

SUPPORTING INFORMATION FOR:

Recent progress in calcium-catalysed polyester synthesis

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Table S1. Reported catalytic results of calcium compounds **1–46** in the ROP of cyclic esters.

Catalyst	Substrate	Solvent	Temperature (°C)	TOF (h ⁻¹)	M _{n, exp} [<i>D</i>] (kDa)
1	TMC	-	86	1,286	-
2	<i>L</i> -LA	-	110	1,124	65.0 [1.02]
2	PDL	-	100	55	28.5 [1.70]
3	<i>rac</i> -LA	THF	20	480	48.2 [1.60]
4	<i>rac</i> -LA	THF	25	194	26.9 [1.19]
5	<i>L</i> -LA	CH ₂ Cl ₂	30	160	90.7 [1.48]
6	<i>L</i> -LA	toluene	30	248	28.5 [1.16]
7	<i>L</i> -LA	CH ₂ Cl ₂	30	119	34.3 [1.22]
8	<i>L</i> -LA	toluene	rt	240	32.4 [1.22]
9	<i>L</i> -LA	CH ₂ Cl ₂	30	25	14.6 [1.43]
10	<i>rac</i> -LA	THF	25	33	13.2 [1.26]
11	<i>rac</i> -LA	THF	25	61	5.35 [1.79]
11	ε-CL	THF	23	8,000	18.6 [1.59]
12	<i>rac</i> -LA	THF	25	38	15.1 [1.36]
13	<i>rac</i> -LA	toluene	20	95	11.4 [1.55]
13	ε-CL	toluene	20	360,000	100.2 [2.11]
14	<i>rac</i> -LA	THF	25	37	12.8 [1.43]
15	<i>L</i> -LA	toluene	70	744	22.8 [1.40]
16	ε-CL	toluene	25	119	85.8 [1.61]
17	ε-CL	CH ₂ Cl ₂	25	5,580	32.0 [1.53]
18	ε-CL	CH ₂ Cl ₂	40	1,092	36.7 [1.53]
19	<i>rac</i> -LA	toluene	20	317	109.3 [2.06]
19	ε-CL	toluene	20	-	111.4 [2.34]
20	ε-CL	CH ₂ Cl ₂	30	1,188	12.0 [1.14]
20	<i>L</i> -LA	THF	25	168	13.0 [1.43]
21	<i>L</i> -LA	THF	20	90	14.4 [1.43]
22	<i>L</i> -LA	THF	20	4	47.5 [1.74]
23	<i>L</i> -LA	-	20	16,600	22.8 [1.07]
24	<i>L</i> -LA	toluene	20	13,950	17.2 [1.25]
25	<i>L</i> -LA	toluene	30	26,100	10.8 [1.17]
26	<i>rac</i> -LA	toluene	25	19	8.4 [2.42]

Table S1. (Continued)

Catalyst	Epoxide	Solvent	Temperature (°C)	TOF (h⁻¹)	M_{n, exp} [<i>Đ</i>] (kDa)
27	ϵ -CL	toluene	60	6.8	26.0 [1.30]
28	<i>L</i> -LA	toluene	60	28,200	6.5 [1.27]
29	<i>L</i> -LA	toluene	30	696	22.2 [1.67]
30	<i>rac</i> -LA	THF	rt	570	3.0 [1.80]
31	<i>rac</i> -LA	toluene	60	3,077	4.8 [1.51]
32	<i>L</i> -LA	THF	23	5.3	13.8 [1.35]
32	ϵ -CL	THF	23	294	28.5 [1.31]
33	ϵ -CL	toluene	25	1920	31.0 [1.75]
34	<i>rac</i> -LA	toluene	25	196	74.1 [1.64]
35	<i>rac</i> -LA	toluene	25	248	70.8 [1.34]
36	<i>rac</i> -LA	toluene	25	495	74.1 [1.64]
37	<i>rac</i> -LA	toluene	25	5520	128.7 [1.57]
38	ϵ -CL	toluene	25	39,376	83.7 [2.47]
38	ϵ -CL	toluene	25	29,403	43.1 [1.44]
38	<i>L</i> -LA	toluene	25	194	24.1 [1.17]
39	<i>rac</i> -LA	THF	rt	10,800	37.8 [1.74]
40	<i>rac</i> -LA	THF	rt	-	40.1 [1.68]
41	<i>L</i> -LA	THF	rt	1.5	3.37 [1.60]
42	<i>rac</i> -LA	THF	rt	1536	162.0 [1.50]
43	<i>rac</i> -LA	THF	rt	1536	181.5 [1.60]
44	<i>meso</i> -LA	toluene	25	196	18.0 [1.63]
45	ϵ -CL	THF	23	1,500	33.2 [1.47]
46	<i>rac</i> -LA	THF	23	130	10.1 [1.19]

Table S2. Reported catalytic results of calcium compounds **47–50** in the ROCOP of epoxides and cyclic anhydrides.

Catalyst	Epoxide	Cyclic anhydride	Solvent	T (°C)	TOF (h⁻¹)	Poly(ester) linkages (%)	M_{n, exp} [<i>Đ</i>] (kDa)
47	CHO	PA	-	100	62	>99	6.0 [1.08]
48	CHO	PA	-	100	25	>99	5.3 [1.11]
49	PO	PA	-	50	4	>99	4.6 [1.13]
50	CHO	PA	THF	65	4.1	>99	5.1 [1.10]
50	CHO	CA	THF	65	3.9	>99%	4.0 [1.20]
50	VCHO	PA	THF	65	3.9	>99%	4.4 [1.20]
50	VCHO	CA	THF	65	3.8	>99%	3.3 [1.40]
50	MUO	PA	THF	65	3.1	>99%	2.4 [1.30]
50	MUO	CA	THF	65	3	>99%	2.3 [1.40]