**Supporting Information**

# Lipase-catalyzed ring opening copolymerization of ε-caprolactone and β-lactam

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**Percent yield calculation:**

Reaction: ε-CL + β-lactam → copolymer + poly(ε-CL) + poly(β-lactam)

**For 1:1 ratio of ε-CL and β-lactam**

mol ε-CL = mol β-lactam = 1.4 mmol

Due to 1:1, ratio mol repeating unit of copolymer = 1.4 mmol

Theoretical yield of copolymer = mol of repeating unit × molar mass of repeating unit

Theoretical yield of copolymer = $1.4 \times 10^{-3}$ mol × 185.12 g/mol = 0.2592 gram

Yield (%) = (actual yield/theoretical yield) × 100%

Yield (%) from experiment 1 = (0.1388/0.2592) × 100% = 53%

Yield (%) from experiment 2 = (0.1228/0.2592) × 100% = 47%

**Average yield (%) from duplicate experiments = (53% + 47%)/2 = 50%**

**For 1:3 or 3:1 ratio of ε-CL:β-lactam**

**a. For 1:3**

mol ε-CL = 0.7 mmol

mol β-lactam = 2.1 mmol

ε-CL act as limiting reagent, therefore mol repeating unit = mol ε-CL = 0.7 mmol

Theoretical yield = $0.7 \times 10^{-3}$ mol × 185.12 g/mol = 0.1296 gram

Yield (%) from experiment 1 = (0.0175/0.1296) × 100% = 13.5%

Yield (%) from experiment 2 = (0.0140/0.1296) × 100% = 10.8%

**Average yield (%) from duplicate experiments = (13.5% + 10.8%)/2 = 12.1%**

**b. For 3:1:**

mol ε-CL = 2.1 mmol

mol β-lactam = 0.7 mmol

β-lactam act as limiting reagent, therefore mol repeating unit = mol β-lactam = 0.7 mmol

