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Comparing *L*-Lactide and ε-Caprolactone Polymerization by Using Aluminum Complexes Bearing Ketiminate Ligands : Steric, Electronic, and Chelating Effects

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Abstract

Our previous studies on the ring-opening polymerization of ε-caprolactone by using aluminum complexes bearing ketimine ligands as pre-catalysts with benzyl alcohol as an initiator showed clearly results about how the steric, electronic, and chelating effect influenced the polymerization rate. Herein, the *L*-lactide polymerization rate of a series of Al complexes bearing ketimine ligands was also investigated, and the polymerization characters between *L*-lactide and ε-caprolactone were compared. The kinetic results revealed complexes with more steric hindrance ligands that demonstrated greater propagation activity of the CL polymerization; however, an opposite trend was obtained in the *L*-lactide polymerization because of the larger size of *L*-lactide hindering its coordination with Al atoms in the crowded surroundings. The electron-withdrawing group of ligands, or less chelating ligands, demonstrated greater propagation activity both in *L*-lactide and ε-caprolactone polymerization.

Keywords: ketimine, aluminum complex, ε-Caprolactone, *L*-Lactide, Ring-opening polymerization

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Introduction

Poly(lactide) (PLA) and poly(ε-caprolactone) (PCL) were designed to reduce the pollution problem

caused by disposable containers and packaging and now are frequently used as popular plastic materials in various fields[1] because of their biodegradability, biocompatibility, and permeability. The main method of their synthesizing PLA and PCL is the ring-opening polymerization (ROP) of cycloesters with various metal catalysts.[2] Aluminum catalysts are for a commonly used type of ROP catalysts because they are low cytotoxic, and easily synthesized, and their precursors are inexpensive. Al complexes have been thoroughly studied to determine their electronic, steric and chelate effects in ROP.[3-5] Several Al complexes[3b,3h, 3g,6] have been reported to be both active for both lactide (LA) and ε-caprolactone (CL) polymerization, but few[3b,3h, 6a-c] of them have been compared to determine the difference in the polymerization characters between LA and CL. The size of LA is larger than that of CL, and LA coordination with Al atom will be hindered more easily from the steric bulky ligands than that of CL. They should be different strategies of catalyst design for LA and CL polymerization. In addition, the copolymerization results of LA and CL also will be influenced by the catalysts with various ligand effects. However, there is no clear report about the differences between LA and CL polymerization. Recently we reported the kinetic analysis of ROP of CL by using alkyl Al complexes bearing varied ketimine ligands[7] as precatalysts with benzyl alcohol (BnOH) as an initiator and the results clearly revealed the connection between the polymerization rate and the ligands of steric, electronic, and chelating effects (**Figure 1**). Determining the polymerization characters between LA and CL is crucial for the design of Al catalysts and the strategy[6b-c,6f-h] of copolymerization of LA and CL. Herein, the ROP of *L*-LA by using the same Al complexes was studied, and the polymerization characters of the ligands of steric, electronic, and chelating effects between LA and CL were compared.

