Characteristics of silica-supported tin(II) methoxide catalysts for ring-opening polymerization (ROP) of L-lactide

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ABSTRACT

Supported Sn(OMe)2 catalysts were prepared on pretreated silica with various tin contents. A series of bulk polymerizations of L-lactide were conducted with homogeneous methoxide catalyst and silica-supported tin alkoxide catalyst to compare with their characteristics of the polylactide (PLA) produced. The conversion of L-lactide with the silica-supported methoxide catalysts was higher than that with the homogeneous catalyst at each monomer/catalyst molar ratio. The highest catalytic activity and propagation constant (k2) was achieved at 180 °C. The spent catalyst was successfully recovered up to 85% by simple filtration of the polymer product. The heterogeneous catalyst system is advantageous for recycling the catalyst and the production of highly purified, metal-free grade PLA.

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1. Introduction

Plastics are a ubiquitous material and have been developed to have excellent performance for new applications. However, most plastics cause serious environmental pollution resulting in special attention to synthesize degradable plastics. Polylactide (PLA) is an aliphatic polyester that is produced from lactic acid derived from renewable resources such as sugar beets or corn [1–3]. Biodegradable PLA is expected to solve environmental pollution problems by forming a natural life cycle because it can be decomposed to carbon dioxide and water by the action of microorganisms in nature [4]. PLA can be synthesized by polycondensation of lactic acid or ring-opening polymerization of lactide, which is a dimer of lactic acid. Ring-opening polymerization of lactide is also a well-known method to produce PLA with high molecular weight [3,5], which has excellent mechanical properties comparable to conventional polymers such as polystyrene (PS) and polyethylene (PE). Homogeneous metal alkoxide catalysts, such as tin, aluminium, zinc and magnesium alkoxides, have been reported as the most common metal-containing species for ring-opening polymerization of lactide [6–10]. However, only a few papers report on the heterogeneous catalyst system, which is thought to be desirable in controlling the polymerization process and the easier separation of the catalyst from the polymer product [11–16].

In this work, the characteristics of heterogeneous tin(II) methoxide catalyst (Sn(OMe)2) using SiO2 as a support are reported. A series of bulk polymerizations of L-lactide were performed with both homogeneous and heterogeneous catalysts to compare the characteristics of the two catalyst systems.

2. Experimental

2.1. Material

L-lactide (PIRASORB, PURAC) and 1-dodecanol (Sigma–Aldrich) were used as received without further purification. Toluene (Sam- jeon Chemical Co., Ltd.) was purified by distillation over sodium metal in a nitrogen atmosphere. Purified toluene was stored over a dried molecular sieve (4A, Sigma–Aldrich). Tin methoxide (Sn(OMe)2) was used as received. All chemicals and catalysts were stored in the glove box.

2.2. Characterization

Tin content of the SiO2-supported Sn(OMe)2 catalysts was determined using inductively coupled plasma (ICP) spectroscopy (ACTIVA, JY HORIVA) after the microwave-assisted digestion of catalyst particles with hydrofluoric acid. Specific surface area
measurements were performed using a BET method (Micromeritics, ASAP 2020) at 78 K with nitrogen as the adsorption gas. Before the adsorption measurement, the samples were degassed at 423 K for 3 h to reach a final pressure of $10^{-4}$ Torr. The number average molecular weight ($M_n$), weight average molecular weight ($M_w$), and polydispersity index (PDI, defined as $M_w/M_n$) of the produced PLA were determined by gel permeation chromatography (GPC, Polymer Laboratory, PL-GPC-120) using CHCl$_3$ as a solvent. The melting temperature of the produced PLA was determined using differential scanning calorimetry (DSC, TA instrument, Q20) from the second heating thermogram at a heating rate of 10 °C/min. A scanning electron microscope (SEM, Carl Zeiss, Supra 40) was used to observe the morphology of the supported catalysts and energy dispersive spectroscopy (EDS) was used to measure the tin content on the surface of the supported catalysts. The thermal analysis of the recovered catalyst was performed by a thermogravimetric analyzer (TGA, TA instrument, Q50).

2.3. Preparation of the supported catalysts

A silica support was calcined at 600 °C under 100 cc/min of nitrogen gas for 10 h before reacting with catalysts. Calcined silica (1.7 g) and the predetermined amount of catalyst were suspended in 100 mL of purified toluene. The mixture was stirred for 3 h at 120 °C. The resulting catalyst was washed four times with 100 mL of toluene, dried under vacuum for 4 h, and stored in a glove box.

