

Supporting information for

β -Diketimate Aluminum Complexes: Synthesis,
Characterization and Ring-Opening
Polymerization of Cyclic Esters

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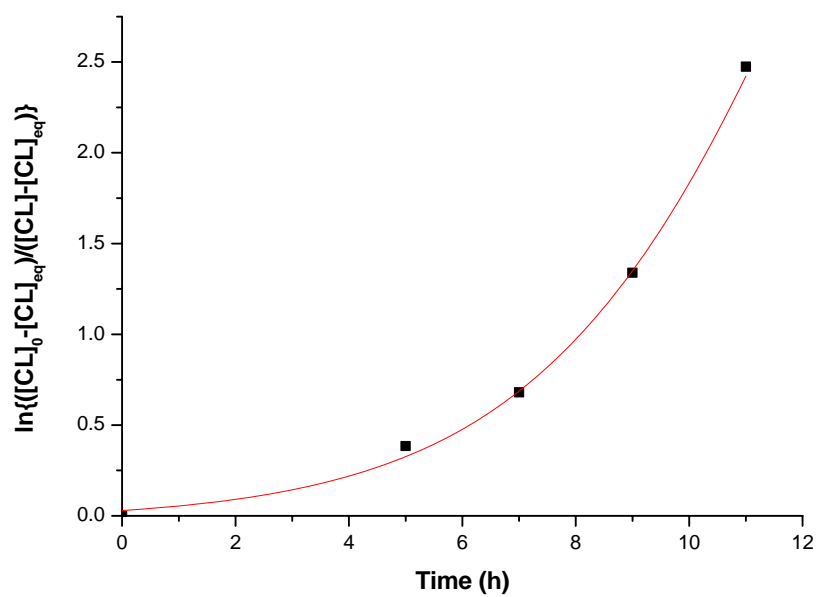


Figure S1. Kinetics of ϵ -caprolactone polymerization initiated with complex **3a**. $[\epsilon\text{-CL}]_0/[\text{Al}]_0 = 100$, $[\epsilon\text{-CL}]_0 = 1.0$ M, toluene, 80 °C.

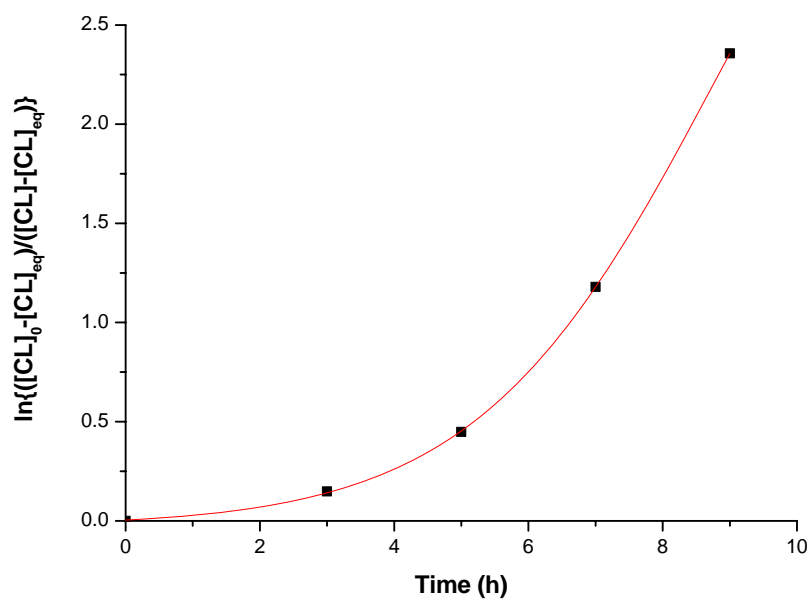


Figure S2. Kinetics of ϵ -caprolactone polymerization initiated with complex **3e**. $[\epsilon\text{-CL}]_0/[\text{Al}]_0 = 100$, $[\epsilon\text{-CL}]_0 = 1.0$ M, toluene, 80 °C.

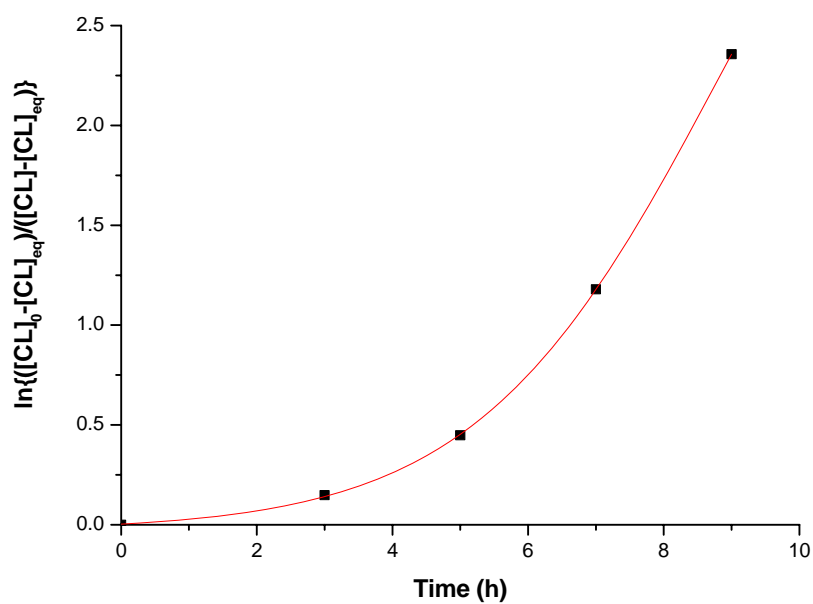


Figure S3. Kinetics of ϵ -caprolactone polymerization initiated with complex **3f**. $[\epsilon\text{-CL}]_0/[Al]_0 = 100$, $[\epsilon\text{-CL}]_0 = 1.0$ M, toluene, 80 °C.

