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Research Note

Elucidating the role of silica surfaces in the ring-opening polymerization of lactide: catalytic behavior of silica-immobilized zinc β-diiminate complexes

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Abstract

New zinc β-diiminate complexes are covalently immobilized on silica supports of different pore sizes and structures and the resulting catalysts are evaluated in the catalytic polymerization of lactide. The homogeneous complexes effectively polymerize lactide to produce high molecular weight polylactic acid (PLA) with a narrow polydispersity. The immobilized catalysts also readily convert lactide; however, only oligomeric products with moderate molecular weights are produced when the complexes are immobilized on porous silica. Control experiments indicate that surface silanols may play an important role in modulating the molecular weight of the PLA, with the surface hydroxyl groups acting as chain-transfer agents. High molecular weight, relatively monodisperse polymer can be obtained using a nonporous supported catalyst.

Keywords: Chain transfer; Polymerization; Porous silica; Zn-BDI; Ring-opening; Lactide

1. Introduction

Polylactic acid (PLA) has for many years been an important biopolymer due to its biocompatibility and biodegradability; however, increasingly it is being considered for more traditional engineering applications. This is a product both of PLA's useful material properties and of the fact that it can be made from renewable resources. Lactide, the cyclic dimer of lactic acid, can be derived from sugars and starches. For instance, Dow-Cargill produces PLA commercially from lactide prepared from corn-derived dextrose [1].

Dow-Cargill's commercial process is a continuous system that utilizes Sn(II) octoate as catalysts in a solution phase or a melt [1]. For biological applications, it is important that the produced polymer be free of residual catalyst, as trace amounts of potentially toxic metal species can be problematic [2–4]. For this reason, substantial research has focused on developing polymerization catalysts that use relatively nontoxic metals such as Fe [2] and Zr [4] (although Sn(II) may be substantially less problematic than Sn(IV)). Another approach to catalyst removal is to develop a technology that ensures that catalyst residue is never deposited in the polymer. This could potentially be achieved using recoverable solid catalysts.

The immobilization of homogeneous catalysts to facilitate easy product separation, catalyst recovery, and recycle constitutes a well-established research area in small molecule catalysis. In contrast, it is significantly less common in polymerization catalysis.[1] There are only a few reports of ring-opening polymerization of lactones and lactides using solid catalysts. Hamaide and co-workers developed silica-based catalysts that utilize grafted aluminum, transition metal, or rare earth alkoxide species as active centers for the ROP of oxygenated heterocycles such as ε-caprolactone [5, 6] and 2,2-dimethyltrimethylene carbonate [7]. Aida, Tatsumi, and co-workers used a similar approach utilizing Al-MCM-41 as a solid catalyst for polymerization of ε-caprolactone and δ-valerolactone [8]. Kadokawa et al. reported the use of Sn-exchanged clays as solid catalysts for lactone polymerization [9]. Finally, Pinnavaia and co-

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[1] Homogeneous catalysts such as metallocenes are routinely immobilized for α-olefin polymerizations but the catalysts are not recovered.

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workers prepared Sn-substituted HMS silicas that effectively polymerized lactide [10]. Here we report the first use of an immobilized metal complex catalyst for the polymerization of lactide. An immobilizable analogue of Coates' Zn–β-diiminate (BDI) catalyst has been prepared and tethered to a variety of different silica supports. The unique new catalysts are evaluated in the catalytic polymerization of lactide and the roles of the silicate surface and porosity are elucidated.

2. Experimental

2.1. Synthesis

Mesoporous SBA-15 was synthesized by literature methods [11], while controlled pore glass (CPG) with an average pore diameter of 246 Å was purchased from CPG, Inc. (NJ). Procedures to functionalize SBA-15 and G–246 with (3-mercaptopropyl)trimethoxysilane (MPTS), capping excess silanols with hexamethyldisilazane (HMDS), and synthesis of complexes **1** and **2** as well as catalyst preparation through methods 1 and 2 (Scheme 1) were previously described in our recent publication [12]. All manipulations during catalyst synthesis and polymerization were carried out in dry nitrogen/argon atmosphere in a dry box or using standard Schlenk techniques.