Theoretical yield = $0.7 \times 10^{-3}$ mol × 185.12 g/mol = 0.1296 gram

Yield from experiment 1 (%) = (0.0625/0.1296) × 100% = 48%

Yield from experiment 2 (%) = (0.0519/0.1296) × 100% = 40%

**Average yield (%) from duplicate experiments = (48% + 40%)/2 = 44%**

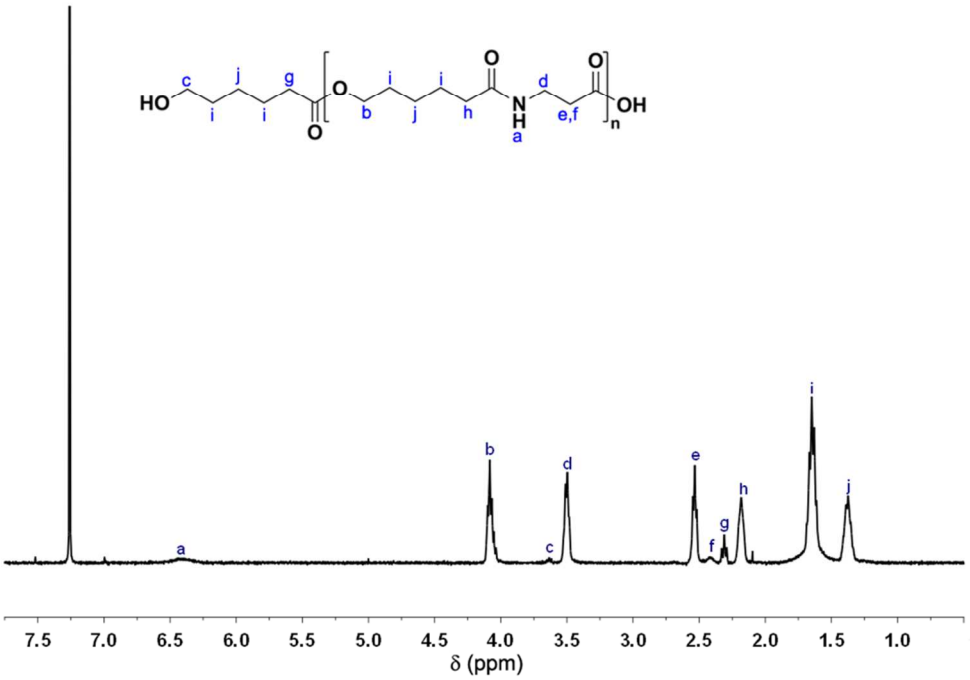



**Figure S1**. $^{1}$H NMR spectrum of poly(ε-CL-*co*-β-lactam) in $CDCl_3$

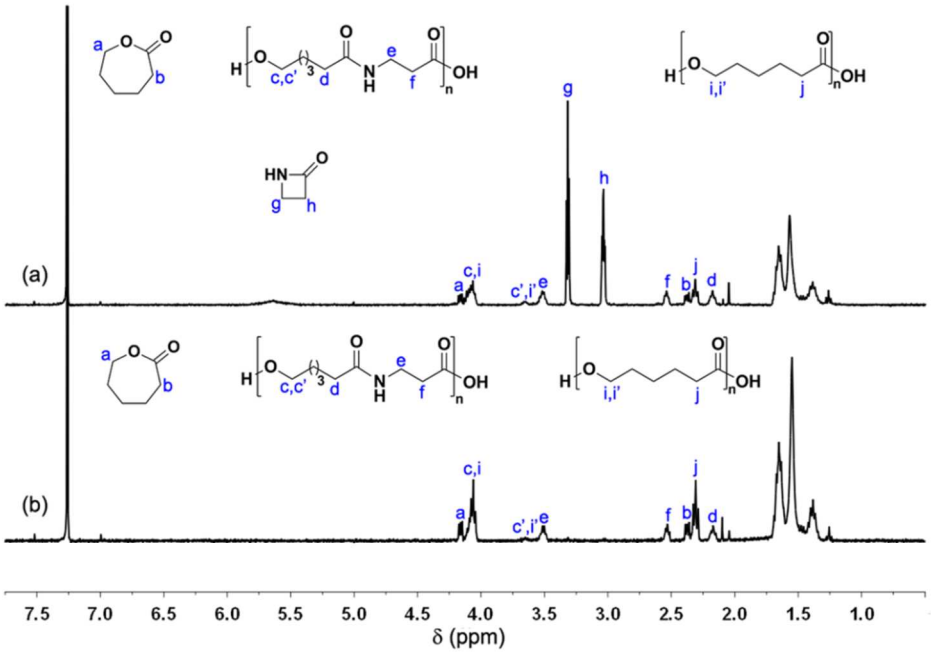



**Figure S2.** $^{1}$H NMR of the evaporated ethyl acetate fraction from the ring opening polymerization of ε-CL and β-lactam in different feed ratios of ε-CL:β-lactam (a) 25:75 and (b) 75:25

