Kinetic Studies on Guanidine-Superbase-Promoted Ring-Opening Polymerization of ε-Caprolactone

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General consideration

All reactions were carried out under air atmosphere in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers. All solvents employed in the reactions were distilled from appropriate drying agents prior to use. Characterization $^1$H NMR (400 MHz) spectra were acquired using a Varian Inova 400 MHz NMR spectrometer. Tetramethylsilane was used as an internal reference with deuterated chloroform as solvent. Molecular weights and polydispersities ($M_w/M_n$; $M_w$: weight average molecular weight, $M_n$: number-average molecular weight) of polymers were determined on a gel permeation chromatograph (GPC, HLC-8320, Tosoh Corporation, Japan) equipped with two HLC-8320 columns (TSK gel Super AWM-H, pore size: 9μm; 6 × 150 mm, Tosoh Corporation) and a double-path, double-flow refractive index(RI) detector (Bryce) at 30 °C. The molecular weights were calculated according to relative calibration with polystyrene standards.

Typical procedure for polymerization reactions

TBD catalyzed ε-caprolactone polymerizations were conducted in flamed dried Schlenk-type glassware on a dual-manifold Schlenk line. In a typical polymerization, ε-CL (1.07 ml, 1 mmol) was added to a solution of TBD (69.6 mg, 0.05 mmol) and 1,4-butandiol (9 μl, 0.001 mmol) in 5mL of toluene under an argon atmosphere at 25 °C. The solution was stirred for 110 mins and directly quenched by addition of benzoic acid(2 mol equiv to base). Conversion was determined by $^1$H NMR= 95%. The polymer was precipitated several times from cold methanol and dried under vacuum until constant weight. $^1$H NMR (CDCl3): δ, 4.05(t, 34H, C(=O)OCH$_2$ PCL backbone), 3.64(t, 1H,CH$_2$OH), 2.30(t, 34H, CH$_2$C(=O)O PCL backbone), 1.69-1.58 (m, 70H, CH$_2$CH$_2$CH$_2$ PCL backbone),1.43-1.33 (m, 35H, CH$_2$CH$_2$CH$_2$ PCL backbone). The yield was 86.4%. GPC analysis calibrated with polystyrene standards: $M_n$=13300 g·mol$^{-1}$, PDI=1.28.
**Table S1** ROP of ε-CL at different reaction times using TBD:1,4-butandiol:ε-CL ratio of 5:2:100

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time (min)</th>
<th>Conv (%)</th>
<th>$M_n$</th>
<th>PDI</th>
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</table>

[a] Reactions were performed in 5 mL toluene.

[b] Measured by $^1$H NMR.

[c] Measured by GPC in THF.

**Table S2** ROP of ε-CL at different reaction times using TBD:1,4-butandiol:ε-CL ratio of 5:1:100

<table>
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<th>Conv (%)</th>
<th>$M_n$</th>
<th>PDI</th>
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<td>1.23</td>
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</table>

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Figure S4. Semilogarithmic plots of the monomer conversion stated as \(\ln([CL]_t/[CL]_0)\) versus the reaction time for the polymerization of \(\varepsilon\)-caprolactone at different concentration of TBD: \([CL]_0/[I]_0 = 100\); 1% TBD; 2% TBD; 5% TBD.
Figure S5. GPC traces for PCL produced at different [M]₀/[I]₀ at room temperature (Table 1, entries 3 – 7).

Figure S6. ln k vs. 1/T in Arrhenius plot to determine the apparent activation energy for ɛ-CL polymerization with n-butanol as the initiator in toluene.