-}i\text{-Pr)}_3/\text{SiO}_2$ , and (c)  $\text{Ti(O-}i\text{-Pr)}_4/\text{SiO}_2$ .

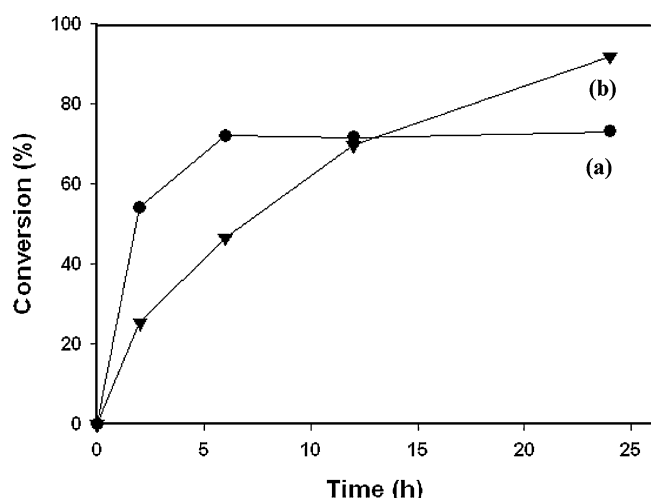


Fig. 2. L-lactide conversion as a function of reaction time for (a)  $\text{TiCl(O-}i\text{-Pr)}_3$  and (b)  $\text{TiCl(O-}i\text{-Pr)}_3/\text{SiO}_2$ : Polymerization conditions; L-lactide/Ti = 100, 20 ml toluene, temperature = 70 °C.

became rough after the supporting process, the morphologies of  $\text{TiCl(O-}i\text{-Pr)}_3/\text{SiO}_2$  and  $\text{Ti(O-}i\text{-Pr)}_4/\text{SiO}_2$  were comparatively regular and spherical. It is thought that the immobilization of titanium alkoxides did not affect the morphology of the support.

### 3.3. Characteristics of polymerization with homogeneous and supported catalysts

A plot of the conversion to PLA versus time in the solution polymerization of L-lactide with homogeneous  $\text{TiCl(O-}i\text{-Pr)}_3$  and  $\text{TiCl(O-}i\text{-Pr)}_3/\text{SiO}_2$  catalysts is shown in Fig. 2. The conversion with homogeneous  $\text{TiCl(O-}i\text{-Pr)}_3$  catalyst remained at around 70% after 6 h of reaction, while that with  $\text{TiCl(O-}i\text{-Pr)}_3/\text{SiO}_2$  increased gradually and the final yield was 30% higher than that with the homogeneous  $\text{TiCl(O-}i\text{-Pr)}_3$  catalyst. If the rate of the polymeriza-

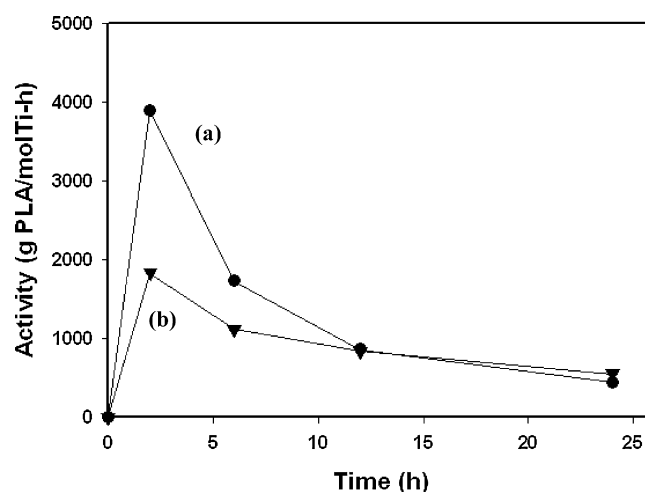


Fig. 3. Activity profiles of (a)  $\text{TiCl(O-}i\text{-Pr)}_3$  and (b)  $\text{TiCl(O-}i\text{-Pr)}_3/\text{SiO}_2$ : Polymerization conditions; L-lactide/Ti = 100, 20 ml toluene, temperature = 70 °C.

tion was fast in the beginning of the reaction, the monomer would have difficulty accessing the active center of the catalyst due to mass transfer limitations. The rate of polymerization with  $\text{TiCl(O-}i\text{-Pr)}_3/\text{SiO}_2$  was slower than that of the homogeneous catalyst but its final conversion was much higher than that with  $\text{TiCl(O-}i\text{-Pr)}_3$  catalyst. It is interesting to note that the catalyst activity of  $\text{TiCl(O-}i\text{-Pr)}_3$  was much higher than that of  $\text{TiCl(O-}i\text{-Pr)}_3/\text{SiO}_2$  at the beginning of the reaction, but it rapidly decreased with time on stream (Fig. 3). In contrast, the maximum catalytic activity of  $\text{TiCl(O-}i\text{-Pr)}_3/\text{SiO}_2$  was 1830 g PLA/(mol Ti-h), which was much lower than that of the  $\text{TiCl(O-}i\text{-Pr)}_3$  catalyst which decreased slowly with increasing time on stream.