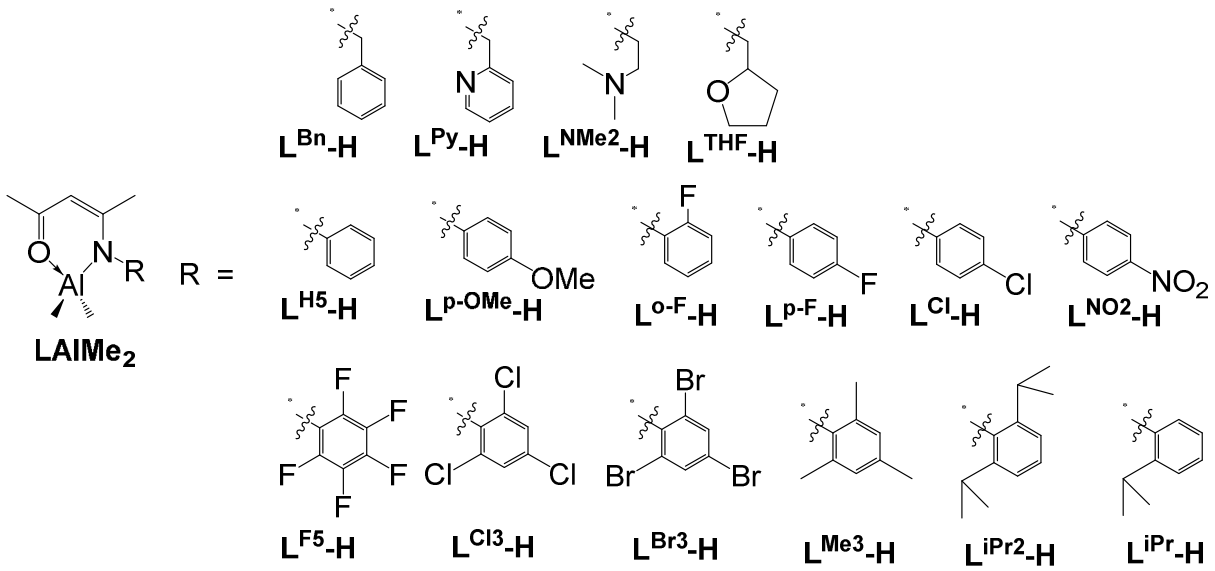


Figure 1. Aluminum complexes with various ketiminates

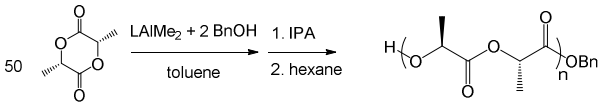
Results and Discussion

Polymerization of *L*-Lactide

The polymerizations of *L*-LA using Al complexes were investigated using two equivalents of BnOH as an initiator at 60 °C; the kinetic data are listed in **Table S1**. As shown in **Table 1**, the catalytic rates of Al complexes with different ligands (ranked according to the k_{obs} obtained using the first-order equation on [LA]) exhibited the following order: $L^{F5} > L^{p\text{-}F} > L^{NO2} > L^{Cl3} > L^{o\text{-}F} > L^{Cl} > L^{Bn} > L^{Br3} > L^{H5} > L^{THF} > L^{Me3} = L^{p\text{-}OMe} > L^{iPr} > L^{Py} > L^{iPr2} > L^{NMe2}$. The *L*-LA polymerization results were similar to those of CL polymerization[7] in that the Mn_{GPC} of these polymers appeared smaller than Mn_{NMR}. It may be that the chain transfer reaction of the polymer chain end occurs during work-up. It was also suggested that Mn_{GPC} of these polymers could compare with Mn_{Cal} to evaluate the extent of transesterification during polymerization. $\mathbf{L^{iPr}AlMe_2}$ and $\mathbf{L^{Py}AlMe_2}$ showed the discrepancy in Mn_{GPC}, Mn_{NMR}, and Mn_{Cal} (entries 13 and 14, **Table 1**), and it seemed there was only one equivalent of BnOH to be an initiator; however, the real reason how the ketiminate ligands influence the above phenomenon was unknown. $\mathbf{L^{NMe2}AlMe_2}$ showed no catalytic reactivity of *L*-LA polymerization (**Table 1**, entry 16). According to the linear relationship between Mn_{GPC} and $([LA]_0 \times \text{conv.})/[BnOH]_0$, the polymerization of LA by using $\mathbf{L^{F5}AlMe_2}$ as the catalyst demonstrated excellent controllability. (**Table 1**, entries 1 and 17-19; **Figure S2**). The comparison

between CL and *L*-LA polymerization was classified according to the steric, electronic, and chelating effects.

Table 1. Polymerization of *L*-LA by using Al complexes as precatalysts.



Entry	$LAlMe_2$ L =	Time /min	Conv.[a] /%	Mn_{Cal}[b]	Mn_{NMR}[a]	Mn_{GPC}[c]	PDI[c]	k_{obs}[d] $\times 10^2$
1	L^{F5}	110	96	3600	5800	4200	1.29	3.83
2	$L^{p\text{-}F}$	120	97	3600	6200	4200	1.13	3.61
3	L^{NO2}	160	99	3700	5200	4900	1.10	3.03
4	L^{Cl3}	140	98	3600	5800	3000	1.11	2.93
5	$L^{o\text{-}F}$	100	88	3300	4300	3200	1.25	2.61
6	L^{Cl}	90	81	3000	8300	6400	1.02	2.44
7	L^{Bn}	150	99	3700	3200	2800	1.15	2.29
8	L^{Br3}	150	93	3500	5000	4100	1.06	1.88
9	L^{H5}	100	99	3700	7200	5500	1.15	1.68
10	L^{THF}	180	91	3400	5400	4800	1.10	1.44
11	L^{Me3}	220	90	3300	4400	2400	1.26	1.09
12	$L^{p\text{-}OMe}$	105	94	3500	3600	3200	1.26	1.09
13	L^{iPr}	260	92	3400	9900	6700	1.08	0.95
14	L^{Py}	350	66	2500	12000	6300	1.03	0.84
15	L^{iPr2}	300	95	3500	3400	2300	1.13	0.76
16[e]	L^{NMe2}	-	-	-	-	-	-	-
17[f]	L^{F5}	150	99	7200	8100	7500	1.05	-
18[g]	L^{F5}	150	99	10800	11200	11100	1.07	-
19[h]	L^{F5}	200	99	14400	16500	14600	1.08	-

Reaction condition: toluene (5 mL), $[LA]_0/[Cat.]_0/[BnOH]_0$ = 50:1:2, [LA] = 1.0 M, at 60 °C. [a] Obtained from ^{1}H NMR analysis. [b] Calculated from the molecular weight of monomer x $[monomer]_0/ 2[Cat]_0$ × conversion yield + *M*w(Pr^iO). [c] Obtained from GPC analysis and calibration based on the polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58. [d] Monitored by ^{1}H NMR to determine the k_{obs} by first-order equation on [LA]. [e] Not available. [f] Reaction condition: toluene (5 mL), $[LA]_0/[Cat.]_0/[BnOH]_0$ = 100:1:2, [LA] = 2.0 M, at 60 °C. [g] Reaction condition: toluene (10 mL), $[LA]_0/[Cat.]_0/[BnOH]_0$ = 150:1:2, [LA] = 1.5 M, at 80 °C. [h] Reaction condition: toluene (10 mL), $[LA]_0/[Cat.]_0/[BnOH]_0$ = 200:1:2, [LA] = 1.0 M, at 80 °C.

