

Supporting Information

for

Comparison of Structurally Analogous Zn₂, Co₂, and Mg₂ Catalysts for the Polymerization of Cyclic Esters

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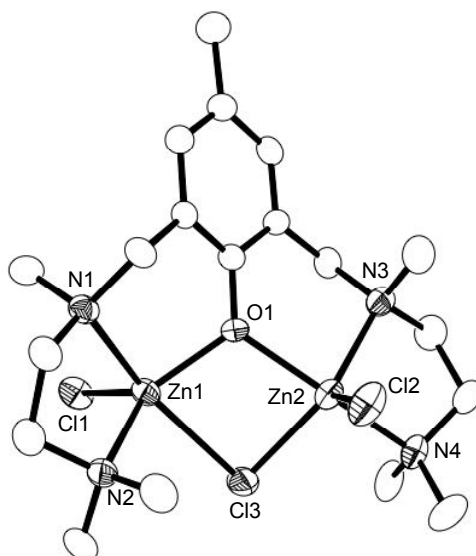


Figure S1. Representation of the X-ray crystal structure of LZn₂Cl₃, showing all nonhydrogen atoms as 50% thermal ellipsoids.

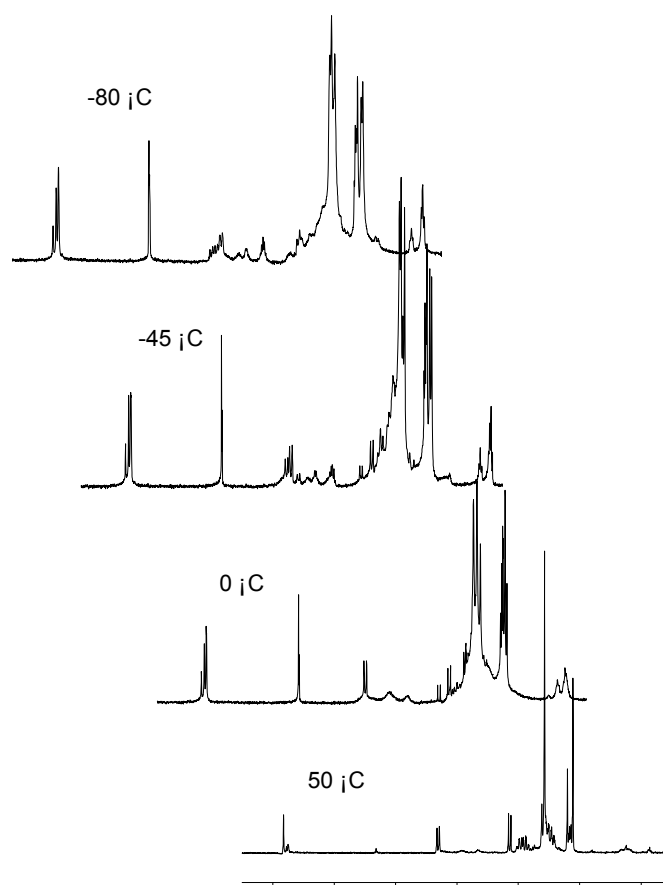


Figure S2. Representative variable temperature ¹H NMR spectra of **1** in CD₂Cl₂ (300 Mhz).

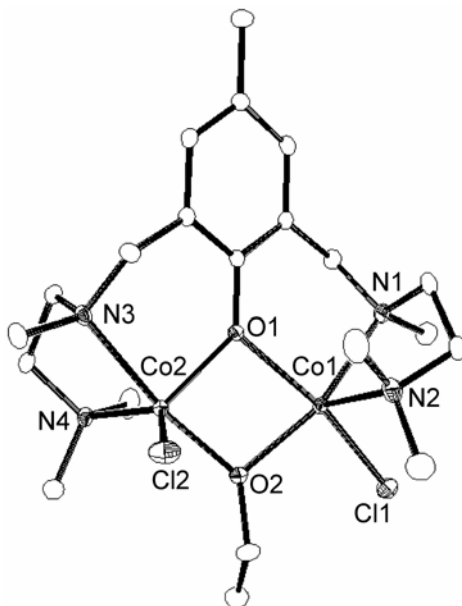


Figure S3. Representation of the X-ray crystal structure of **2**. All atoms except hydrogens are shown as 50% thermal ellipsoids.