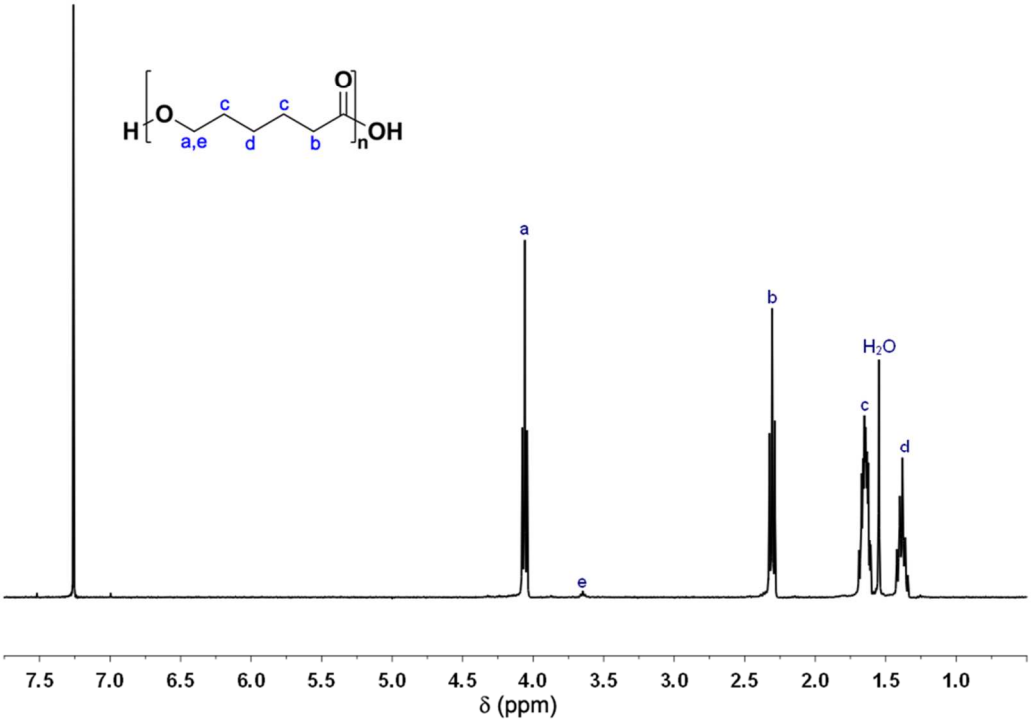



**Figure S3.** $^{1}$H NMR spectrum of poly(ε-caprolactone) in $CDCl_3$

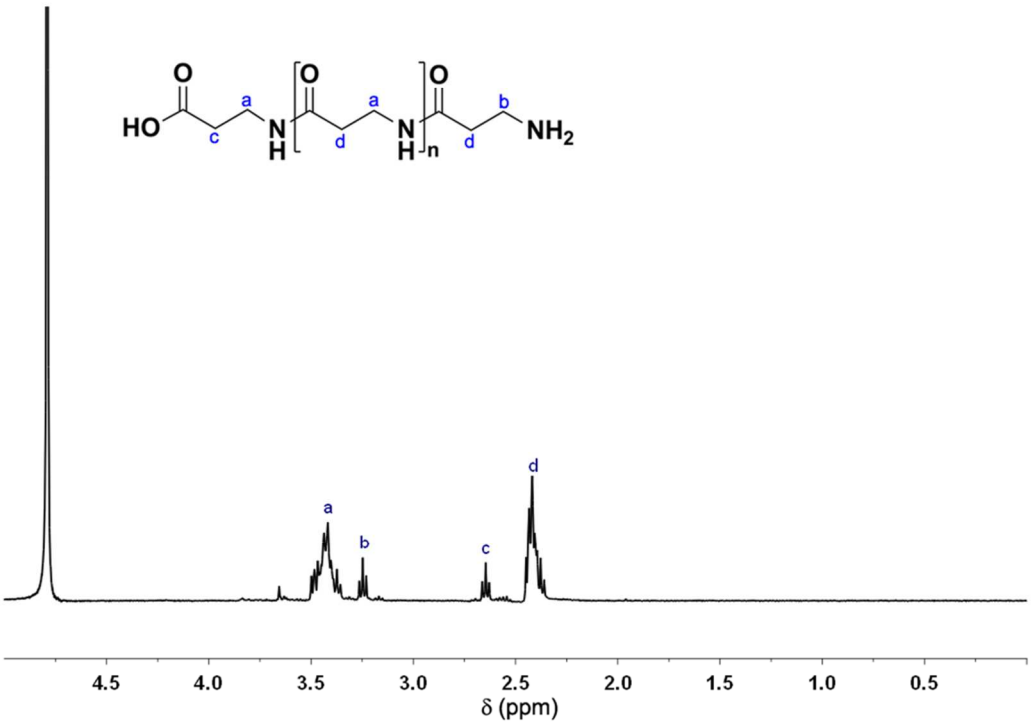



**Figure S4.** $^{1}$H NMR spectrum of poly(β-lactam) in $D_2O$

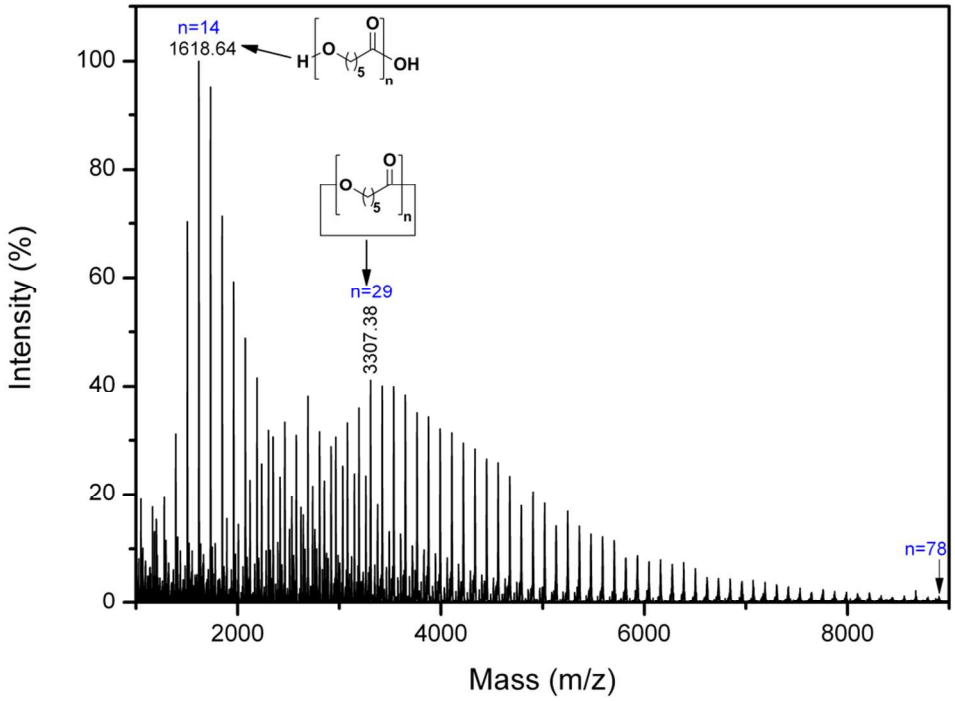



**Figure S5.** MALDI-ToF spectrum of poly(ε-caprolactone)

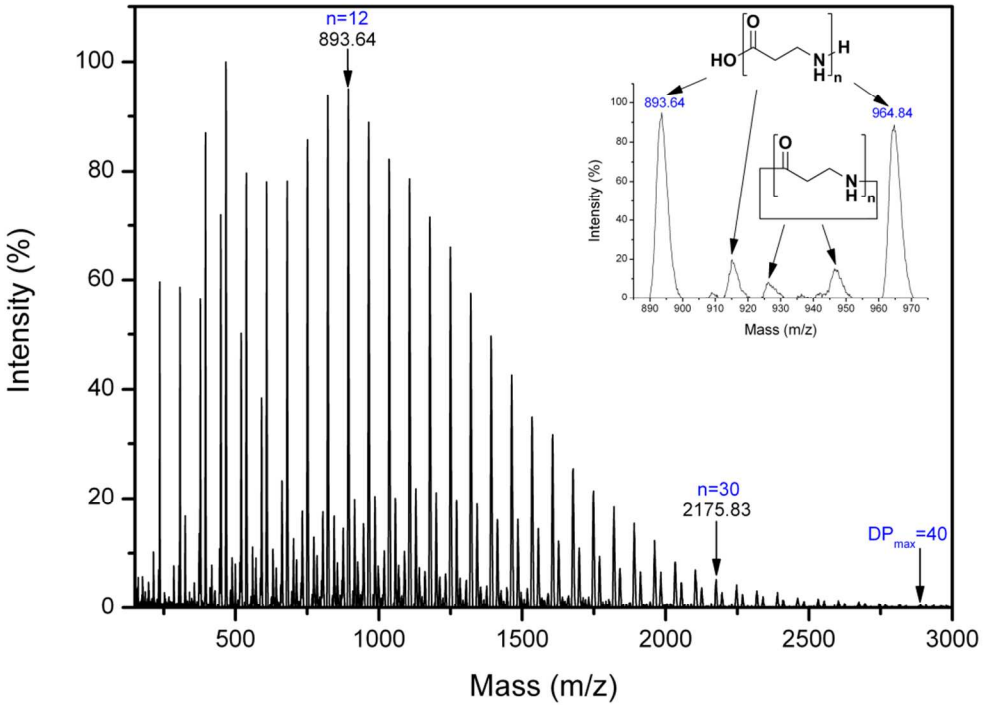



**Figure S6.** MALDI-ToF spectrum of poly(β-lactam)

**Table S1.** Structures of poly(ε-CL-*co*-β-lactam) resulted from the reaction with feed ratio 50:50 of ε-CL:β-lactam.

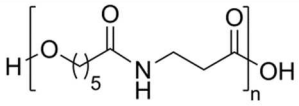
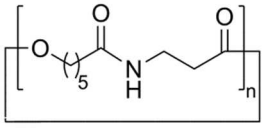
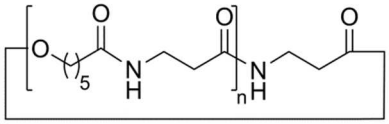
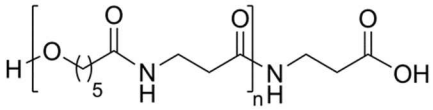
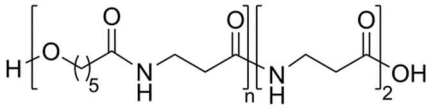
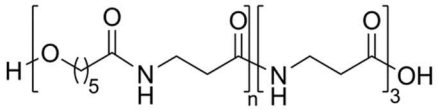