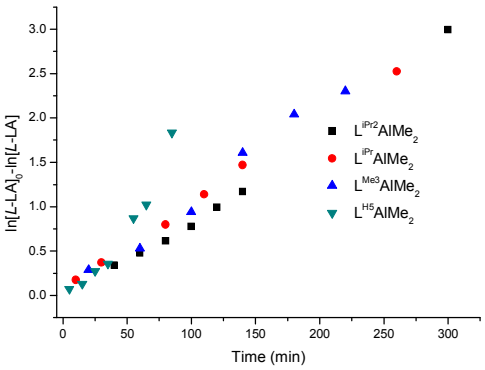


Figure 2. First-order kinetic plots for *L*-LA polymerizations versus time for various Al complexes (steric effect)

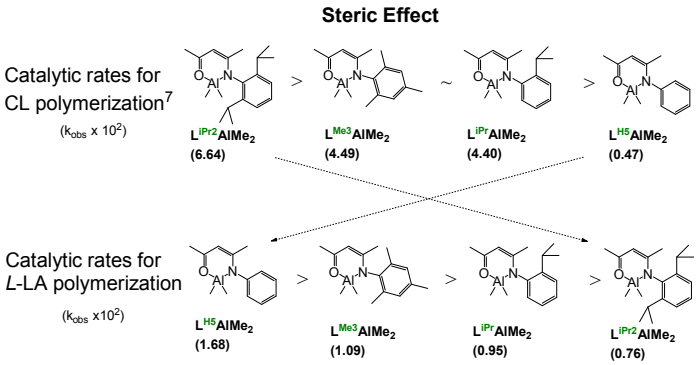


Figure 3. Comparison between the *L*-LA and CL polymerization (Steric effect)

Figures 2, **4**, **6**, and **8** show the kinetic results of the *L*-LA polymerization from using various Al complexes as the catalysts, as well as the linear plots of $\ln([LA]_0/[LA])$ versus time, showing that polymerization proceeds with first-order dependence on monomer concentration. As shown in **Figure 3**, when the steric bulk of ligands increased, $k_{(obs)}$ showed an obvious increase in CL polymerization, but an opposite trend was observed in *L*-LA polymerization. The steric effect increased the catalytic activity of CL polymerization, possibly because the dimerization of Al alkoxide and the disproportionation (**Figure 10**) could be restrained by steric bulky ligands.[7] However, the size of *L*-LA is larger than CL and the coordination of *L*-LA to the Al catalytic center could be hindered by the steric bulky ligands shown in **Figure 11**. Similar catalytic trends of the literatures for *L*-LA[8] and CL[3j,4e-f,5d-e] polymerization have been reported.

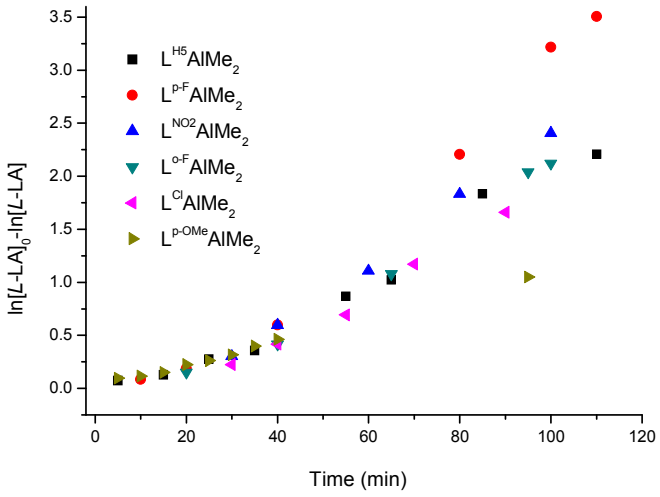


Figure 4. First-order kinetic plots for *L*-LA polymerizations versus time for various Al complexes (electronic effect)

