Use of Pyrazoles as Ligands Greatly Enhances the Catalytic Activity of Titanium *Iso*-Propoxide for the Ring-Opening Polymerization of *L*-Lactide: A Cooperation Effect

Tzu-Fang Wang,[a] Someswara Rao Kosuru,[a] Shu-Chun Yu,[a] Yung-Chi Chang,[a] Hsin-Yu Lai,[a] Yu-Lun Chang,[a] Kuo-Hui Wu,[bc] Shangwu Ding,[ad] Hsuan-Ying Chen,*[ade]

[a] *Department of Medicinal and Applied Chemistry, Drug Development and Value Creation Research Center, Kaohsiung Medical University, Kaohsiung, Taiwan, 80708, R.O.C.*

[b] *Department of Chemistry, Graduate School of Science, The University of Tokyo, Tokyo 113-0033, Japan.*

[c] *Department of Chemistry, National Sun Yat-sen University, Kaohsiung, Taiwan, 80424, R.O.C.*

[d] *Department of Medical Research, Kaohsiung Medical University Hospital, Kaohsiung 80708, Taiwan, R.O.C.*

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Table S1 Kinetic study of LA polymerization with various ratio of $TiO^{i}Pr_4$ and ^{thio}Pz at 60 ^{o}C

	[LA]:[$TiO^{i}Pr_4$]:[^{thio}Pz]				
time	100:1:0.5 ([LA]=1 M)	100:1:1 ([LA]=1 M)	100:1:2 ([LA]=1 M)	100:1:4 ([LA]=1 M)	100:1:1 ([LA]=2 M)
min		Conv.			
2					0.20
3					0.35
4					0.45
5		0.43			0.62
6					0.68
7	0.27				0.73
8					0.81
10					0.87
13	0.44				
15		0.60	0.59		
20	0.57			0.59	
21			0.64		
22		0.74			
26			0.68		
27	0.66			0.65	
30		0.80			
40				0.69	
43	0.80				
45		0.86			
50	0.85			0.73	
60			0.75		
125			0.84		
k_{obs} min^{-1} (error)	0.0358 ()	0.036 (4)	0.008 (1)	0.013 (1)	0.232 (8)
I.P/ min (error)	0	0	0	0	1 (1)
R^2	0.998	0.985	0.986	0.987	0.997

Table S2 Kinetic study of LA polymerization with TiO^iPr_4 and various pyrazole derivatives in toluene 5 mL, [LA] = 2.0 M at 60 °C ([LA] : $[TiO^iPr_4]$ = 50:1)

	[LA]:[TiO^iPr_4]:[Pz] (50:1:1)				
time	Ligand free	^{H}Pz	^{Me}Pz	^{Cl}Pz	^{Bu}Pz
min	Conv.				
2		0.35	0.26		0.26
3		0.46			0.46
4	0.32	0.59		0.41	0.56
5		0.67	0.54	0.54	0.75
6	0.41			0.62	
7		0.83			
8	0.54	0.88	0.77		
9					0.95
10	0.66			0.81	
11			0.90		
12	0.72				
13			0.94		
14				0.89	
15	0.86				
16					
18					
22	0.96				
k_{obs} min^{-1} (error)	0.161 (9)	0.285 (14)	0.233 (13)	0.166 (8)	0.394 (21)
I.P/ min (error)	3 (1)	1 (1)	1 (1)	0	1 (1)
R^2	0.991	0.995	0.995	0.996	0.996

	[LA]:[TiO^iPr_4]:[Pz] (50:1:1)				
time	^{Ph}Pz	^{fur}Pz	^{py}Pz	^{MeO}Pz	Tz
min	Conv.				
1		0.27			
1.5		0.38			
2	0.27	0.45		0.24	
3	0.38	0.63		0.37	
4	0.43	0.78	0.43	0.50	0.35
5	0.63	0.86		0.60	0.40
6			0.54		0.49
7					0.50
8			0.63		
9	0.92				
10	0.94		0.73	0.92	
11					
12					0.63
13					
15			0.88		
18					0.79
22					
24					0.90
k_{obs} min^{-1} (error)	0.334 (23)	0.418 (20)	0.152 (10)	0.288 (16)	0.120 (15)
I.P/ min (error)	1 (1)	0	1 (1)	2 (1)	1 (1)
R^2	0.991	0.995	0.992	0.995	0.963