2.4. Bulk polymerization of l-lactide

The bulk polymerizations of l-lactide were conducted at different reaction temperatures with time on stream. L-lactide (2 g), the predetermined amount of homogeneous (denoted as HCAT) or heterogeneous (denoted as SCAT-x, x is wt.% of Sn supported on SiO$_2$) catalysts, and 0.0026 g of 1-dodecanol (0.1 mol/L based on monomer) as an initiator were introduced into a 20 mL glass reactor equipped with a magnetic stirrer. After polymerization, the reactor was quenched with ice water and 5 mL of methanol was added to terminate the reaction. Methylene chloride (CH$_2$Cl$_2$: 5 mL) was added to dissolve the polymer and the resulting mixture was separated by precipitating in an excess amount of methanol. When needed, the catalyst was separated by filtration from the polymer mixture using a membrane filter with a 1 μm pore size before the precipitation step. Finally, the polymer and/or filtered catalyst were washed with an excess of methanol and dried at 50 °C under vacuum for 12 h.

3. Results and discussion

3.1. Characteristics of SiO$_2$-supported Sn(OMe)$_2$ catalysts

SiO$_2$ is typically calcined at high temperature to remove water and regulate the concentration of hydroxyl groups on the surface. The surface properties of SiO$_2$, such as the pore volume, mechanical strength, and density of silanol groups, also change with the calcination temperature and time [17]. The SiO$_2$ support was calcined at 600 °C for 10 h at which the condensation of germinals and vicinals occurred to form stable and isolated silanol groups [18–20].

The supported catalysts were prepared by reacting Sn(OMe)$_2$ with SiO$_2$ in toluene medium. Table 1 shows Sn contents and the BET surface areas of the silica-supported tin catalysts. The pristine SiO$_2$ support has a specific surface area of 286 m$^2$/g, while the specific surface areas of SCAT-x were 261–237 m$^2$/g. The specific surface areas of SCAT-x decreased with an increasing amount of Sn(OMe)$_2$ in the catalyst. The efficiency of immobilization, which is defined as the ratio of Sn supported and Sn reacted, was observed as 0.54–0.64. The Sn/Si molar ratio of SCAT-2.14 on the surface was 0.0268 and that of the entire catalyst particle was 0.0112, which indicates that a major portion of Sn(OMe)$_2$ was distributed on the surface of the SiO$_2$ particle.

<table>
<thead>
<tr>
<th>Support/catalyst</th>
<th>Tin methoxide (g)</th>
<th>Silica (g)</th>
<th>Sn content (wt.%</th>
<th>Immobilization efficiency (%)</th>
<th>Specific surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>6.08</td>
</tr>
<tr>
<td>SCAT-x</td>
<td>0.1036</td>
<td>1.7</td>
<td>2.14</td>
<td>53.5</td>
<td>267.9</td>
</tr>
<tr>
<td></td>
<td>0.1553</td>
<td>1.7</td>
<td>3.57</td>
<td>59.6</td>
<td>261.3</td>
</tr>
<tr>
<td></td>
<td>0.2071</td>
<td>1.7</td>
<td>5.09</td>
<td>61.7</td>
<td>254.9</td>
</tr>
</tbody>
</table>

3.2. Characteristics of ROP of l-lactide over HCAT and SCAT-x

Ring-opening polymerizations of l-lactide in the bulk phase were performed at 180 °C over HCAT or SCAT-x at l-lactide/catalyst molar ratios of 20,000, 40,000, and 60,000. The conversion profiles of l-lactide to time are shown in Fig. 1. When the molar ratio of the monomer/catalyst was 20,000, the l-lactide conversion rapidly increased in the beginning of the reaction and then the conversion was saturated at approximately 93% in 2 h. The reaction time to reach the saturation level of conversion was prolonged to 4 h with SCAT, while the saturation level was not observed at the molar ratio of 40,000 with HCAT. The saturation of the conversion was hardly observed at a molar ratio of 60,000 with both SCAT and HCAT. SCAT showed a higher activity at all monomer/catalyst ratios, regardless of the supported amount of Sn(OMe)$_2$. The higher catalytic activity over SCAT contributes to better dispersion of the catalyst component to reduce the mass transfer limitation of the monomer [21].

3.3. Effect of polymerization temperature

Series of bulk polymerizations of l-lactide were performed at various temperatures and a l-lactide/catalyst molar ratio of 40,000 to observe characteristics of the catalyst. As shown in Table 2, the polymerization with HCAT and SCAT showed similar reaction behaviors with respect to the reaction temperature. The catalytic conversion of those catalysts substantially increased with increasing reaction temperature. The conversion at 150 °C was significantly less than that at 180 and 200 °C. As shown in Table 2, the final conversion at 200 °C was less than that of the conversion at 180 °C. The higher polymerization rate at the beginning of the reaction was unfavorable for the higher conversion.