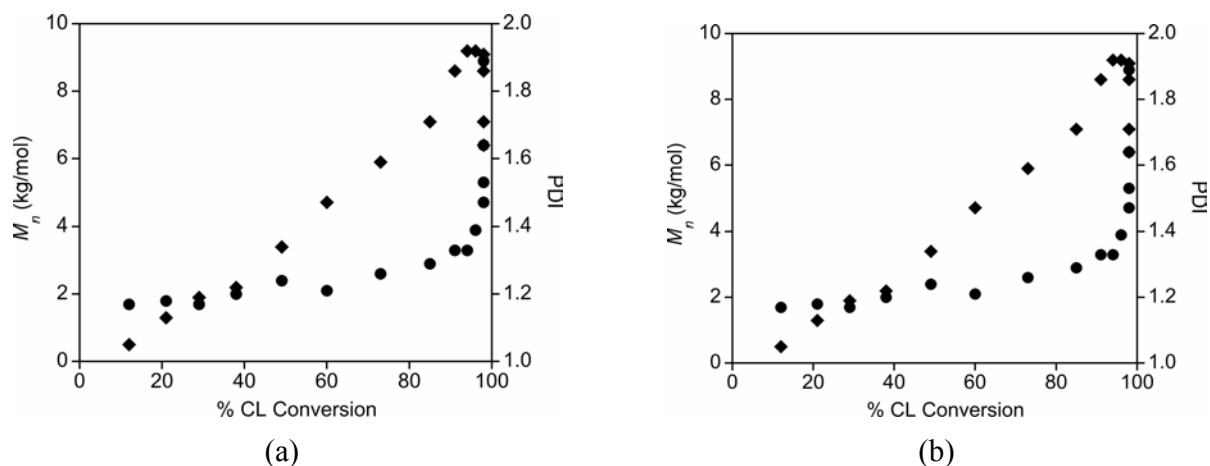


Figure S4. Plots of M_n (vs. polystyrene standards, diamonds) and PDI (circles) versus conversion for the polymerization of CL by (a) **2** or (b) **3**. Conditions: $[CL]_0 = 1$ M, $[2]_0 = 0.025$ M, $[3]_0 = 0.019$ M THF, 25 °C.