Table S3 Kinetic study of LA polymerization with $TiO^{i}Pr_4$ and various pyrazole derivatives in CH_2Cl_2 2.5 mL, [LA] = 2.0 M at room temperature ([LA] : $[TiO^{i}Pr_4]$:[Pz] = 100:4:4)

	[LA]:[$TiO^{i}Pr_4$]:[Pz] (100:4:4)				
time	Ligand free	^{H}Pz	^{Me}Pz	^{Cl}Pz	^{Bu}Pz
min	Conv.				
30		0.29			0.26
65				0.34	
70		0.37			0.46
75			0.36		
120				0.44	
180	0.51		0.48		
225		0.57			0.69
230				0.57	
265		0.66			
270	0.56				
305				0.62	
310					0.85
370		0.76			0.88
390	0.63				
450		0.80			
590				0.80	
660			0.70		
720				0.85	
1335	0.79		0.79		
1670	0.81		0.85		
4290	0.85				
$k_{obs} \times 10^3$ min^{-1} (error)	0.27 (8)	3.09 (14)	0.85 (8)	2.22 (4)	5.27 (43)
I.P/ min (error)	0	0	0	0	0
R^2	0.86	0.996	0.987	0.999	0.990

	[LA]:[TiO^iPr_4]:[Pz] (100:4:4)					
time	^{Ph}Pz	^{thio}Pz	^{fur}Pz	^{py}Pz	^{MeO}Pz	Tz
min	Conv.					
35		0.31			0.25	
40			0.27			
70	0.35			0.44		
100				0.49		
115			0.43			
160		0.47			0.51	
180	0.55		0.53			
225		0.53			0.61	
240						0.50
270	0.60					
280				0.60		
330						0.63
365						0.68
395		0.70				
425			0.83			
450				0.74		
510					0.81	
515		0.78				
540			0.90			
600				0.83		
660	0.72	0.84		0.87	0.85	
1335	0.89					
1350						0.80
1670						0.87
k_{obs} $\times 10^3$ min^{-1} (error)	1.30 (11)	2.39 (5)	4.00 (13)	2.36 (17)	2.56 (18)	0.77 (12)
I.P/ min (error)	0	0	0	0	0	0
R^2	0.989	0.999	0.998	0.989	0.993	0.963

Table S4. Selected bond lengths (Å) and bond angles (deg) of $^{Me}Pz_2Ti_2O^iPr_7$

Bond lengths	Ti(1)	Ti(2)
Ti-O	Ti(1)–O(1) (terminal) 1.801(4)	Ti(2)–O(3) (bridge) 2.086(3)
	Ti(1)–O(2) (terminal) 1.793(3)	Ti(2)–O(4) (terminal) 1.811(4)
	Ti(1)–O(3) (bridge) 2.019(4)	Ti(2)–O(5) (terminal) 1.800(4)
	Ti(1)–O(7) (bridge) 2.021(3)	Ti(2)–O(6) (terminal) 1.905(3)
		Ti(2)–O(7) (bridge) 2.086(3)
Ti-N	Ti(1)–N(1) 2.199(4)	Ti(2)–N(3) 2.235(4)
	Ti(1)–N(4) 2.136(4)	
Bond angles	Ti(1)	Ti(2)
∠O-Ti-O	O(1)–Ti(1)–O(2) 98.18(19)	O(4)–Ti(2)–O(5) 98.13(19)
	O(1)–Ti(1)–O(7) 92.28(16)	O(4)–Ti(2)–O(3) 94.14(16)
	O(2)–Ti(1)–O(3) 96.48(17)	O(4)–Ti(2)–O(6) 98.83(17)
	O(3)–Ti(1)–O(7) 73.23(13)	O(5)–Ti(2)–O(7) 96.24(16)
		O(5)–Ti(2)–O(6) 99.65(16)
		O(3)–Ti(2)–O(7) 70.59(13)
∠O-Ti-N	O(1)–Ti(1)–N(1) 92.46(16)	O(4)–Ti(2)–N(3) 93.19(16)
	O(2)–Ti(1)–N(1) 95.49(16)	O(5)–Ti(2)–N(3) 92.33(16)
	O(3)–Ti(1)–N(1) 82.2(15)	O(3)–Ti(2)–N(3) 78.37(14)
	O(7)–Ti(1)–N(1) 85.83(14)	O(7)–Ti(2)–N(3) 78.74(14)
	O(1)–Ti(1)–N(4) 99.60(17)	
	O(2)–Ti(1)–N(4) 94.38(16)	
	O(3)–Ti(1)–N(4) 83.13(15)	
	O(7)–Ti(1)–N(4) 82.02(15)	
∠N-Ti-N	N(1)–Ti(1)–N(4) 163.16(16)	