2.1.1. Method 1

Complex **1** (100 mg, 0.129 mmol) was added into a toluene suspension (30 ml) of dry SBA-15 (400 mg) or CPG-246 (600 mg) and was stirred for 20 h at room temperature. The solid catalyst was collected by filtration and washed with anhydrous toluene and dry hexanes in a dry box and then dried under high vacuum.

2.1.2. Method 2

Complex **2** (120 mg, 0.207 mmol), AIBN (20 mg) and thiol-functionalized SBA-15 (500 mg) or CPG-246 (700 mg), was mixed in chloroform (30 ml). The mixture was refluxed overnight. After cooling to room temperature, the product was recovered by filtration and washed with hexanes and toluene in a dry box followed by drying under high vacuum.

2.2. Characterization

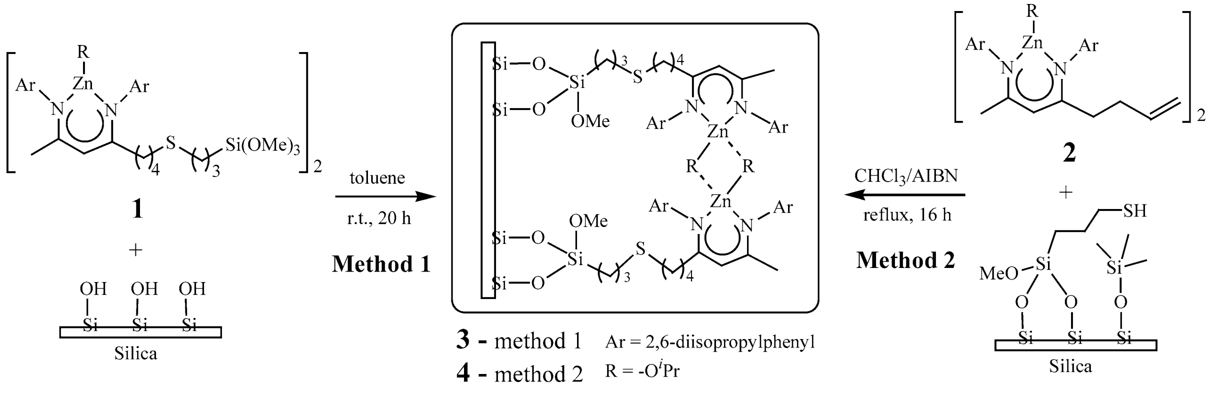
The pore size and BET surface areas of SBA-15 were calculated from data gathered from N_2 physisorption experiments at 77 K using a Micromeritics ASAP 2010 system. TGA/DSC and elemental analyses were used to determine the loadings of thiol functionalized SBA-15 and CPG, as well as the organic loadings of catalysts **3** and **4** made through methods 1 and 2 (Scheme 1). Immobilization of the complexes via covalent attachment on silica supports was monitored using FT-Raman spectroscopy. Number-average molecular weight as well as the molecular weight distribution of PLA was determined by gel-permeation chromatographic analysis and referenced against polystyrene standards.

2.3. Catalysis

In a typical polymerization, catalyst **3** or **4** (∼150 mg) and L-lactide (200 mg) were mixed in 4 ml of dichloromethane (DCM) or toluene in a flask equipped with a condenser. The reaction was allowed to stir at the desired temperature for the necessary reaction time (Table 1) under dry argon. After reaction, a small sample of the crude mixture was withdrawn to determine the conversion by ^{1}H NMR. Approximately 1 ml of methanol was then added to quench the polymerization and the mixture was filtered and washed with DCM to remove the silica catalyst from the soluble polymer. The filtrate was concentrated and PLA was collected through precipitation from the addition of methanol.