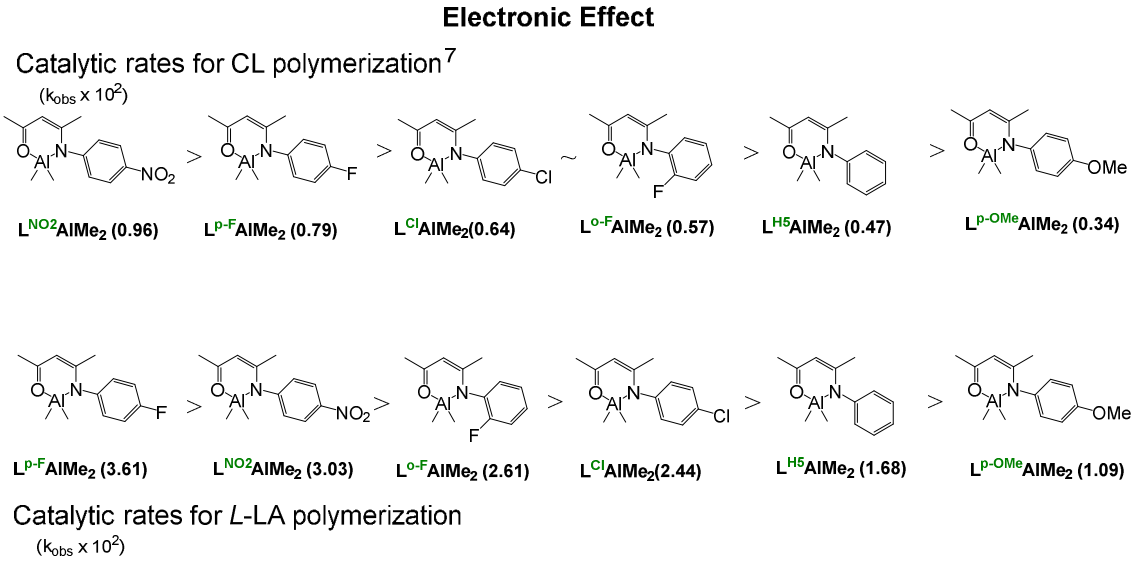


Figure 5. Comparison between the *L*-LA and CL polymerization (electronic effect)

As shown in **Figure 5**, the electron-withdrawing groups, such as the halide and nitro groups, slightly increased the catalytic activity of the CL polymerization compared with $L^{H5}AlMe_2$, but substantially increased the catalytic activity of the *L*-LA polymerization. In addition, it was found that p-nitro substituent showed higher polymerization rate than p-F, and p-chloro substituent showed higher polymerization rate than o-F in case of CL; however, this trend was changed in case of L-LA. The results revealed that the electron-withdrawing groups enhanced the Lewis acidity of

Al atom shown in **Figure 12**, thereby increasing the positive charge of the carbonyl group of the cycloesters and the initiation. *L*-LA was more sensitive than CL for the described activation during the polymerization process.

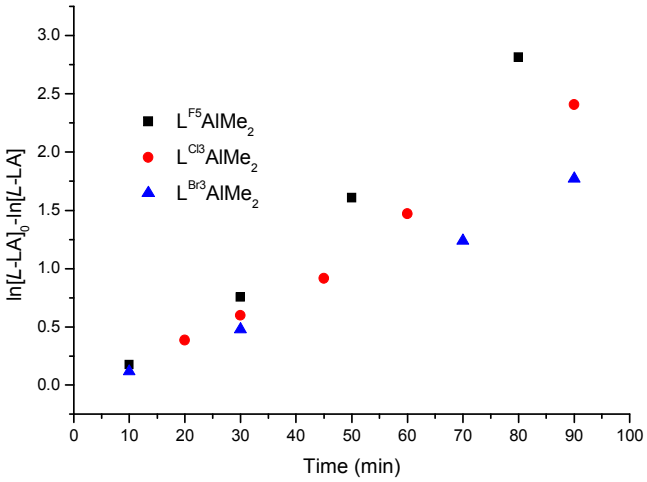


Figure 6. First-order kinetic plots for *L*-LA polymerizations versus time for various Al complexes (steric + electronic effect)

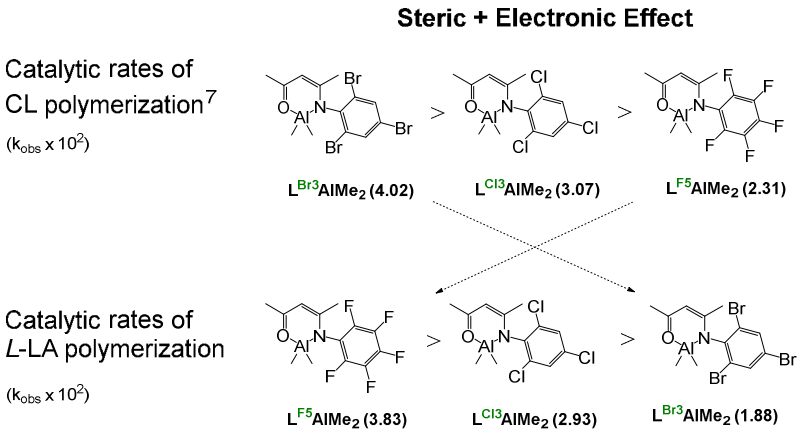


Figure 7. Comparison between the *L*-LA and CL polymerization (steric + electronic effect)

As shown in **Figure 7**, the combination of the steric and electronic effect in Al complexes was tested for CL polymerization, revealing that the steric effect is more effective than the electronic effect, and that $L^{Br3}AlMe_2$ with the largest steric bulky ligand showed the highest polymerization rate. It may be that side reactions including the dimerization of Al alkoxide and the

disproportionation during CL polymerization process occur easily for Al complexes bearing electron withdrawing groups, and the steric bulky ligand could reduce the above reactions. However, an opposite phenomenon was observed in *L*-LA polymerization because both less steric bulky and electron-withdrawing ligands both increased the catalytic activity. In addition, LA with larger size than CL also could reduce the dimerization and the disproportionation when LA coordinates with Al atom.