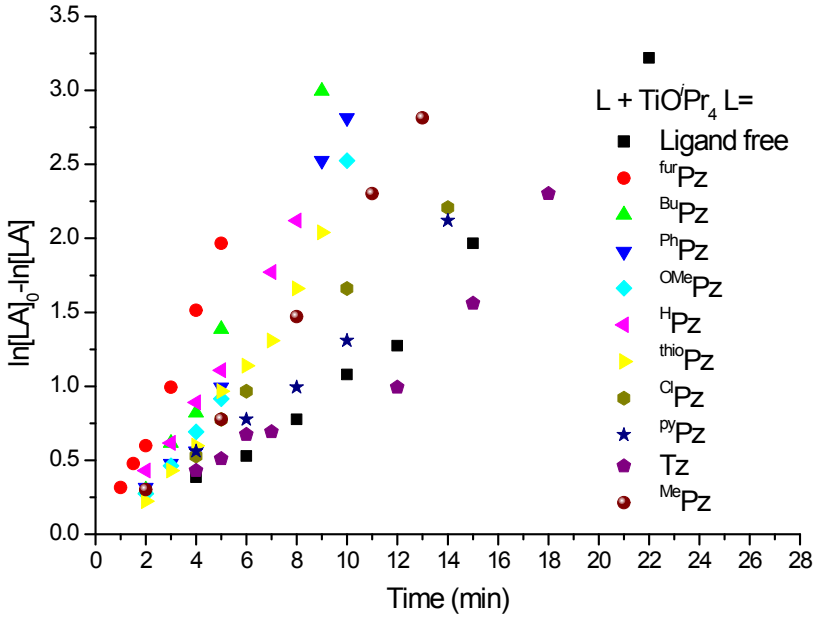

Figure S1. First-order kinetic plots of LA polymerization with TiO^iPr_4 and various **pyrazole derivatives** in toluene 5 mL, [LA] = 2.0 M at 60 °C ([LA] : [TiO^iPr_4]:[Pz] = 50:1:1, **Table 2**).