3. Results and discussion

β-Diiminate zinc alkoxide complexes described originally by Coates and co-workers [13,14] and subsequently by others [15] were chosen as useful metal complex catalysts for immobilization due their ability to catalyze the living polymerization of lactide to produce polylactic acid with narrow molecular weight distributions. Furthermore, these catalysts are also capable of promoting the polymerization of



Scheme 1.

Table 1
Silica supported catalysts **3** and **4** for lactide polymerization

Entry[a]	Catalyst/support	Capping[b]	Loading[c]	Solvent[d]	[Monomer]/[catalyst]	Time (h)	Conversion/%[e]	M_n^{EX}	M_n^{TH}	M_w/M_n
1	**3**, SBA-15	no	0.16	Toluene	58	24	65	1285	5430	1.12
2	**3**, SBA-15	no	0.16	DCM	58	24	59	2375	4930	1.09
3	**3**, SBA-15	yes	0.16	Toluene	58	18	52	4330[f]	4345	1.49
4	**3**, SBA-15	yes	0.16	DCM	58	18	48	4725[f]	4010	1.38
5	**3**, CPG	no	0.09	Toluene	103	24	76	1395	11,270	1.09
6	**3**, CPG	no	0.09	DCM	103	24	68	2595	10,085	1.12
7	**3**, CPG	yes	0.09	Toluene	103	17	58	5015[f]	8600	1.44
8	**3**, CPG	yes	0.09	DCM	103	17	51	4860[f]	7565	1.28
9	**4**, SBA-15	yes	0.17	Toluene	58	20	46	2105	3840	1.51
10	**4**, SBA-15	yes	0.17	DCM	58	20	41	1745	3425	1.47
11	**4**, CPG	yes	0.07	Toluene	132	21	61	3245	11,595	1.42
12	**4**, CPG	yes	0.07	DCM	132	21	53	3480	10,075	1.35
13	**1**	n.a.	n.a.	DCM	180	0.5	94	27,550	24,365	1.18
14	**2**	n.a.	n.a.	DCM	100	0.5	96	15,630	13,825	1.09

[a] Homogeneous complexes **1** and **2**, reactions were carried out at 25 °C.
[b] Capping means no surface-silanol remaining.
[c] Loading unit is of mmol/g support, determined by TGA and verified with elemental analysis.
[d] Reactions were performed in toluene at 80 °C or DCM at 45 °C.
[e] Calculated by integration of methine resonances in ^{1}H NMR of the polymer, estimated error is ±0.5%.
[f] Bimodal distribution.

epoxides with CO_2 to prepare polycarbonates, making them very versatile catalytic centers [12,16–19].

Recently, we have prepared immobilized BDI-Zn catalysts in the Zn-amide and Zn-methoxy forms immobilized on silica and demonstrated that the supported catalysts exhibit good reactivity in the copolymerization of cyclohexene oxide and carbon dioxide [12]. Here the synthetic methodology has been modified to incorporate Zn-isopropoxy species that are effective for lactide polymerization in place of the amide and methoxy species noted above. Reaction of zinc amide, $Zn[N(SiMe_3)_2]_2$, with terminal olefin-modified 2,6-diisopropylphenyl-substituted β-diimine ligand, produces the zinc amide complex in quantitative yield. The sterically bulky amido group of this complex was transformed into an isopropoxide group (complex **2**), as this is a more suitable initiating group for lactide polymerization. Complex **1** was synthesized similarly from a MPTS-modified ligand. Both complexes **1** and **2** were highly active for the polymerization of L-lactide in homogeneous media (Table 1). In 30 min at 25 °C, **2** polymerized L-lactide to 96% conversion ($[\mathbf{2}] = 2.0 \times 10^{-3}$ M, $[\mathrm{LA}]/[\mathbf{2}] = 100$), and GPC revealed an M_n of 15,630 and a polydispersity index (PDI) of 1.09. **1** also polymerized L-lactide to 94% conversion ($[\mathbf{1}] = 2.0 \times 10^{-3}$ M, $[\mathrm{LA}]/[\mathbf{1}] = 180$), with an $M_n = 27{,}550$ and $\mathrm{PDI} = 1.18$. The narrow polydispersity and the good correlation of the experimentally determined M_n with the theoretical value show that **1** and **2** have good control over the polymerization, illustrating that the modified homogeneous catalysts behaved similarly to the original Coates Zn-BDI catalyst [14].