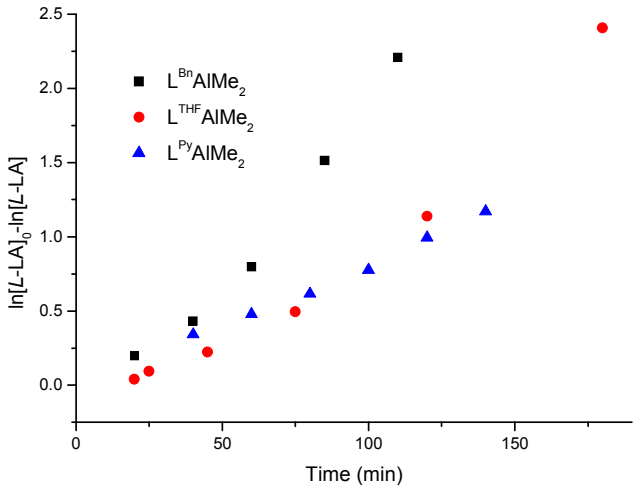


Figure 8. First-order kinetic plots for *L*-LA polymerizations versus time for various Al complexes (chelating effect)

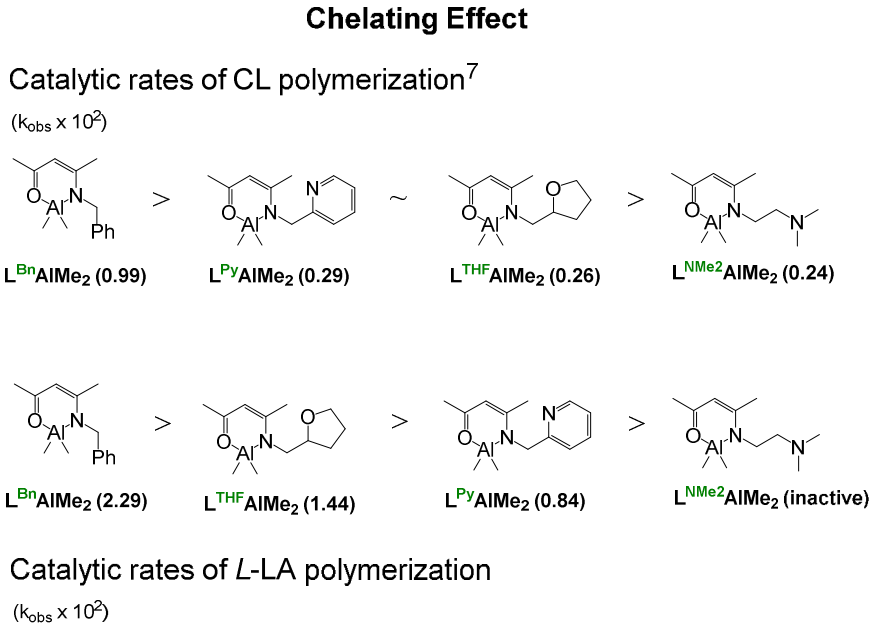


Figure 9. Comparison between the *L*-LA and CL polymerization (chelating effect)

As shown in **Figure 9**, the chelating effects, such as those of the 2-pyridinylmethyl, 2-tetrahydrofuranylmethyl, and 2-dimethylaminoethyl groups, reduced the catalytic rate compared with $\mathbf{L^{Bn}AlMe_2}$. A similar catalytic trend was observed in *L*-LA polymerization and $\mathbf{L^{NMe2}AlMe_2}$ was inactive. The possible reason of the inaction of *L*-LA polymerization by using $\mathbf{L^{NMe2}AlMe_2}$ as a catalyst may be that the two methyl groups on the chelating amino group increased the repulsion between LA and the ketiminate ligand and further decrease the LA coordination with Al atom.

The results showed that steric bulky ligands reduced the catalytic activity of *L*-LA polymerization because the larger size of *L*-LA was difficult to coordinate with Al atom in the crowded surroundings, although the steric bulky ligands could avoid the dimerization of Al alkoxide and the disproportionation and increase the catalytic activity of CL polymerization. In addition, *L*-LA and CL polymerization showed a similar catalytic trend of electronic and chelating effects.

