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

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Electronic Supplementary Information Available: Polymer characterization data, and details of the kinetic study.

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Table S1 Kinetic study of *L*-LA polymerization with various Al complexes in toluene 5 mL, [*L*-LA] = 1.0 M at 60 °C

Time Min	L^{iPr2}	L^{iPr}	L^{Me3}	L^{H5}	L^{F5}	L^{Cl3}	L^{Br3}	$L^{p\text{-}F}$	L^{NO2}	$L^{o\text{-}F}$	L^{Cl}	L^{Bn}	$L^{p\text{-}OMe}$	L^{THF}	L^{Py}
	PLA conversion														
5				0.07									0.09		
10		0.16			0.16		0.11	0.08					0.11		
15				0.12									0.14		
20			0.25			0.32		0.17		0.14		0.18	0.20	0.04	
25				0.24									0.23	0.09	
30		0.31			0.53	0.45	0.38		0.26		0.20		0.27		
35				0.30									0.33		
40	0.29							0.45	0.45	0.34	0.34	0.35	0.37		0.29
45						0.60								0.20	
50					0.80										
55				0.58							0.50				
60	0.38		0.41			0.77			0.67			0.55			0.38
65				0.64						0.66					
70							0.71				0.69				
75														0.39	
80	0.46	0.55			0.94			0.89	0.84						0.46
85												0.78			
90						0.91	0.83				0.81				
95										0.87			0.65		
100	0.54		0.61					0.96	0.91	0.88					0.54
110		0.68					0.88	0.97				0.89			
120	0.63													0.68	0.63
140	0.69	0.77	0.80												0.69
150							0.93								
180			0.87											0.91	
220			0.90												
260		0.92													
300	0.95														
k_{obs} x10^2	1.04 (4)	0.95 (2)	1.09 (7)	1.68 (17)	3.83 (19)	2.94 (16)	2.04 (11)	3.61 (24)	3.03 (9)	2.61 (18)	2.44 (13)	2.29 (20)	1.09 (2)	1.44 (14)	0.84 (4)
R^2	0.99	0.99	0.99	0.98	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.98	0.99
Ip min	18.8	0	2.3	6.3	7.6	9.7	5.7	14.7	20.8	0	0	17.9	0	26.5	2.7

Ip = induction period

Table S2 ROP process of LA with a wide range of [$L^{F5}AlMe_2$ + 2 BnOH] in toluene 5 mL, [*L*-LA] = 1.0 M at 60 °C[a]

[Al]/[BnOH]/[LA]							
0.5:1:50		**1:2:50**		**1.5:3:50**		**2:4:50**	
Time (min)	Conv. (%)	Time (min)	Conv. (%)	Time (min)	Conv. (%)	Time (min)	Conv. (%)
15	0.09	10	0.16	20	0.47	8	0.28
35	0.27	30	0.53	25	0.61	10	0.33
55	0.51	50	0.80	30	0.73	20	0.64
70	0.61	80	0.94	50	0.91	30	0.84
85	0.70					35	0.90
100	0.78					40	0.94
k_{obs}							
0.0168 (7)		0.0383 (19)		0.0588 (21)		0.0770 (37)	
R							
0.99		0.99		0.990		0.99	

[a] Obtained from ^{1}H NMR analysis.

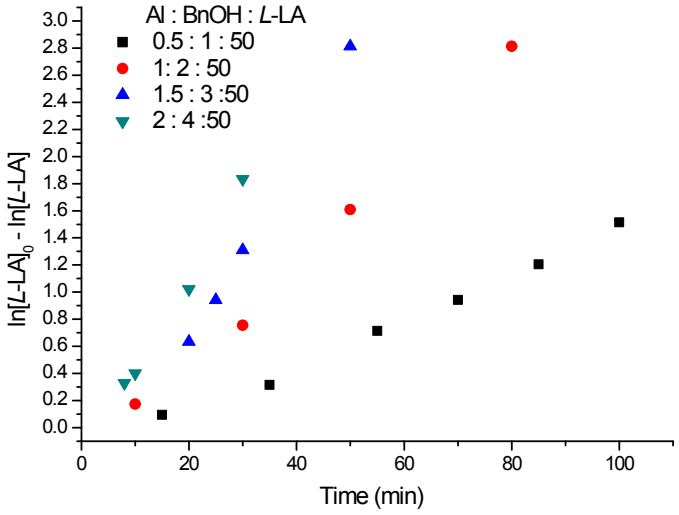


Figure S1 First-order kinetic plots for CL polymerizations with time in toluene (5 mL) with different concentration of [$L^{F5}AlMe_2$ + 2 BnOH]

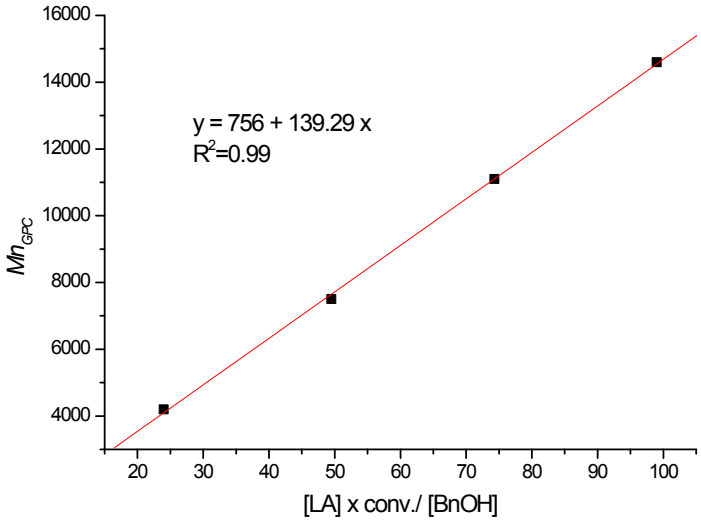


Figure S2. Linear plot of Mn_{GPC} vs. $[LA]_0 \times$ conv. / $[BnOH]_0$, with polydispersity indexes indicated by closed circles (**Table 1**, entries 1 and 17-19)