Silica-immobilized catalysts have been made using two synthetic routes. Method 1 (catalyst **3**) was based on a direct reaction of the $-Si(OMe)_3$ group of **1** with surface silanols to form a Si–O–Si bond with the concomitant release of methanol. In contrast, method 2 (catalyst **4**) involves a coupling reaction between the double bond and a surface-immobilized thiol group.

Two different silica materials with different pore sizes and pore connectivities were used as hosts for the zinc catalysts, SBA-15 and CPG–246. SBA-15 is a well-defined, hexagonal mesoporous silica material with straight mesopores that are connected through small, random micropores. The SBA-15 used in this study has an average mesopore size of 105 Å and a surface area of 830 m^2/g. Hexagonal mesoporous silicas of this type are useful model supports because they have well-defined, tailorable mesopore systems with low polydispersity. However, for industrial application and maximizing reaction rates, these supports are not optimal due to the one-dimensional nature of the pores.

For this reason, a different silica material with larger, interconnected pores was also studied. This second silica material that was employed is controlled pore glass (CPG), a lower surface area (~ 80 m^2/g) mesoporous solid with an average pore size of 246 Å and a narrow pore size distribution. This material has pores that are interconnected randomly. The total silanol content for SBA-15 determined by TGA is approximately 4.0 mmol/g silica, whereas for CPG, it is only about 1.0 mmol/g silica.

To verify that the complexes were covalently immobilized onto the silica support, the silica materials were analyzed using FT-Raman spectroscopy before and after complex addition. For instance, the immobilization of complex **2** on silica (method 2) was followed by FT-Raman spectroscopy (Fig. 1). The spectrum for thiol-functionalized SBA-15 shows a peak 2575 cm^{-1}, characteristic of the S–H stretching (Fig. 1A). The FT-Raman spectrum of the pure complex **2** showed a peak at 1641 cm^{-1} for the C=C stretching (Fig. 1B). The disappearance of the –SH and C=C

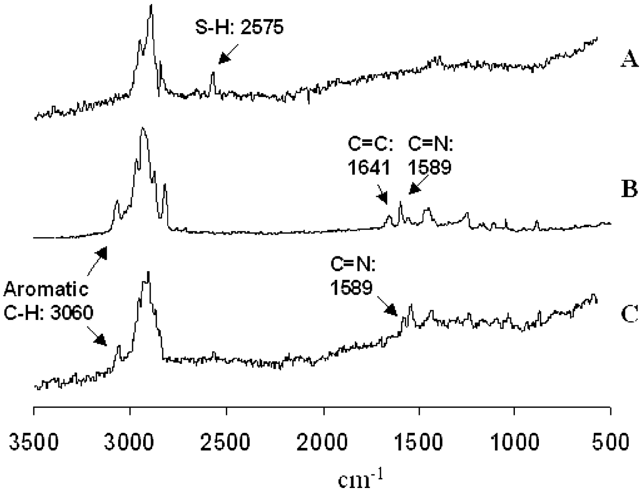


Fig. 1. FT-Raman spectra of (A) SBA-15-SH-capped; (B) complex **2**; and (C) solid catalyst after immobilization of **2** on SBA-15-SH-capped. Raman samples were prepared in a dry box with ~ 20 mg of the solid sample placed into a J. Young Raman tube for analysis under dry N_2.

stretching signals after the coupling reaction as shown in Fig. 1C and the addition of an aromatic C–H-stretching band at 3060 cm^{-1} indicate that the β-diiminate ligand was immobilized on the silica surface.