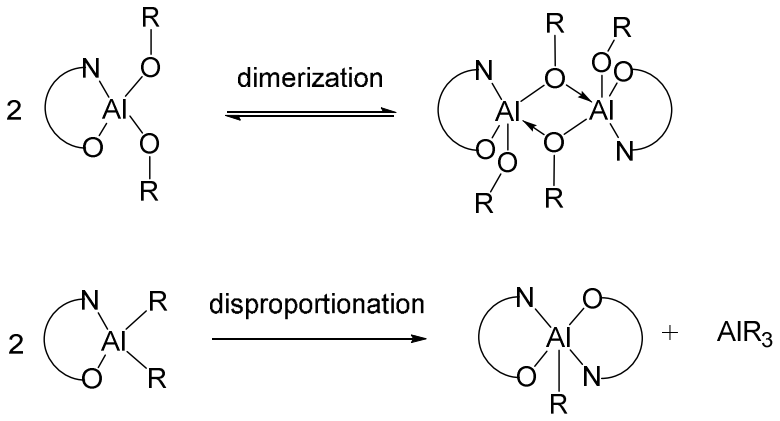


Figure 10. The mechanism of the dimerization and the disproportionation

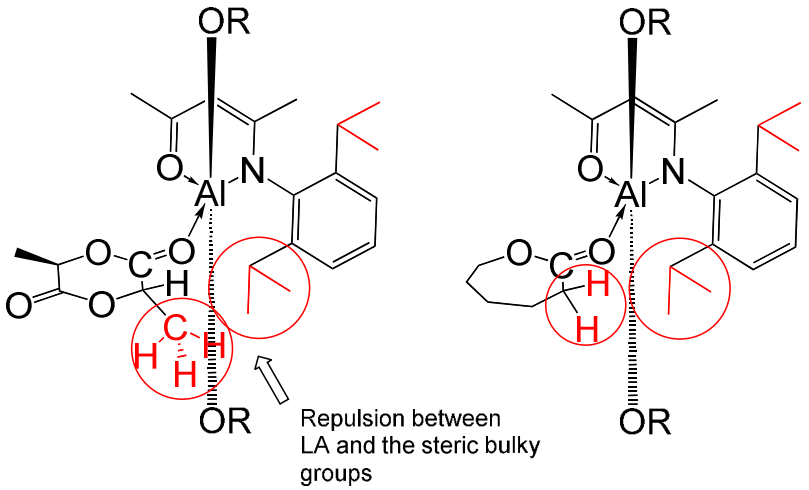


Figure 11. The possible reason that the steric bulky groups on the ligands decrease the catalytic activity of the LA polymerization

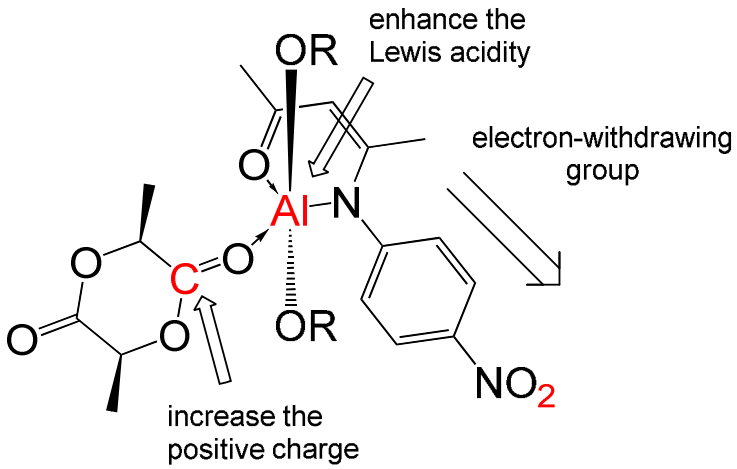


Figure 12. The possible reason that the electron-withdrawing groups on the ligands increase the catalytic activity of the LA polymerization

Kinetic Study of the Polymerization of *L*-LA catalyzed using $L^{F5}AlMe_2$

Kinetic studies were performed with respect to the ratio of $[L\text{-LA}]_0/[\mathbf{L^{F5}AlMe_2} + 2\ \text{BnOH}]$ ($[L\text{-LA}] = 1.0$ M in toluene) at 60 °C, as shown in **Table S2**. The preliminary results indicated a first-order dependency on [*L*-LA] (**Figure S1**). By plotting k_{obs} vs. $[\mathbf{L^{F5}AlMe_2} + 2\ \text{BnOH}]$ with the assumption that the order of $[\mathbf{L^{F5}AlMe_2} + 2\ \text{BnOH}]$ is 1, k_{app} values of 2.01 were determined for *L*-LA (**Figures 13**). The polymerization of *L*-LA by using $\mathbf{L^{F5}AlMe_2}$ at 60 °C demonstrated the following rate law:

$$d[L\text{-LA}]/dt = 2.01 \times [L\text{-LA}][\mathbf{L^{F5}AlMe_2} + 2\ \text{BnOH}]$$

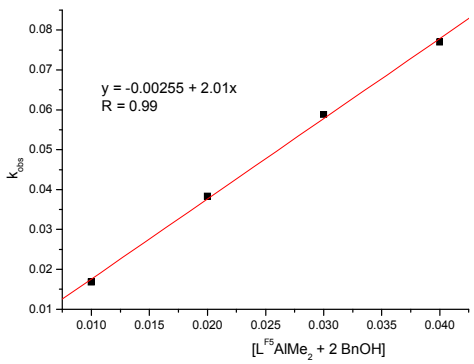


Figure 13. Linear plot of k_{obs} versus [$L^{F5}AlMe_2$ + 2 BnOH] for the polymerization of *L*-LA with [*L*-LA] = 1.0 M in toluene (5 mL) at 60 ^{o}C

Mechanistic studies of polymerization

Our research reported that the methyl groups of the aluminum complex are not good initiators and the real catalytic species is "$LAlOBn_2$" because the crystal structure of $\mathbf{L^{H5}AlOBn_2}$ was observed by the reaction of BnOH and $\mathbf{L^{H5}AlMe_2}$. To prove the methyl groups of the aluminum complex could be replaced by BnOH, the ^{1}H NMR spectrum of the active species of $LAlMe_2$/BnOH catalytic systems for LA polymerization was studied (**Figure 14**). **Figure 14 (A)** is $\mathbf{L^{Cl}AlMe_2}$ and the ratio of the integration between peak **b** and peak **f** is 2:6. **Figure 14 (B)** is the mixture of $\mathbf{L^{Cl}AlMe_2}$ and BnOH (1:2), and it revealed two methyl groups were replaced by BnOH because of the absence of peak **f**. **Figure 14 (C)** is the mixture of LA, $\mathbf{L^{Cl}AlMe_2}$, and BnOH (4:1:2), and the proton peak of the methine on LA, β-H of $\mathbf{L^{Cl}AlMe_2}$, and the methylene on BnOH overlapped in peak **c**. The ratio of peak **b** and **f** is 2:1.5 and it revealed that most methyl groups on Al atom were replaced by BnOH during the LA polymerization. According to the kinetic characteristics and ^{1}H NMR study, the possible mechanism (**Figure 15**) is that two BnOHs replace the methyl groups to be benzyl alkoxides, and one LA coordinated to an aluminum center. Benzyl alkoxide initiates LA to be the new alkoxide, and repeating the coordination of LA and initiation by alkoxide resulted in a PLA product.