The apparent propagation rate constant ($k_p$) was calculated to compare the polymerization characteristics over supported catalysts [22]. If the polymerization rate ($\text{mol} \cdot L^{-1} \cdot h^{-1}$) is the first order reaction for the monomer and catalyst concentration, the polymerization rate will be represented by the following equation:

$$
R_p = -\frac{d[M]}{dt} = k_p[M]^n
$$
\[
\frac{\ln (1-x)}{[C]} = k_p t
\]

where \([M]_0\) is the monomer concentration and \([C^*]\) is the active catalyst concentration. Alternatively, if the catalyst deactivation effect is assumed to be negligible at the beginning of the reaction, the equation can be integrated to

- Fig. 1. L-lactide conversion as a function of reaction time at a monomer/catalyst molar ratio of (a) 20,000, (b) 40,000, and (c) 60,000. Polymerization conditions: temp = 180 °C, 0.1 mol% initiator base on the monomer.

- Table 2

<table>
<thead>
<tr>
<th>Tin content of the catalyst (wt%)</th>
<th>Temperature (°C)</th>
<th>Conversion at the saturated point (%)</th>
<th>(k_p) (L/mol h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCAT</td>
<td>150</td>
<td>17.6</td>
<td>272.8</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>92.3</td>
<td>2940.0</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>91.3</td>
<td>3717.8</td>
</tr>
<tr>
<td>SCAT-2.14</td>
<td>150</td>
<td>65.6</td>
<td>1076.1</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>92.9</td>
<td>2999.6</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>90.3</td>
<td>3052.9</td>
</tr>
<tr>
<td>SCAT-3.57</td>
<td>150</td>
<td>58.1</td>
<td>728.5</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>92.9</td>
<td>3002.2</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>90.8</td>
<td>3149.8</td>
</tr>
<tr>
<td>SCAT-5.09</td>
<td>150</td>
<td>48.4</td>
<td>641.7</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>94.3</td>
<td>3377.0</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>87.1</td>
<td>2760.2</td>
</tr>
</tbody>
</table>

where the calculated \(k_p\) values using an Arrhenius plot. Table 2 shows the calculated \(k_p\) based on the results of polymerization of lactide with tin methoxide catalysts. The propagation rate constants of reactions with catalysts significantly increased with increasing reaction temperature. Note that the apparent propagation rate constants were calculated based on the initial rate of the reaction. The conversions of lactide were similar when the temperature was 180 °C and \(k_p\) values of SCAT-x were slightly greater than those of the HCAT.

- 3.4. Characteristics of the obtained polymer

A white and thin plate-shaped polymer was obtained after vacuum drying at the initial time of polymerization, while a white and agglomerated polymer was obtained at the final time of polymerization. Table 3 shows the characteristics of the PLA produced from both the HCAT and SCAT. The molecular weight of PLA was approximately 20,000–56,000 g/mol for 1 h polymerization at 180 °C and 31,000–95,000 g/mol for 5 h at the same condition. The molecular weights after 5 h of polymerization were approximately 2 times greater than those of molecular weights of 1 h, and the polydispersity indexes (PDI) also increased with polymerization time.

When the homogeneous catalysts are supported to form heterogeneous catalysts, the stability of active sites may be affected, resulting in changes of the molecular weights. The PDI of the polymer tends to increase in many cases, because the active sites may be in different electronic environments during immobilization [23–25], which leads to the formation of multi-active sites with different chain transfer rates. However, if the molecular weights and PDIs of HCAT and SCAT are compared, the PDIs were nearly unchanged, while the molecular weights of PLA produced by SCAT decreased. The immobilization of Sn(OME)\(_2\) over SiO\(_2\) may not affect the chemical nature of the active sites (Sn) or it is physically adsorbed on the SiO\(_2\) surface. The decrease of the molecular weights over the SCATs was unexpected and may be attributed to the characteristics of the lactide polymerizations. The acidic nature of SiO\(_2\) may accelerate the chain transfer rate, resulting in a decrease of the molecular weight of PLA [26].