Silica-immobilized catalyst **3** prepared on both SBA-15 and CPG was investigated for the polymerization of L-lactide. Polymerizations were performed in both toluene and dichloromethane and the results are summarized in Table 1. Unlike the epoxide/CO_2 copolymerization previously reported [12], in which the polycarbonates generated from the homogeneous and the immobilized zinc BDI catalysts have similar molecular weights around 20,000, PLAs produced homogeneously and heterogeneously differ distinctly. In the lactide case, at 80 °C in toluene after 24 h, SBA-15-immobilized catalyst **3** (Table 1, entry 1) polymerized L-lactide to 65% conversion to yield a polymer with narrow PDI (1.12) but with an M_n of only 1285. Similarly, CPG-immobilized **3** yielded a PLA with $M_n = 1395$ and PDI = 1.09 (Table 1, entry 5). This is in sharp contrast to the molecular weight of 27,550 for PLA generated from the homogeneous complex **1**. The same trend is observed when complex **2** is immobilized on silica supports using method 2. Homogeneous catalyst **2** generated PLA with M_n =15,630, while both SBA-15 and CPG-immobilized **4** yielded PLAs with significantly lower molecular weights ($M_n = 2105$, Table 1, entry 9, and 3245, Table 1, entry 11, respectively). Although the supported catalysts were studied under conditions that should result in slightly lower molecular weights than the homogeneous systems due to the lower [LA]/Zn ratio, the observed molecular weights with the solid catalysts are lower than would be theoretically expected. As noted in Table 1, homogeneous catalysts give slightly higher molecular weights than would be expected, whereas heterogeneous systems give substantially lower molecular weights. This is opposite to the trend seen in epoxide/CO_2 copolymerization [12].

We have previously reported that in the case of epoxide/CO_2 copolymerization [12], the polymer filling of the catalyst pores and starvation of the active sites for CO_2 limit the kinetics of the immobilized catalyst system, leading to lower catalytic productivities and copolymer content (more polyether linkages). In the lactide case, we hypothesized that the silica support may play another important role, that of a chain-transfer agent. It was hypothesized that the flexible and hydrophilic PLA chains may interact with the surface Si–OH groups and cause a significant amount of transesterification resulting in chain transfer producing PLAs with significantly lower molecular weights than their homogeneous analogs. In contrast, in the case of cyclohexene oxide (CHO) and CO_2 copolymerization [12], the steric constraints from the bulky cyclohexene group may prevent the interaction of growing polymer chains with the surface silanols. To probe this, the remaining, accessible surface silanols (Si–OHs) of catalyst **3** were capped with –$SiMe_3$ groups, using a known reaction with excess hexamethyldisilazane. Based on TGA analysis, ~ 0.15 and ~ 0.06 mmol of silanols were consumed in this reaction over the SBA-15 and CPG supported catalyst. The resulting catalyst **3** with a drastically reduced surface silanol content (capped) on both SBA-15 and CPG polymerized the L-lactide in otherwise identical conditions to yield PLAs with markedly higher molecular weights $M_n = 4330$ (Table 1, entry 3) and 5015 (Table 1, entry 7) using toluene as the solvent, presumably due to the decrease of interactions between the propagating chain with the surface silanols. However, it is noteworthy that a bimodal molecular weight distribution is observed for the PLAs produced by both systems, with a lower number-average molecular weight portion at 240 and 500, respectively (lower molecular weight portion accounted for ~ 15% of the total polymer). This bimodal molecular weight distribution may be indicative of multiple types of active species that result from side reactions with HMDS. Interestingly, bimodal molecular weight distributions were never observed over the related catalysts for polycarbonate production [12]. In both cases, the formation of multiple types of sites as a result of catalyst decomposition during the immobilization manipulations cannot be ruled out, as the zinc metal centers cannot be easily probed directly by spectroscopic investigations. Since catalyst **4** was surface-silanol free already (capping was performed after the thiol functionalization of the silica support), higher molecular weight PLAs were obtained for both SBA-15 and CPG supported **4** (Table 1, entries 9 and 11) than entries 1 and 5 under the same conditions, which is consistent with the assumption that the weakly acidic surface Si–OH groups cause early chain termination via chain transfer.