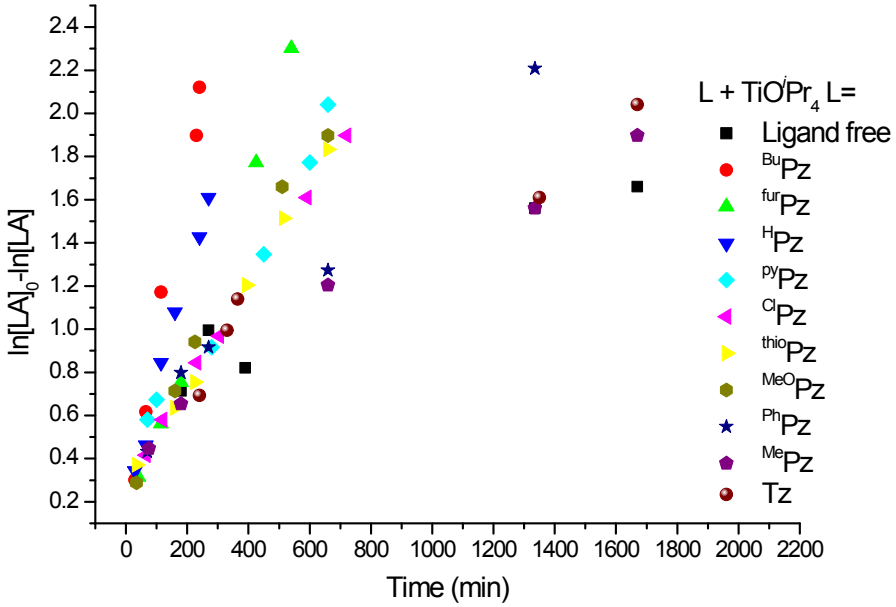

Figure S2. First-order kinetic plots of LA polymerization with TiO^iPr_4 and various **pyrazole derivatives** in CH_2Cl_2 2.5 mL, [LA] = 2.0 M at room temperature ([LA] : [TiO^iPr_4]:[Pz] = 25:1:1, **Table 3**).

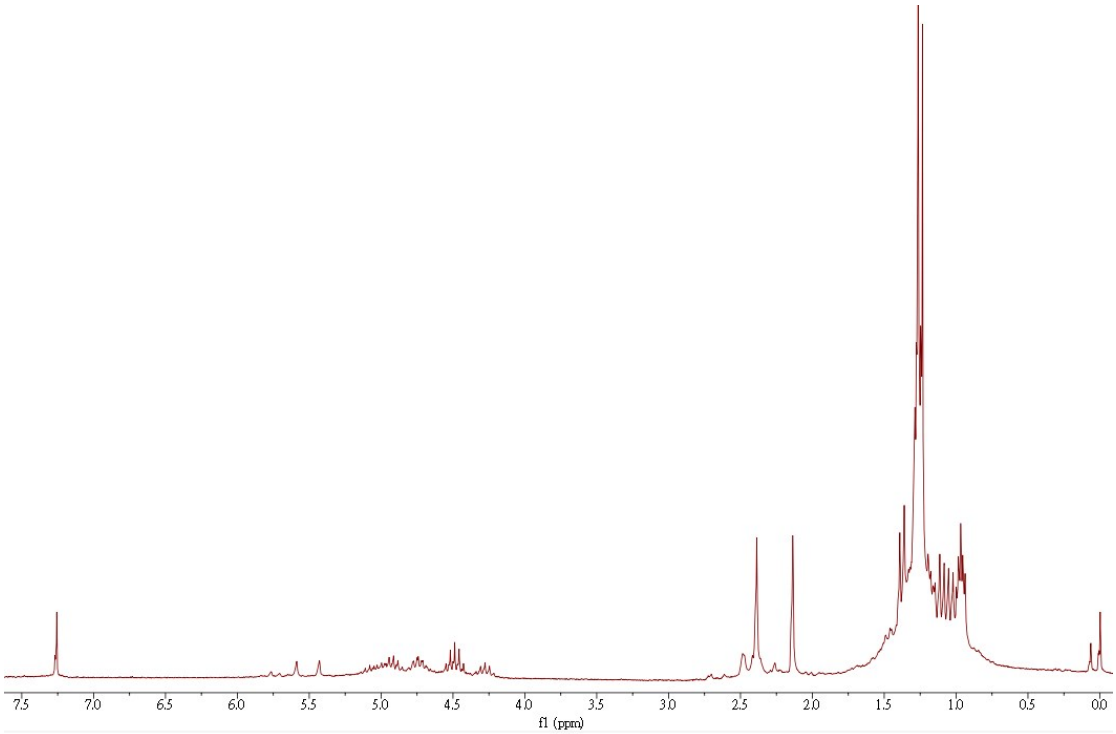

Figure S3. ^{1}H NMR spectrum of $^{Me}Pz_2Ti_2O^{i}Pr_7$ in $CDCl_3$

Reference