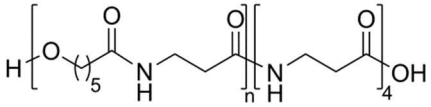
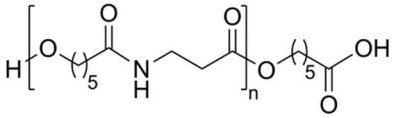
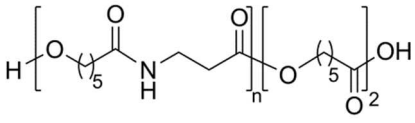
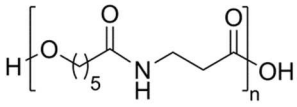
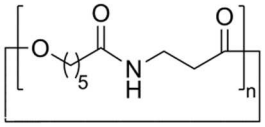
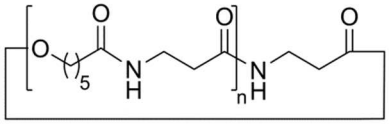
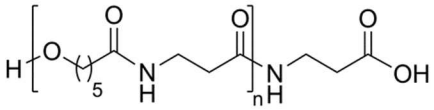
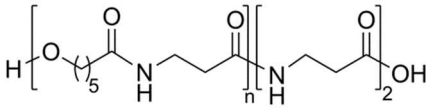
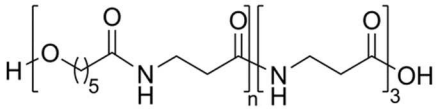
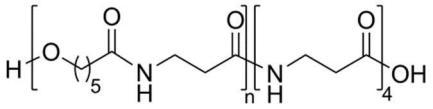
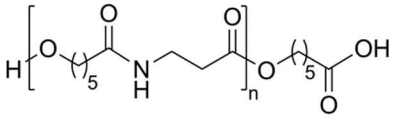
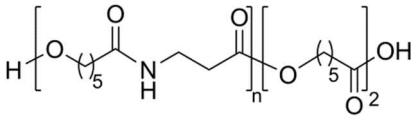
| Symbol adduct | Structures | Mass of end group (amu) |
|---|---|---|
| $H^+$ : ■<br>$Na^+$ : ■ |  | 18 |
| $H^+$ : ● |  | 0 |
| $H^+$ : ⊗ |  | 71 |
| $H^+$ : ◆ |  | 89 |
| $H^+$ : ▼ |  | 160 |
| $H^+$ : * |  | 231.1 |
| $H^+$ : ♥ |  | 302.2 |
| $H^+$ : ♠ |  | 132.1 |
| $H^+$ : ▲ |  | 246.1 |