The catalytic activity of supported catalysts **3** and **4** was also investigated using dichloromethane as the polymerization solvent. Recently, on a nonporous silica supported BDI-Zn system [20], dramatic improvements in the polydispersity of the resulting PLA (PDI narrowing from 2.01 to 1.05) were observed when ROP of lactide was performed in DCM instead of toluene. As shown in Table 1, PLAs generated in DCM generally have narrower polydispersities and higher number-average molecular weights than polymers obtained from toluene. For example, in otherwise identical conditions, catalyst **3** immobilized on SBA-15 generated a PLA with an M_n of 2375 in DCM (45 °C), and an M_n of 1285 in toluene (80 °C) (Table 1, entries 1 and 2, respectively). Higher M_n was also observed in CPG supported **3**, with $M_n = 2595$ in DCM and 1395 in toluene (Table 1, entries 5 and 6). As expected, the surface-silanol-free catalysts also performed better in DCM than in toluene; PLA with a narrower PDI ($M_n = 4725$, PDI $= 1.38$, Table 1, entry 4) was generated in DCM compared to the PLA obtained in toluene ($M_n = 4330$, PDI $= 1.49$, Table 1, entry 3). Again, with the catalysts that were capped after immobilization, bimodal molecular weight distributions were observed, with lower molecular weight portions at 358 and 240, entries 4 and 3, respectively. Despite the increased molecular weight reported using DCM, it was observed that the polymerization rate is slower in DCM than in toluene. This observation is in line with the work of Coates and co-workers, who reported that among three solvents (DCM, THF, and benzene-d_6) investigated for the ring-opening polymerization of β-butyrolactone, the rate is slowest in dichloromethane [21].

The CPG supported catalysts **3** and **4** allowed for higher conversions, slightly improved molecular weights and narrower polydispersities compared to SBA-15 supported catalysts.[2] This is presumably due to the porosity of the CPG—the larger, three-dimensionally interconnected pore structure facilitates the diffusion of the monomer into the catalyst sites and the resulting PLA away from the sites.

To shed light on the state of the polymer produced as a function of reaction time, several data points were taken for a polymerization utilizing catalyst **3** on SBA-15 (uncapped) under the same conditions as in Table 1, entry 1. A plot of polymer molecular weight as a function of conversion is shown in Fig. 2. From this, it is evident that the molecular weight of the resulting PLA is almost independent of the reaction time after 2 h, while conversion increases steadily with the reaction time. This is an indication that the catalyst is not causing polymer degradation by producing high molecular weight polymer at the outset of the polymerization followed by subsequent degradation of the polymer chains. Furthermore, the polymerization clearly not a “living” prosses.

Like the new silica-based catalysts reported here, it is noteworthy that all the porous silica catalysts reported in the open literature for lactone or lactide polymerization yield polymers with exceeding low molecular weights [5–9].[3] Over acidic Al-MCM-41 mesoporous silicates (27 Å pores), Aida and co-workers oligomerized lactones to number-average molecular weights of 1000–8200 over exceedingly long reaction times (up to 60 days) [8]. For long reaction times and low alcohol concentrations, higher M_n’s were observed with larger M_w/M_n after reaction for up to 138 days. Using Sn-exchanged clays for polymerization, only oligomeric products were reported for δ-valerolactone polymerization [9]. Similar observations (primarily oligomeric products) were made for lactone or cyclic carbonate polymerization with silica-supported metal alkoxides [5–7]. The similarity of all these observations leads to the hypothesis that there is something inherent about silica-based catalysts that gives only low molecular weight products. Hence, to probe the role of porosity and the influence of the silica surface on molecular weight, several additional experiments were undertaken. Control studies (Table 2) indicate that production of low molecular weight PLAs is unique to catalytic sites immobilized inside the mesopores of the support. For example, in control experiment one, unfunctionalized, calcined SBA-15 (100 mg) is physically mixed with complex **2** (20 mg, [**2**] $= 2 \times 10^{-3}$ M, [LA]/[**2**] $= 200$) and added to a DCM solution. With added L-lactide, the monomer is polymerized efficiently to nearly 100% conversion within an hour, and GPC revealed an M_n of 33,200 g/mol and molecular weight distribution of 1.04. Under these conditions, all of the complex cannot adsorb onto the support and free complex **2** effectively polymerizes lactide to high molecular weights. In control experiment two, intimate physical interactions between the complex and the support are promoted by adding a smaller amount of complex **2** (10 mg) to calcined, bare SBA-15 (60 mg) in DCM for 30 min, followed by evaporation of the solvent. When this physically immobilized complex is used to polymerize L-lactide in DCM, only low molecular weight PLA was produced ($M_n = 770$, PDI $= 1.05$), indicating that sites sequestered into the pores

