Electronic Supplementary Material (ESI) for Dalton Transactions


# Supporting Information

# Well-controlled ring-opening polymerization of cyclic esters initiated by dialkylaluminum β-diketiminates

**Di Li, Ying Peng*, Chao Geng, Kaipeng Liu, Dexu Kong**

State Key Laboratory of Fine Chemicals, School of Pharmaceutical Science and Technology, Dalian University of Technology, Dalian 116024, P. R. China.

E-mail: ypeng@dlut.edu.cn; Fax: +86-411-8498-6186

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# Contents

**Table S1** Activity table for ε-caprolactone polymerization initiators **2a–2h** in the absence of BnOH[a]

| Entry | Initiator | ε-CL/Al | Time | Conv.(%)[b] | $M_{cald}\times10^{-4}$ [c] | TOF/$h^{-1}$ [d] | Activity |
|---|---|---|---|---|---|---|---|
| 1 | **2a** | 100 | 2 h | 65 | 0.74 | 33 | poor |
| 2 | **2b** | 100 | 2 h | 90 | 1.03 | 45 | poor |
| 3 | **2c** | 100 | 30 min | 99 | 1.13 | 198 | good |
| 4 | **2d** | 100 | 2 h | 47 | 0.54 | 24 | poor |
| 5 | **2e** | 100 | 2 h | 94 | 1.07 | 47 | poor |
| 6 | **2f** | 100 | 2 h | trace | / | / | low |
| 7 | **2g** | 100 | 30 min | 90 | 1.03 | 180 | moderate |
| 8 | **2h** | 100 | 30 min | 99 | 1.13 | 198 | good |
| 16 | **2c** | 800 | 2 h | 93 | 8.49 | 47 | good |

[a] Polymerization conditions: ε-CL, 1.0 M, in toluene at 80 °C; Ar atmosphere. [b] Determined by $^1$H NMR spectroscopy. [c] $M_{Cald} = ([\varepsilon\text{-CL}]_0/[Al]_0) \times 114.14 \times$ conv.%. [d] TOF = number of molecules of a given product/((number of active sites)*(time)).

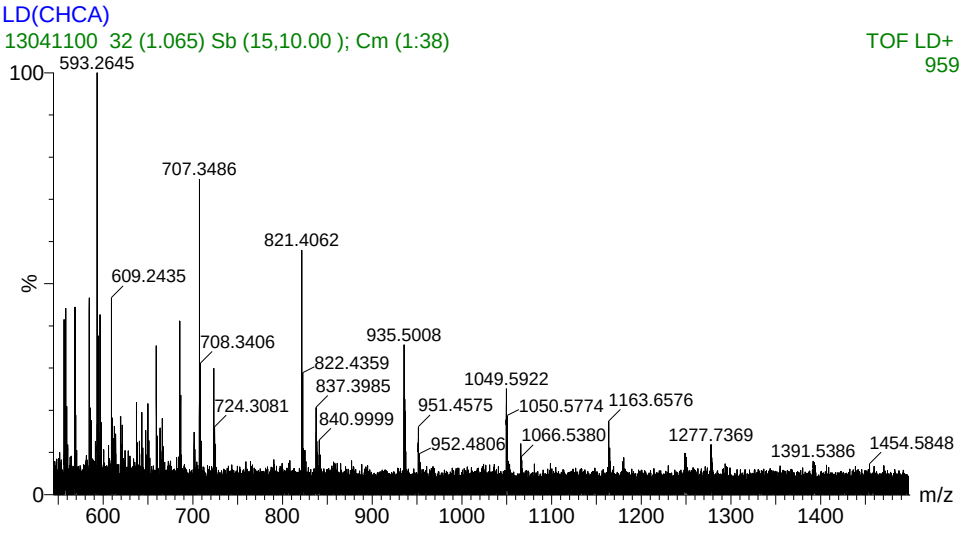


**Fig. S1** MALDI-TOF mass spectrum of PCL initiated by complex **2c** in toluene at 60 °C

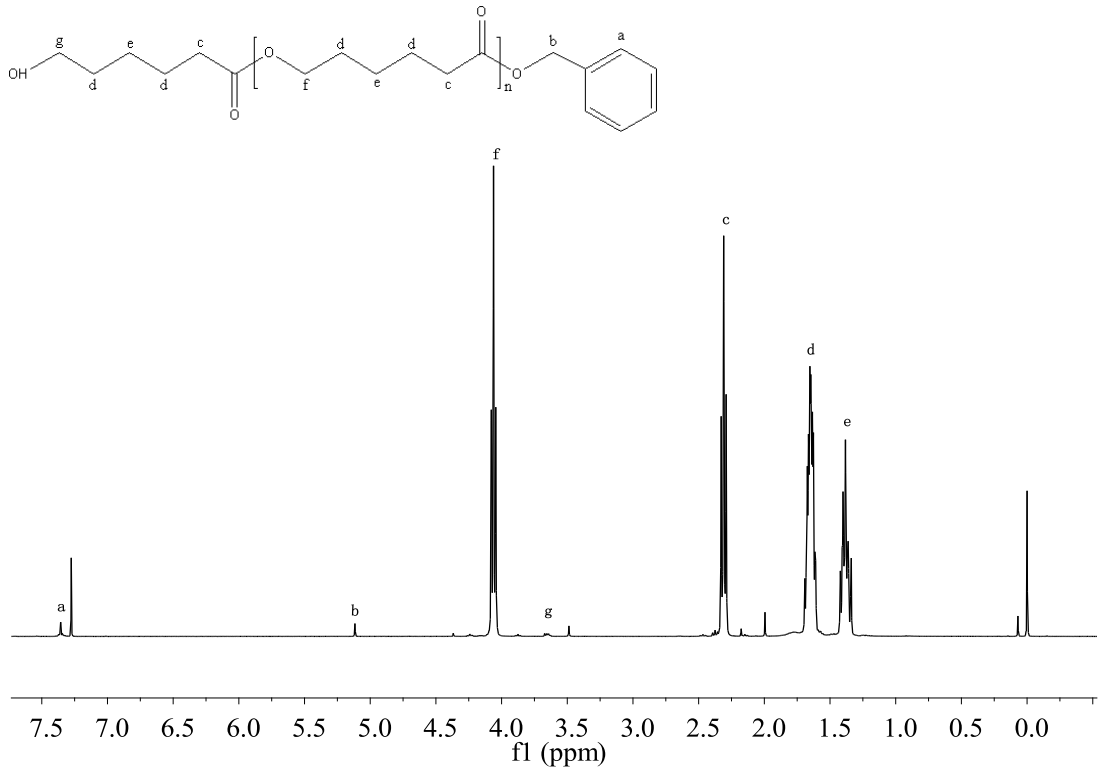


**Fig. S2** $^{1}$H NMR spectrum of PCL initiated by complex **2c**/BnOH in toluene at 80 °C after 30 min.