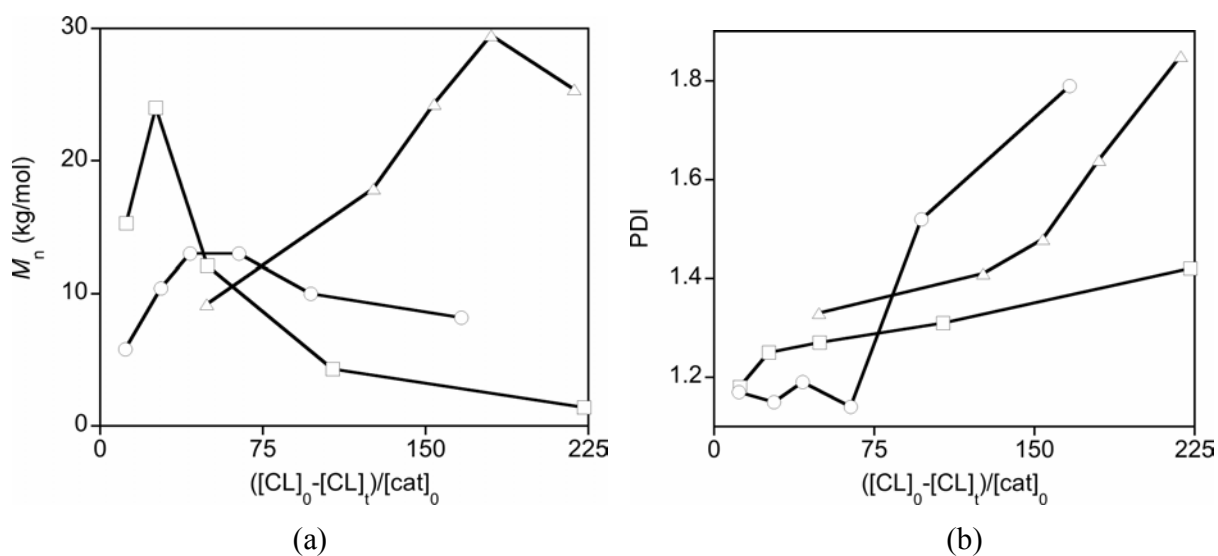


Figure S5. Dependence of (a) M_n (vs. polystyrene standards) and (b) PDI on $([CL]_0 - [CL]_t)/[cat]_0$ for the polymerization of CL by **1** (squares), **2** (circles), or **3** (triangles). Conditions: $[CL]_0 = 1$ M, THF, 25 °C.

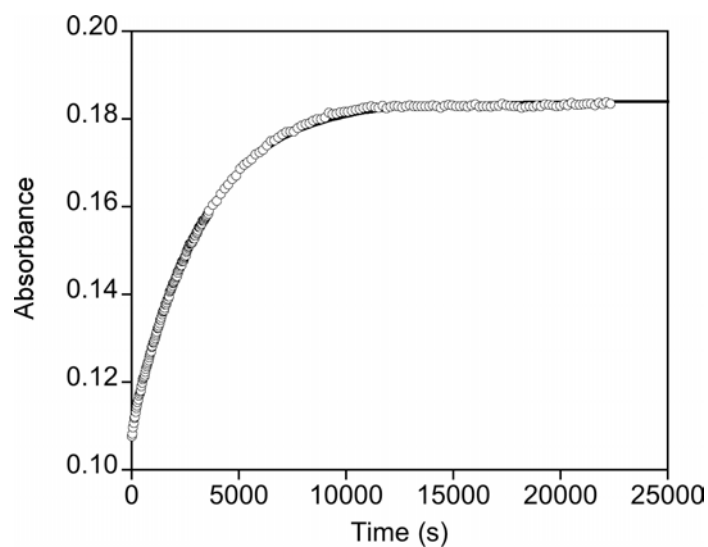


Figure S6. Illustrative time course for the polymerization of CL by **3** as monitored by ReactIR (PCL growth at 1206 cm^{-1}). Conditions: $[3]_0 = 10$ mM, $[CL]_0 = 1$ M, THF, 25 °C. The fit shown is to the first order equation $(A_0 - A_\infty)\exp(-kt) + A_\infty$, and yields $k_{\text{obs}} = 3.1 \times 10^{-4}\text{ s}^{-1}$ ($R = 0.9994$).