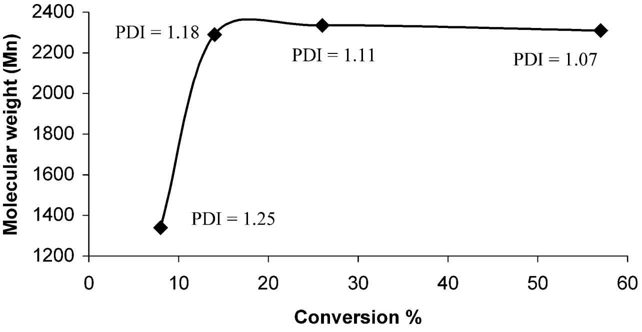


Fig. 2. Number-average molecular weigh (M_n) as a function of conversion with catalyst **3** supported on SAB-15 (uncapped) under the same conditions as entry 1, Table 1. Data points correspond to times of 0.5, 2, 4, and 20 h.

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[2] Although true initial rates were not measured, under otherwise identical conditions, CPG supported **3** (no capping) gave a conversion of 28% after 2 h, while SBA-15 supported **3** yielded 23% conversion; for **4**, CPG gave 24% conversion, while SBA-15 resulted in 17% conversion.

[3] Pinnavaia’s Sn-HMS catalyst is the outlier, with a relatively high molecular weight of 36,000 reported over this silica catalyst, although this is only a single data point [10].

Table 2
Control experiments—ROP of L-lactide

Entry	Catalyst	Method[a]	Time (h)	[Monomer]/[catalyst]	Conversion (%)	M_n	M_w/M_n
Control 1	SBA-15 + **2**	In situ	1.0	200	100	33,200	1.04
Control 2	SBA-15 + **2**	Premixing	1.0	200	85	770	1.05
Control 3	Uncalcined SBA-15 + **1**	Method 1	3.0	80	100	12,460	1.18

[a] In control 1, **2**, SBA-15, and L-lactide are physically mixed in situ (no covalent attachment); while in control 2, **2** was premixed with SBA-15 and solvent was evaporated and subsequently mixed with L-lactide (no covalent attachment). Uncalcined SBA-15 has mesopores still blocked with surfactant and only external surface silanols are available for immobilization (covalent attachment). All reactions are carried out in a DCM solution at 45 °C.

of the support result in oligomeric products. However, when complex **1** is covalently tethered (via method 1), exclusively on the external surface of uncalcined, bare SBA-15 that had its pores still plugged with surfactant the resulting supported catalyst polymerized L-lactide to nearly 100% conversion in 3 h yielding PLA with a high M_n of 12,460 and PDI of 1.18. This observation clearly demonstrates that the silica porosity has an important effect on the catalytic behavior of the supported Zn-BDI sites—when the zinc is immobilized inside the mesopores, only low molecular PLA was generated, while significantly higher molecular weight PLA was obtained when Zn is immobilized on the external surface of the silica support.[4] As a final control experiment, commercial PLA was mixed with bare SBA-15 and heated to 45 °C in a DCM solution for 5 h, and no detectable decomposition of the PLA occurred as judged by both TGA (melting point) and GPC, indicating that bare silica will not break down the PLA once it is formed. PLA formed from complex **2** is also very stable, with no change of the polymer observed after mixing with silica or heating alone in a THF solution at 50 °C for 5 h. These results indicate that the reduced molecular weights are likely a consequence of polymer/active species interactions with silanol groups during the catalytic insertion process and that the polymers are not degraded by the silica or catalyst after synthesis.