Table 3 shows the characteristics of the produced PLA with both the homogeneous and heterogeneous titanium alkoxide catalysts. The molecular weight of PLA produced with  $\text{TiCl(O-}i\text{-Pr)}_3/\text{SiO}_2$  was 2.5 times higher than the PLA made with  $\text{TiCl(O-}i\text{-Pr)}_3$ . The

Table 3  
Characteristics of PLA produced with heterogeneous and heterogeneous titanium alkoxide catalysts.

Run <sup>a</sup>	Catalyst	Conversion (%)	$M_n$ (g/mol)	$M_w$ (g/mol)	PDI	$T_m$ (°C)
1	$\text{TiCl(O-}i\text{-Pr)}_3$	72	9,650	13,600	1.41	161.5
2	$\text{TiCl(O-}i\text{-Pr)}_3/\text{SiO}_2$	70	29,500	36,200	1.23	166.2
3	$\text{Ti(O-}i\text{-Pr)}_4$	66	9,590	15,100	1.57	154.3
4	$\text{Ti(O-}i\text{-Pr)}_4/\text{SiO}_2$	74	30,300	36,300	1.20	165.6

<sup>a</sup> Polymerization conditions: L-lactide/Ti = 100, 20 ml toluene, temperature = 70 °C, T = 12 h.

molecular weight of PLA produced with  $\text{TiCl}(\text{O-}i\text{-Pr})_3$  at 70 °C for 12 h was 13,600 g/mol, while that of the PLA made with  $\text{TiCl}(\text{O-}i\text{-Pr})_3/\text{SiO}_2$  under the same conditions was 36,200 g/mol. The molecular weights of the PLAs produced with  $\text{Ti}(\text{O-}i\text{-Pr})_4$  and  $\text{Ti}(\text{O-}i\text{-Pr})_4/\text{SiO}_2$  under the same conditions were 15,100 and 36,300 g/mol, respectively. It is thought that the higher L-lactide/Ti ratio is responsible for the higher molecular weights. The total amount of titanium of the catalyst was not used as only a partial amount of titanium on the silica surface was used for the polymerization in the case of the supported catalysts. The molecular weight increase of the polymers made using the supported catalyst is valuable from a commercial point of view. The molecular weight distributions of the produced PLA with both  $\text{TiCl}(\text{O-}i\text{-Pr})_3/\text{SiO}_2$  and  $\text{Ti}(\text{O-}i\text{-Pr})_4/\text{SiO}_2$  were narrower than those with the homogeneous catalyst (Runs 2 and 4). It is currently unclear why the transesterification reaction might be restrained, but it may be due to changes of the environment of the active sites during the immobilization.

Table 3 shows the melting temperatures of the PLAs produced with the homogeneous and heterogeneous titanium alkoxide catalysts. The  $T_m$  values of the polymers produced by the supported catalysts were around 165 °C, which are 5–10 °C higher than those produced by the homogeneous catalyst. It is thought that the higher molecular weight of the polymer produced by supported catalyst resulted in these differences in the melting temperatures.

#### 4. Conclusions

Silica-supported catalysts were prepared by reacting  $\text{TiCl}(\text{O-}i\text{-Pr})_3$  and  $\text{Ti}(\text{O-}i\text{-Pr})_4$  with pretreated silica. Lactide polymerization was conducted with silica-supported titanium alkoxide catalysts in a different catalyst system. It was observed that the immobilization of titanium alkoxides did not affect the morphology of the support. The morphologies of  $\text{TiCl}(\text{O-}i\text{-Pr})_3/\text{SiO}_2$  and  $\text{Ti}(\text{O-}i\text{-Pr})_4/\text{SiO}_2$  catalysts were comparatively regular and spherical. The activity of the supported catalysts was lower than that of the homogeneous

catalysts. However, the final conversion using the supported catalysts was higher than that of the homogeneous catalysts. The mass transfer limitation of the monomer may be responsible for the discrepancy between the catalytic activity and the conversion. Both  $\text{TiCl}(\text{O-}i\text{-Pr})_3/\text{SiO}_2$  and  $\text{Ti}(\text{O-}i\text{-Pr})_4/\text{SiO}_2$  catalysts produced similar PLA molecular weights and PDIs. The silica-supported titanium alkoxide catalysts produced superior molecular weight, melting point, and final conversion to PLA. The molecular weights of PLA produced with the silica-supported catalysts were 2.5 times higher than those produced with the homogeneous catalysts.

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