**Table S2.** Structures list of the symbols for figure S8 and figure S9

| Symbol adduct | Structures | Mass of end group (amu) |
|---|---|---|
| $H^+$ : ■<br>$Na^+$ : ■ |  | 18 |
| $H^+$ : ● |  | 0 |
| $H^+$ : ⊗ |  | 71 |
| $H^+$ : ◆<br>$Na^+$ : ◆ |  | 89 |
| $H^+$ : ▼<br>$Na^+$ : ▼ |  | 160 |
| $H^+$ : ✻<br>$Na^+$ : ✻ |  | 231.1 |
| $H^+$ : ♥ |  | 302.2 |
| $H^+$ : ♠ |  | 132.1 |
| $H^+$ : ▲ |  | 246.1 |

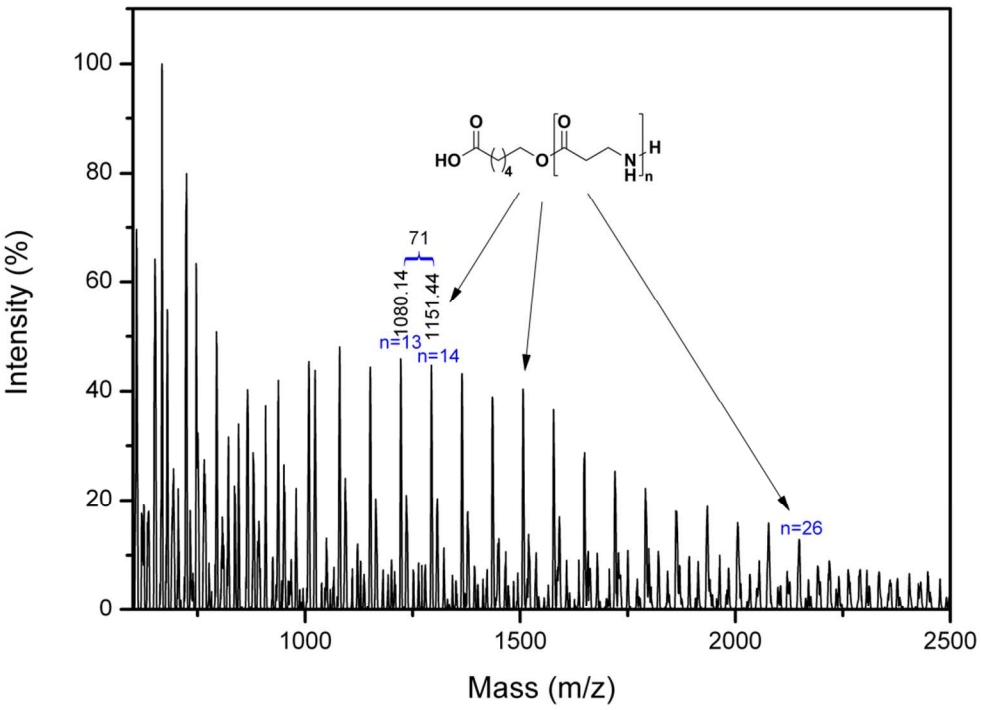



**Figure S7.** MALDI-ToF spectrum of the side product dissolved in formic acid

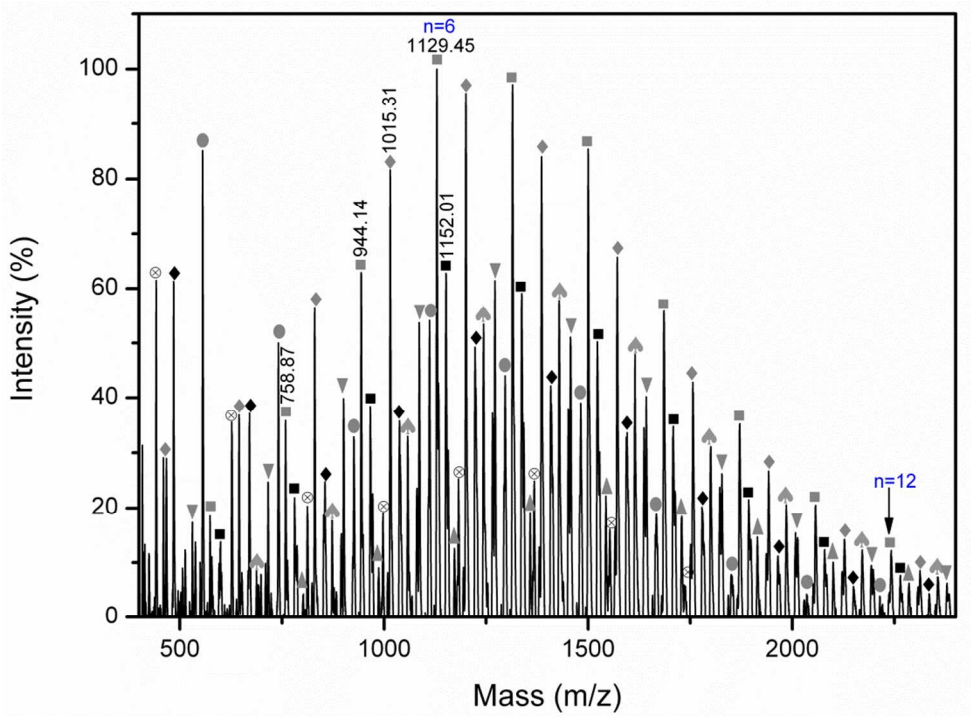



**Figure S8.** MALDI-ToF spectrum of poly(ε-CL-*co*-β-lactam) with addition of NaTFA

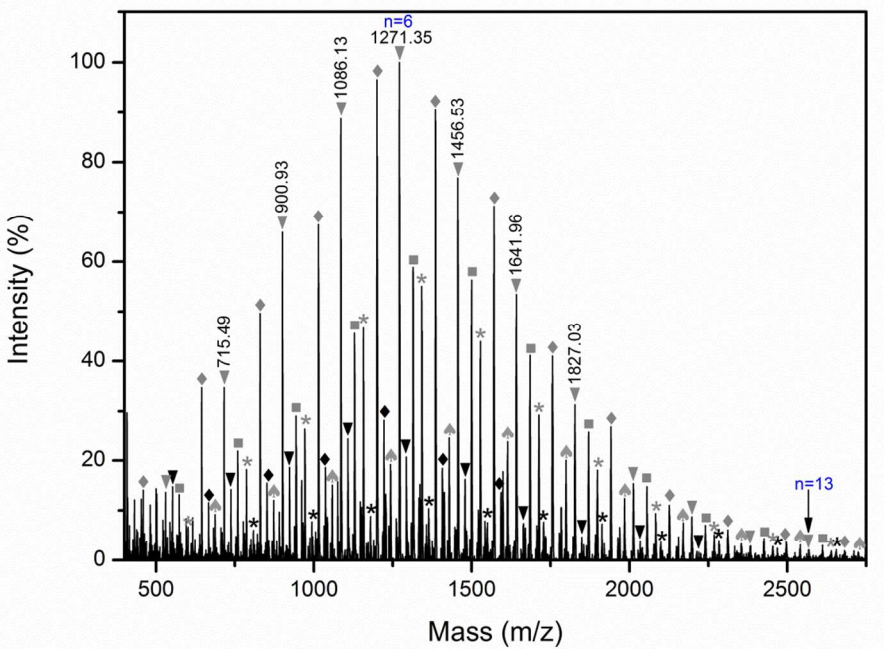



**Figure S9.** MALDI-ToF spectrum of poly(ε-CL-*co*-β-lactam) from the reaction with feed ratio 75:25 of β-lactam:ε-CL

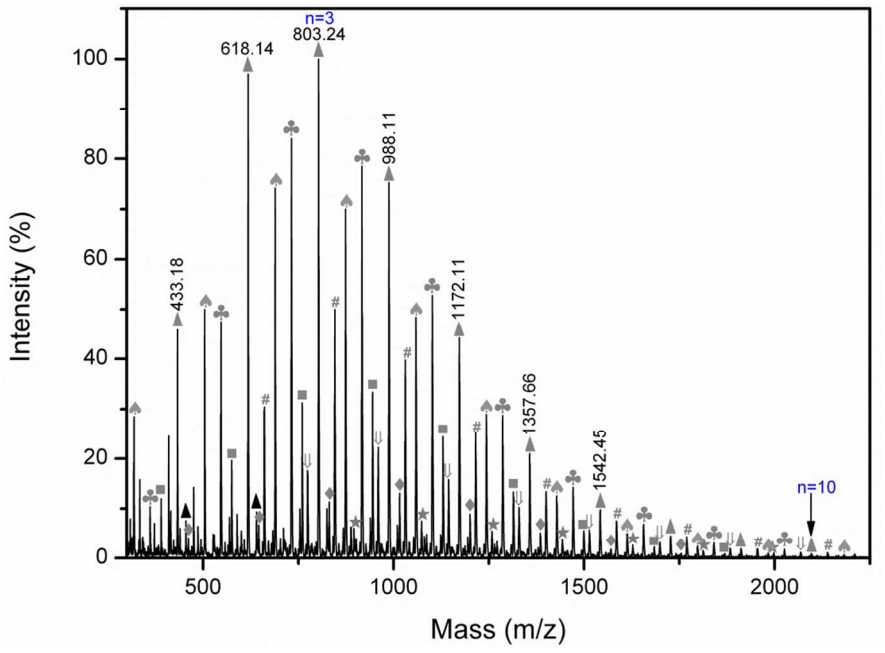