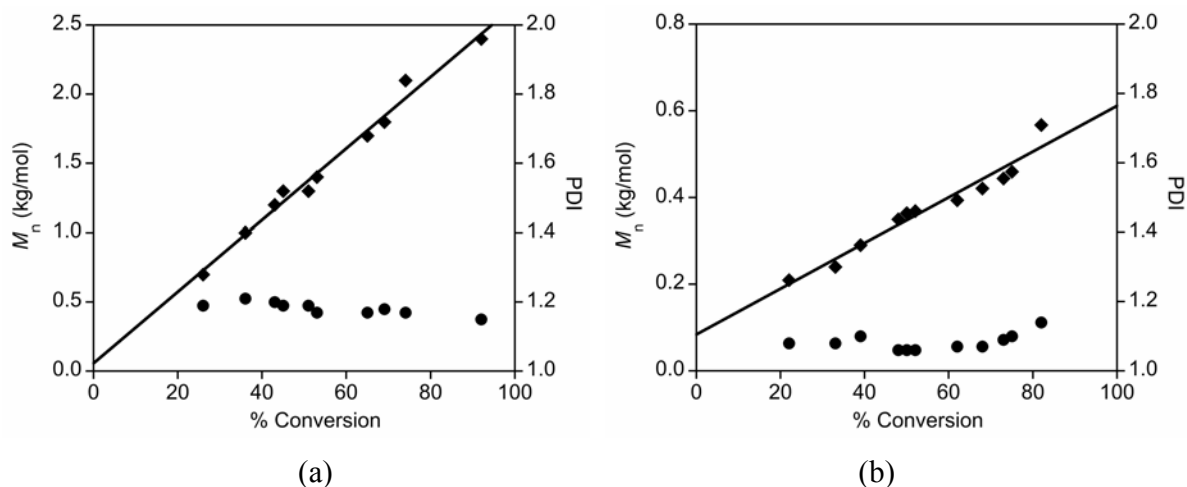


Figure S7. Plot of M_n (diamonds) and PDI (circles) vs. conversion for the polymerization of LA by (a) **2** and (b) **3**. Conditions: $[LA]_0 = 1$ M, CH_2Cl_2 , 25 °C, $[2]_0 = 100$ mM, $[3]_0 = 200$ mM.

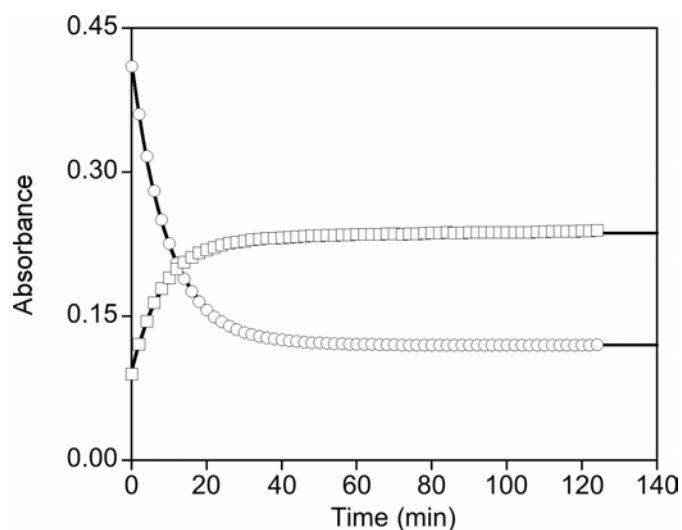


Figure S8. Illustrative time course for the polymerization of LA by **1** as monitored by ReactIR (PLA growth at 1131 cm^{-1} and LA decay at 1240 cm^{-1}). Conditions: $[1]_0 = 5$ mM, $[LA]_0 = 1$ M, CH_2Cl_2 , 25 °C. The fits shown are to the first order equation $(A_0 - A_\infty)\exp(-kt) + A_\infty$, and yield $k_{obs} = 1.8 \times 10^{-3} s^{-1}$ ($R = 0.997$, PLA growth) and $k_{obs} = 1.7 \times 10^{-3} s^{-1}$ ($R = 0.999$, LA decay).

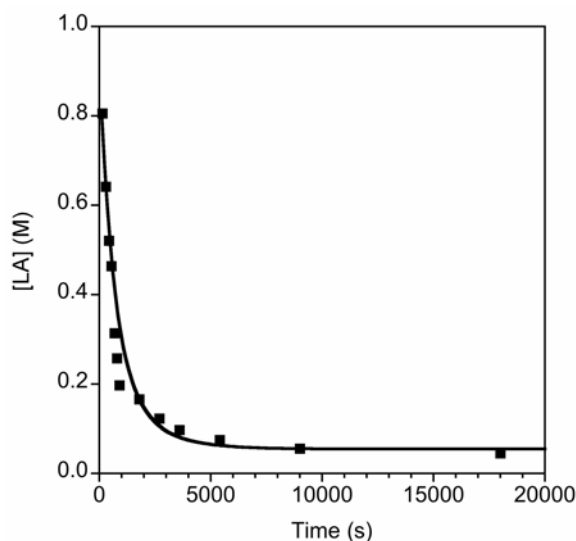
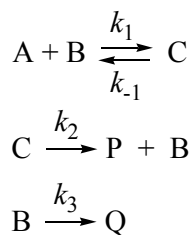