The hypothesized structure of the catalyst as described in Scheme 1 includes both halves of the dimer covalently bound to the surface. However, it is possible that only one of the two metal complexes of the dimer may react with the surface. If this occurs, the unreacted complex could become a homogeneous species if the dimer is broken upon the onset of the catalytic cycle. Recent investigations into the homogeneous catalyst system indicate that a monomeric complex is likely the active species [14,21–23]. To probe whether the immobilized catalyst **3** has all silyl groups reacted to the surface through at least one Si–O–Si linkage, a leaching test with complex **1** supported on SBA-15 (method **1**, no capping) was performed. After starting the polymerization and allowing it to continue for 30 min (DCM, 45 °C) the solution was separated from the supported solid catalyst via centrifuge and the solution was allowed to stir at the same temperature for an additional 15 h. The crude mixture before separation had a conversion $\sim 8 \pm 0.5\%$ (based on ^{1}H NMR), and the soluble part had an identical conversion ($\sim 8 \pm 0.5\%$) even after the additional 15 h of reaction time. This suggested that there were no leached active species in solution after separation of the supported catalyst. This implies that complex **1** was covalently tethered to the silica surface, presumably adopting the dimeric structure for catalyst **3** as shown in Scheme 1, or a mixture of monomers or dimers for catalyst **4**.[5] When complex **1** was immobilized on SBA-15 using method 1 under conditions where the complex should be a monomer in solution (high temperature, 80 °C for 16 h), the resulting catalyst **3** polymerized L-lactide under the same conditions used in Table 1, entry 1, to yield PLA with a conversion of 61% and M_n of 1460 (PDI = 1.08). Thus, catalyst **3** polymerizes lactide in a consistent manner, regardless of whether the original homogeneous complex, **1**, was immobilized under conditions where it is likely dimeric or monomeric in solution. Taken together, these results imply that all or nearly all of the complexes are covalently immobilized on the supports. Furthermore, the catalytic results are consistent with an active species that is monomeric in metal complex, not dimeric, although either monomeric or dimeric species may be originally immobilized on the surface.

4. Conclusions

In summary, the catalytic reactivity of mesoporous silica-supported catalysts **3** and **4,** which are the first silica-immobilized transition metal complexes reported for lactide polymerization, was influenced by a number of factors including the porosity of the silica support and the polymerization solvent, as well as, to a lesser extent, catalyst preparation methods. Immobilized catalysts gave moderate polymerization rates compared to their homogeneous analogues, potentially due to transport effects. The structure of the support was illustrated to have a strong influence on the ability to produce high molecular weight PLAs. High molecular weight PLA was only produced on a catalyst pre-

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[4] GPC analysis of the SBA-15 block copolymer surfactant showed an average molecular weight of 5445 and a PDI of 1.37, indicating that the polymer recovered was polylactic acid produced by the zinc sites and not leached structure-directing agent. ^{1}H NMR analysis of the polymer also indicates that the polymer is PLA.

[5] Catalyst **3** is prepared by immobilization at room temperature, conditions where the complex primarily adopts a dimeric form in solution. Catalyst **4** is immobilized at higher temperatures, where monomeric species are more commonly observed in solution [21].

pared on a nonporous support. Surface silanols are shown to contribute to premature chain transfer, resulting lower molecular weight, oligomeric products. If oligomeric products are desired, immobilized catalysts offer the opportunity for enhanced catalyst removal from the product polymer.

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