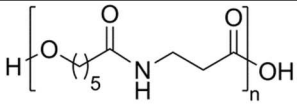
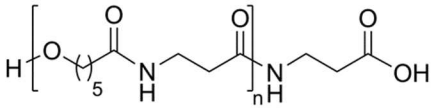
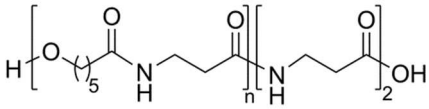
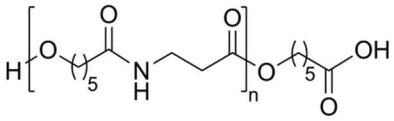
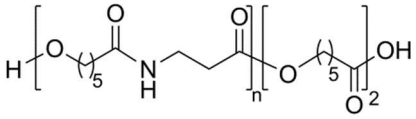
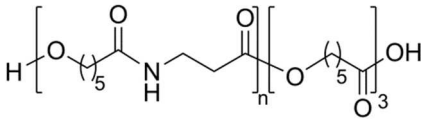
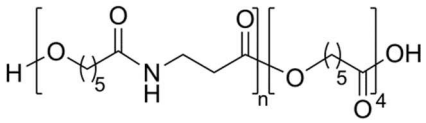
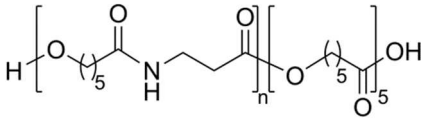
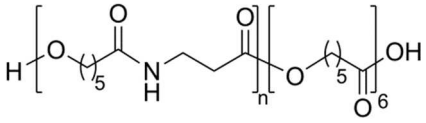
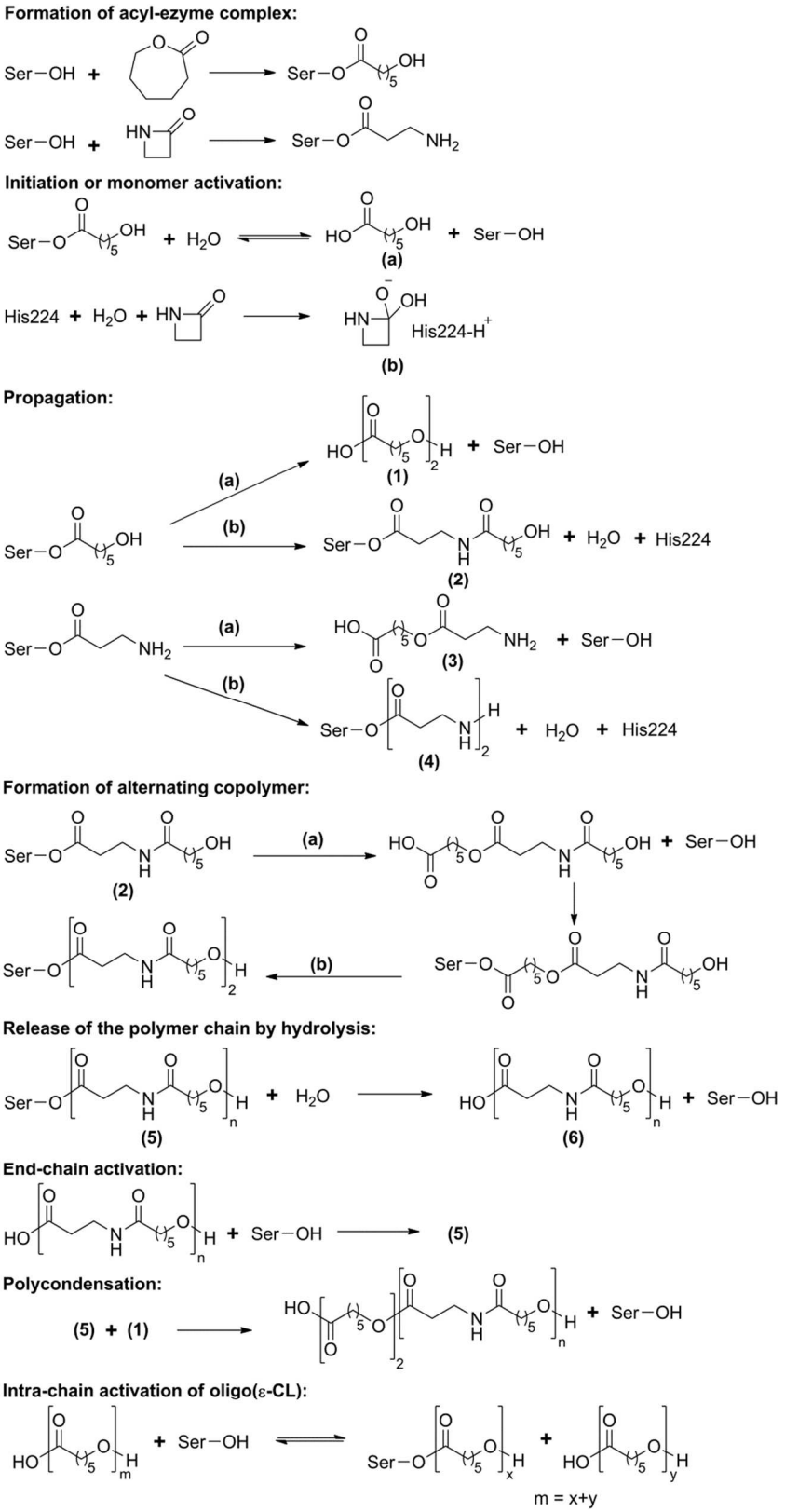