Figure S9. Plot of time course for LA polymerization catalyzed by **2** using $[2]_0 = 300$ mM. The data were collected by ^1H NMR spectroscopy. Conditions: $[\text{LA}]_0 = 1$ M, CH_2Cl_2 , 25 °C. The line is a simulation of the data constructed using the program KINTEKSIM and the following kinetic model:



where A = LA, B = M-OR (the catalytically active species), C = the adduct between M-OR and LA, P = the polymer chain (increased in length by one LA subunit), and Q = deactivated catalyst. The rate constants that yield the simulation shown are $k_1 = 300 \text{ M}^{-1}\text{s}^{-1}$, $k_{-1} = 1000 \text{ s}^{-1}$, $k_2 = 0.02 \text{ s}^{-1}$, and $k_3 = 0.0006 \text{ s}^{-1}$. Simulations that did not include the catalyst deactivation step did not accurately replicate the data at long reaction times. Simulations of data acquired using $[3]_0$ or different values for $[2]_0$ were of poorer quality and yielded inconsistent values for the rate constants. As a result, only initial rate data were analyzed as described in the text.

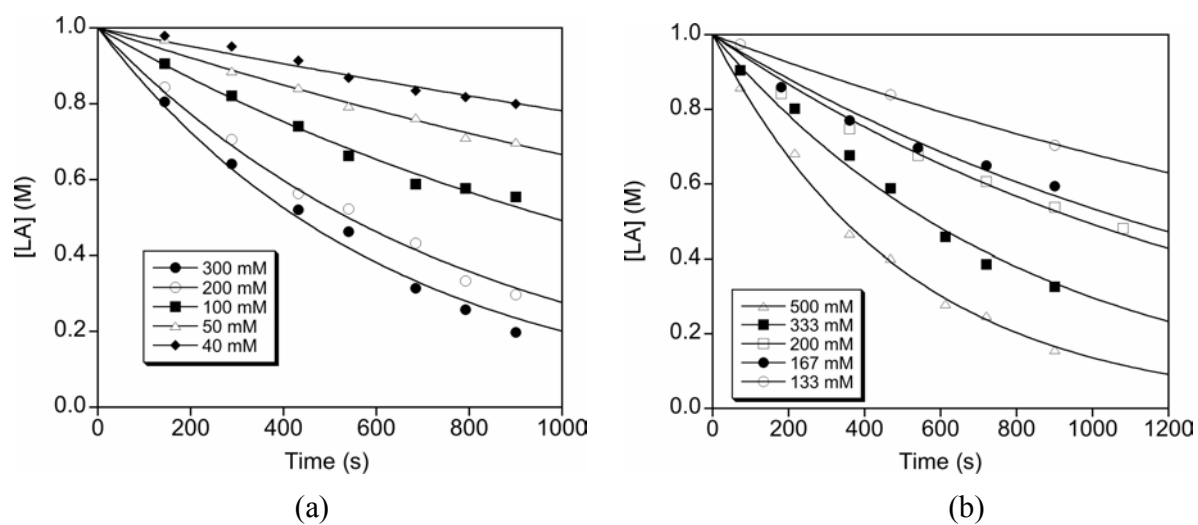


Figure S10. Initial rate data for the polymerization of LA by (a) **2** and (b) **3**, for the values of $[2]_0$ and $[3]_0$ shown. Conditions: $[LA]_0 = 1$ M, CH_2Cl_2 , 25 °C. The indicated fits are to the first order exponential $[LA]_t = \exp(-k_{obs}t)$, and yield k_{obs} values that are plotted in Figure 6.