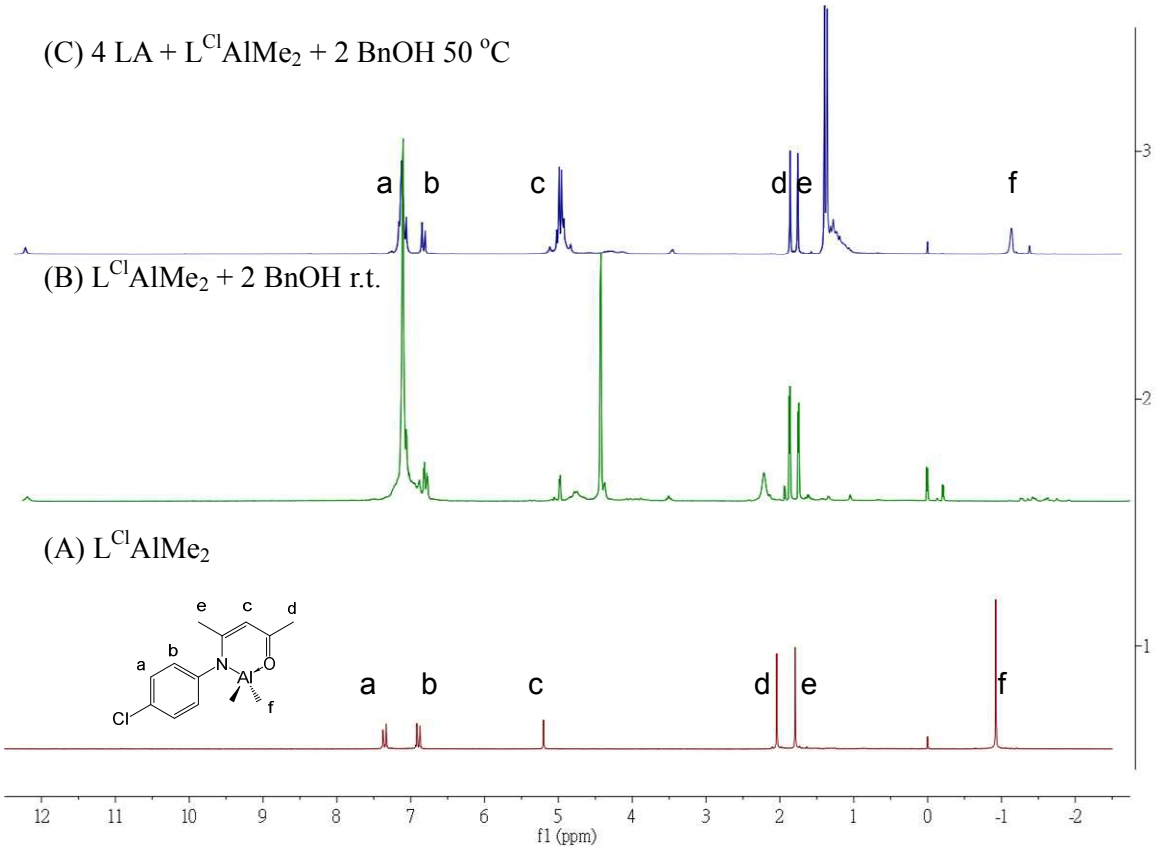


Figure 14. ^{1}H NMR spectrum of (A) $L^{Cl}AlMe_2$, (B) $L^{Cl}AlMe_2$ + 2 BnOH at r.t., (C) 4 LA + $L^{Cl}AlMe_2$ + 2 BnOH at 50 °C in $CDCl_3$)

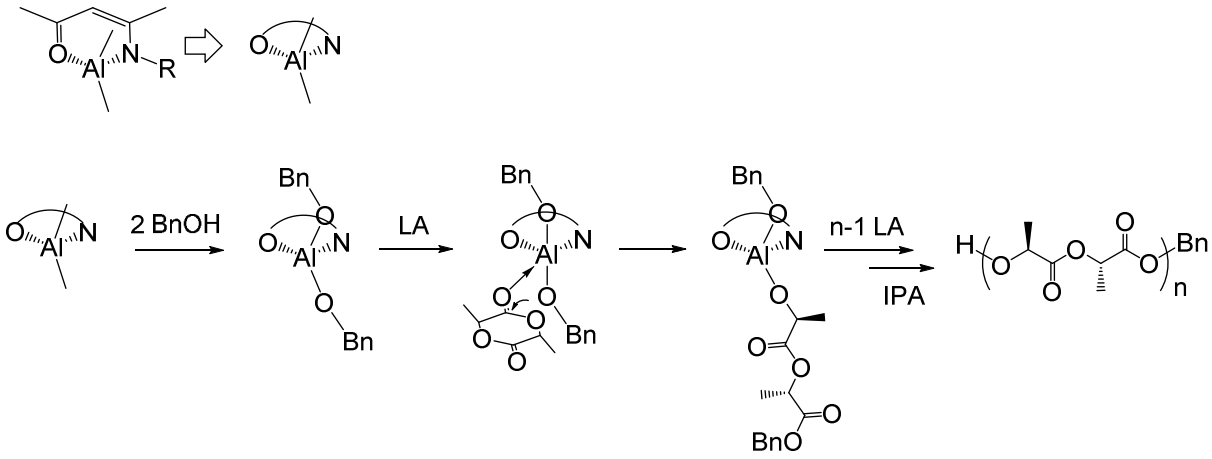


Figure 15. Possible mechanism of LA polymerization by using Al complexes bearing a ketiminate ligand