- 3.5. Separation of the catalyst from the polymer product

An advantage of the heterogeneous catalytic process is that a solid catalyst can be recovered from the polymer product, which facilitates the production of highly pure PLA and recycling of the catalysts [27–31]. In this work, we successfully separated the spent catalyst by simple filtration of the product mixture after polymerization. Approximately 70% of the initial catalyst amount was recovered from the polymer product. Fig. 2(a) and (b) shows the
Table 3
Characteristics of PLA produced with homogeneous and supported catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction time (h)</th>
<th>Conversion (%)</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>PDI</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCAT</td>
<td>1</td>
<td>38.25</td>
<td>26,500</td>
<td>40,000</td>
<td>1.51</td>
<td>172.3</td>
</tr>
<tr>
<td>SCAT-2.14</td>
<td></td>
<td>49.40</td>
<td>19,100</td>
<td>31,600</td>
<td>1.66</td>
<td>170.8</td>
</tr>
<tr>
<td>SCAT-3.57</td>
<td></td>
<td>43.35</td>
<td>44,000</td>
<td>56,100</td>
<td>1.28</td>
<td>174.4</td>
</tr>
<tr>
<td>SCAT-5.09</td>
<td></td>
<td>58.25</td>
<td>20,000</td>
<td>34,500</td>
<td>1.72</td>
<td>171.1</td>
</tr>
<tr>
<td>HCAT</td>
<td>5</td>
<td>92.25</td>
<td>49,200</td>
<td>95,500</td>
<td>1.94</td>
<td>176.7</td>
</tr>
<tr>
<td>SCAT-2.14</td>
<td></td>
<td>92.85</td>
<td>32,000</td>
<td>59,200</td>
<td>1.85</td>
<td>173.1</td>
</tr>
<tr>
<td>SCAT-3.57</td>
<td></td>
<td>92.90</td>
<td>31,400</td>
<td>60,100</td>
<td>1.91</td>
<td>173.9</td>
</tr>
<tr>
<td>SCAT-5.09</td>
<td></td>
<td>94.30</td>
<td>34,800</td>
<td>68,300</td>
<td>1.96</td>
<td>174.4</td>
</tr>
</tbody>
</table>

* Polymerization conditions: 1-lactide/catalyst = 40,000, temperature = 180 °C

Fig. 2. SEM images of the (a) fresh catalyst and (b) separated catalyst after the polymerization. EDS mapping images of catalyst: (c) one particle of (a) and (d) one particle of (b).

morphology of the fresh and recovered catalyst, respectively. The surface of the recovered catalyst was coated by PLA, but the particle morphology was unchanged during the polymerization. To confirm that the separated particles originated from the supported catalyst, EDS analyses were performed to compare the surface Sn content of the fresh catalyst and the separated particles. The Sn content of the fresh catalyst (SCAT-2.14) was measured as 6.07 wt.% and the recovered catalyst was 5.11 wt.%. The EDS analysis clearly confirmed that the separated particles were the same catalyst. Note that the Sn content from the EDS analysis resulted from the particle surface.

The amount of polymer coated on the surface of the catalyst was analyzed by thermogravimetry (TG). As shown in Fig. 3, approximately 4% weight loss was observed in the TG thermogram. The residual mass can be considered to be that of the catalyst because the PLA decomposes under 400 °C [32]. The catalyst was also separated after the polymerization with various solvents. From the results of TG, the recovery efficiencies were in the range of 74 to 85%.

Table 4
Separation of catalyst from the polymer product with different solvents.

<table>
<thead>
<tr>
<th>Run</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chloroform</td>
<td>74.4</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>75.1</td>
</tr>
<tr>
<td>3</td>
<td>Tetrahydrofuran</td>
<td>72.8</td>
</tr>
<tr>
<td>4</td>
<td>Dichloromethane</td>
<td>78.5</td>
</tr>
<tr>
<td>5</td>
<td>Acetonitrile</td>
<td>85.0</td>
</tr>
<tr>
<td>6</td>
<td>1,4-Dioxane</td>
<td>80.6</td>
</tr>
</tbody>
</table>

* Polymerization conditions: SCAT-2.14 catalyst = 0.02 g, monomer = 2 g, polymerization temp. = 180 °C, reaction time = 2 h.

* Calculated from TG analysis.

Fig. 3. TGA and DTA thermograms of the separated catalyst.
85% for each solvent as shown in Table 4. These results show that the supported catalysts can be used economically by recycling and can improve the purity of the produced PLA.

4. Conclusions

Silica-supported catalysts were prepared by reacting Sn(OMe)\textsubscript{2} with various amounts of tin over pretreated silica. Bulk polymerization of l-lactide was performed with homogeneous and silica-supported tin methoxide catalysts in a different monomer/catalyst molar ratio. The supported catalysts showed greater conversion than that of the homogeneous catalyst at each monomer/catalyst molar ratio. The polymerization with Sn(OMe)\textsubscript{2} and Sn(OMe)\textsubscript{2}/SiO\textsubscript{2} catalysts showed similar reaction behaviors with respect to the reaction temperature. The catalytic conversion and \( k_0 \) of those catalysts increased with increasing reaction temperature, but the greatest conversion was achieved at 180 °C. The PDIs of PLA were nearly unchanged, while the molecular weights of PLA produced by SCAT decreased. The immobilization of Sn(OMe)\textsubscript{2} over SiO\textsubscript{2} did not affect the chemical nature of the active sites. The spent catalyst was successfully recovered up to 85% by simple filtration of the product mixture after polymerization. Recycling of the catalyst or highly purified, metal-free grade of PLA can be processed with the heterogeneous catalyst system.

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References