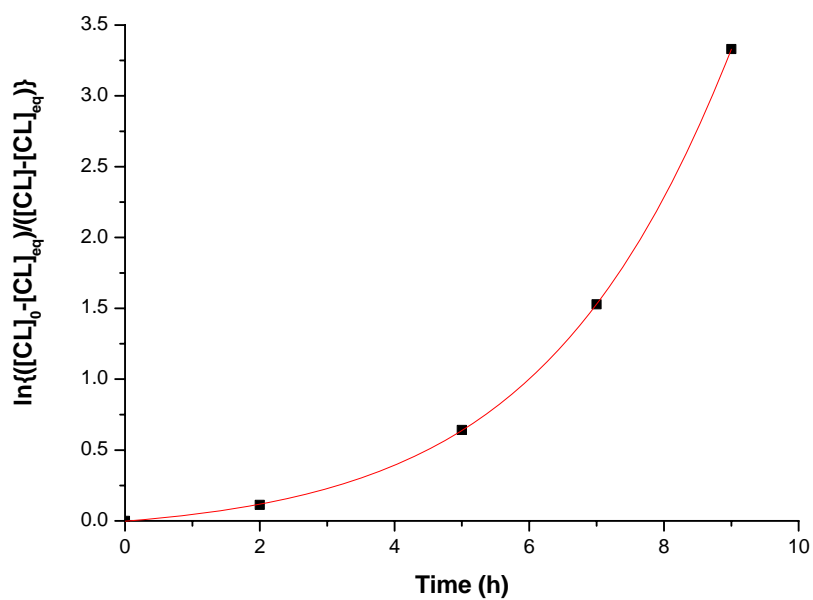
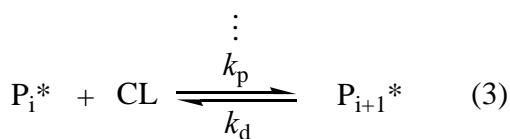
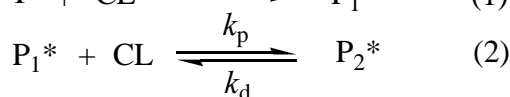
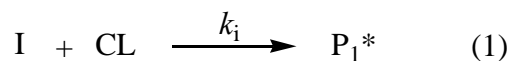


Figure S4. Kinetics of ϵ -caprolactone polymerization initiated with complex **3g**. $[\epsilon\text{-CL}]_0/[Al]_0 = 100$, $[\epsilon\text{-CL}]_0 = 1.0$ M, toluene, 80 °C.

Kinetic experiments were carried out under the same conditions as those in Table 4 with complexes **3a**, **3e**, **3f**, and **3g** as initiators respectively, monomer conversions were monitored by ^1H NMR at specified time intervals. The kinetic of ε -caprolactone polymerization was analyzed in terms of the following kinetic scheme,



where I stands for the initiator, P_i^* stands for the growing species with the polymerization degree equal to i. If we define $[\text{P}_n^*] = \sum([\text{P}_i^*])$, then $[\text{I}]_0 = [\text{I}] + [\text{P}_n^*]$. Since in all cases the semilogarithmic plots of $\ln\{([\text{CL}]_0 - [\text{CL}]_{\text{eq}})/([\text{CL}]_t - [\text{CL}]_{\text{eq}})\}$ versus time indicate a very slow initiation step, we further assume that within a very short time interval ($t \rightarrow 0$), $[\text{P}_n^*]$ keeps constant, thus the following set of differential equations can be deduced:

$$-d[\text{I}]/dt = k_i[\text{I}][\text{CL}] \quad (4)$$

$$-d[\text{CL}]/dt = k_i[\text{I}][\text{CL}] + k_p([\text{I}]_0 - [\text{I}])([\text{CL}] - [\text{CL}]_{\text{eq}}) \quad (5)$$

$$-d[\text{CL}]/dt = k_i([\text{I}]_0 - [\text{P}_n^*])[\text{CL}] + k_p[\text{P}_n^*]([\text{CL}] - [\text{CL}]_{\text{eq}}) \quad (6)$$

$[\text{P}_n^*]$ as the concentration of growing polymer chains can be calculated from the observed number of polymer chains----either by end group analysis with ^1H NMR spectroscopy or by GPC method, relative to the theoretical ones (assuming that each aluminum center initiates one polymer chain). However, due to the quite high molecular weights of obtained polymer samples or with polystyrene as standards, both methods can only give rough values of $[\text{P}_n^*]$, which causes serious errors during calculation, for example, negative value of k_i .