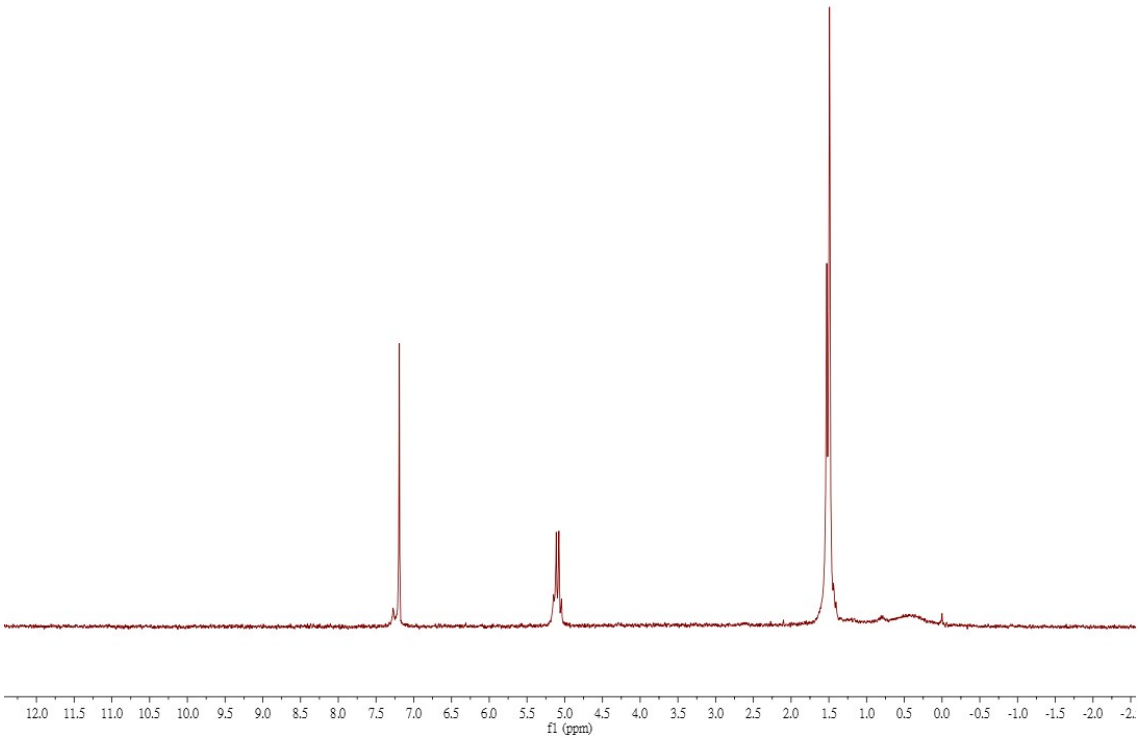
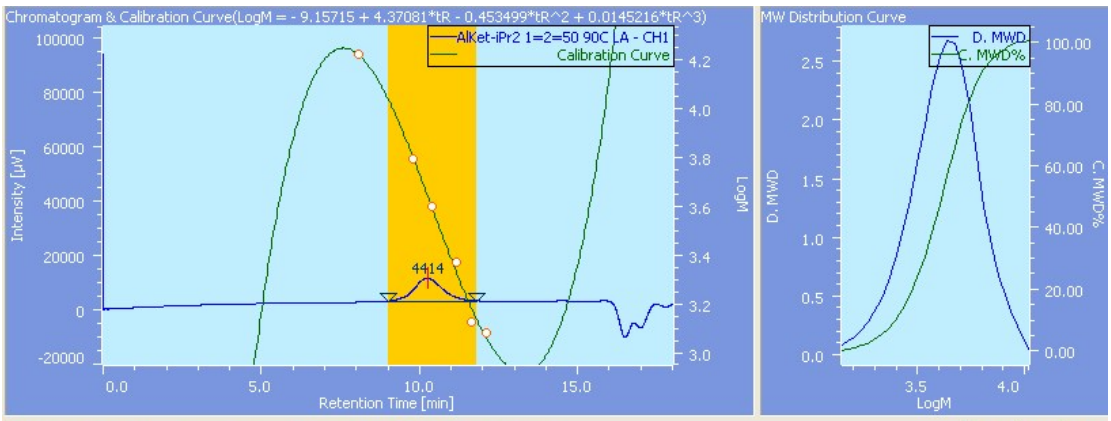


Figure S3. ^{1}H NMR spectrum of PLA by using $L^{iPr2}AlMe_2$ as a catalyst (**Table 1**, entry 15)



MW Calculation Results: AlKet-iPr2 1=2=50 90C LA

#	Range	CH	Baseline Range	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	Range Value	Percentage	Warning
1	9.0000 - 11.8000	1	9.0000 - 11.8000	10.2250	4414	3896	4440	4995	4440	1.1398	1.1250	544614	100.00	

Figure S4. GPC results of PLA by using $L^{iPr2}AlMe_2$ as a catalyst (**Table 1**, entry 15)