Conclusions

The polymerization characters between *L*-LA and CL were examined using Al complexes

bearing ketiminate ligands as the model catalysts. The different polymerization characters between *L*-LA and CL indicated that steric bulky ligands increased the catalytic activity of CL polymerization because of the precautions against the dimerization and the disproportionation of Al complexes; However, *L*-LA polymerization exhibited the opposite behavior because *L*-LA with the larger bulk was difficult to coordinate with Al atoms under the packed circumstances. Other effects exhibited a similar catalytic trend between *L*-LA and CL polymerization in that the electron-withdrawing groups enhanced the polymerization rate, and *L*-LA polymerization was more sensitive than that of CL in the electronic effect. The chelating groups could compete with *L*-LA or CL during the monomers coordination with Al atom and reduce the polymerization rate. These results are crucial for the design of Al catalysts in *L*-LA and CL polymerization. In addition, this information is important for the study of the selectivity of PLA-*grade*-PCL copolymerization[9] because steric bulky ligands could restrain the LA polymerization and contrary to increase the CL polymerization.

Experimental Section

Standard Schlenk techniques and a N_2-filled glovebox were used throughout the isolation and handling of all the compounds. Solvents, deuterated solvents were purified prior to use. 2,4-Pentanedione, *p*-toluenesulfonic acid, 2-flouroaniline, 4-flouroaniline, 2,3,4,5,6-pentaflouroaniline, 4-nitroaniline, 2,4,6-tribromoaniline, 2,4,6-trichloroaniline, 4-chloroaniline, aniline, 4-methoxyaniline, 2,6-diisopropylaniline, 2-isopropylaniline, 2,4,6-trimethylaniline, pyridin-2-ylmethanamine, (tetrahydrofuran-2-yl)methanamine, phenylmethanamine, *N*,*N*-dimethylethane-1,2-diamine, deuterated chloroform, and *L*-LA were purchased from Acros. Benzyl alcohol was purchased from Alfa. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini2000-200 (200 MHz for ^{1}H and 50 MHz for ^{13}C) spectrometer with chemical shifts given in ppm from the internal TMS or center line of $CDCl_3$. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. GPC measurements were performed on a Jasco PU-2080 PLUS HPLC pump system equipped with a differential Jasco RI-2031 PLUS

refractive index detector using THF (HPLC grade) as an eluent (flow rate 1.0 mL/min, at 40 °C). The chromatographic column was JORDI Gel DVB 103 Å, and the calibration curve was made by primary polystyrene standards to calculate Mn(GPC). All the Al complexes bearing the ketiminate ligands[7] were prepared following literature procedures.

General procedures for the polymerization of *L*-lactide

A typical polymerization procedure was exemplified by the synthesis of entry 1 (**Table 1**) using complex $\mathbf{L^{F5}AlMe_2}$ as a catalyst. The polymerization conversion was analyzed by ^{1}H NMR spectroscopic studies. Toluene (5.0 mL) was added to a mixture of complex $\mathbf{L^{F5}AlMe_2}$ (0.1 mmol), BnOH (0.2 mmol), and *L*-lactide (5 mmol) at 60 ^{o}C. At indicated time intervals, 0.05 mL aliquots were removed, trapped with $CDCl_3$ (1mL), and analyzed by ^{1}H NMR. After the solution was stirred for 110 min, the reaction was then quenched by adding a drop of *iso*-propanol, and the polymer precipitated as white solid when pouring into *n*-hexane (30.0 mL). The isolated white solid was dissolved in CH_2Cl_2 (5.0 mL) and then *n*-hexane (70.0 mL) was added to give purified crystalline solid. Yield: 0.59 g (82 %). By plotting $\ln([L\text{-LA}]_0/[L\text{-LA}])$ vs. time, the slope is k_{obs} and intercept is induction period.

Electronic supplementary information (ESI) available: Polymer characterization data, and details of the kinetic study.

Acknowledgment This study is supported by Kaohsiung Medical University "Aim for the top 500 universities grant" under Grant No. KMU-DT103007, NSYSU-KMU JOINT RESEARCH PROJECT (NSYSU KMU 103-I004), NSYSU-KMU JOINT RESEARCH PROJECT, (#NSYSUKMU 104-P006), and the Ministry of Science and Technology (Grant MOST 104-2113-M-037 -010). We thank Center for Research Resources and Development at Kaohsiung Medical University for the instrumentation and equipment support.

Keywords: ring-opening polymerization; *ε*-caprolactone; *L*-lactide aluminum complexes

Reference

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Graphic abstract