**Figure S10.** MALDI-ToF spectrum of poly(ε-CL-*co*-β-lactam) from the reaction with feed ratio 25:75 of β-lactam:ε-CL

**Table S3.** Structures of poly(ε-CL-*co*-β-lactam) from the reaction with feed ratio 25:75 of β-lactam:ε-CL

| Symbol adduct | Structures | Mass of end group (amu) |
|---|---|---|
| $H^+$ : ■ |  | 18 |
| $H^+$ : ◆ |  | 89 |
| $H^+$ : ▼<br>$Na^+$ : ▼ |  | 160 |
| $H^+$ : ♠ |  | 132.1 |
| $H^+$ : ▲<br>$Na^+$ : ▲ |  | 246.1 |
| $H^+$ : ♣ |  | 360.2 |
| $H^+$ : # |  | 474.2 |
| $H^+$ : ⇓ |  | 588.3 |
| $H^+$ : ★ |  | 702.4 |




**Scheme S1**. Proposed reaction mechanism of CAL-B-catalyzed formation of poly(ε-CL-*co*-β-lactam).

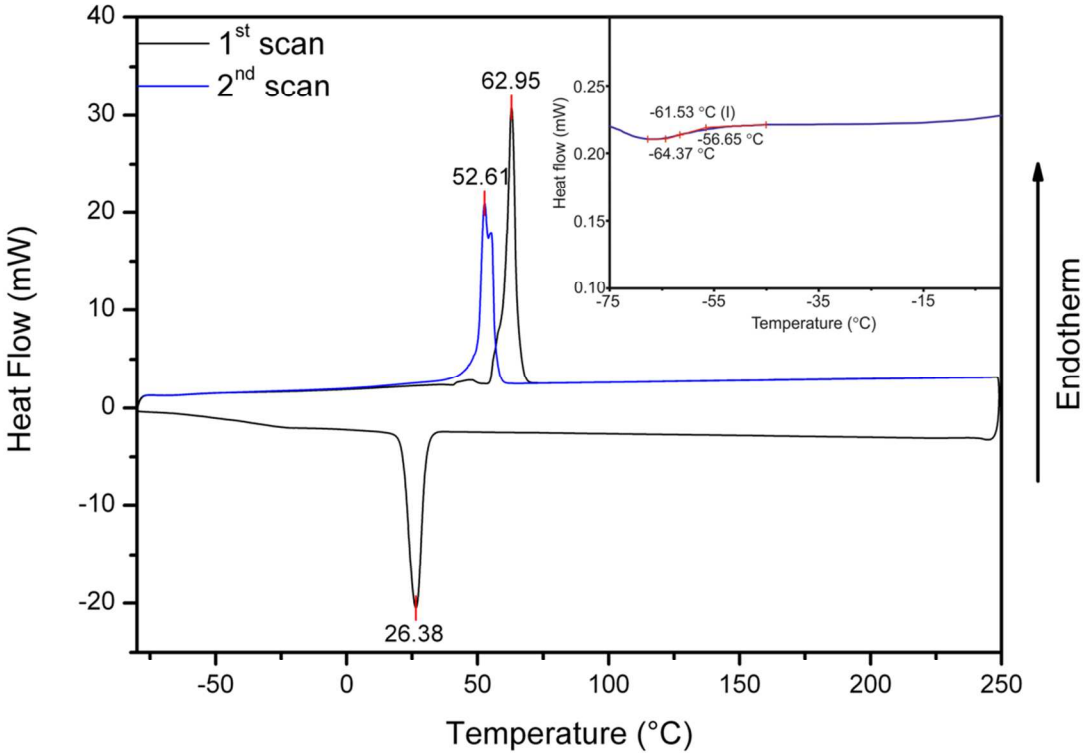



**Figure S11.** DSC curves of poly(ε-caprolactone)

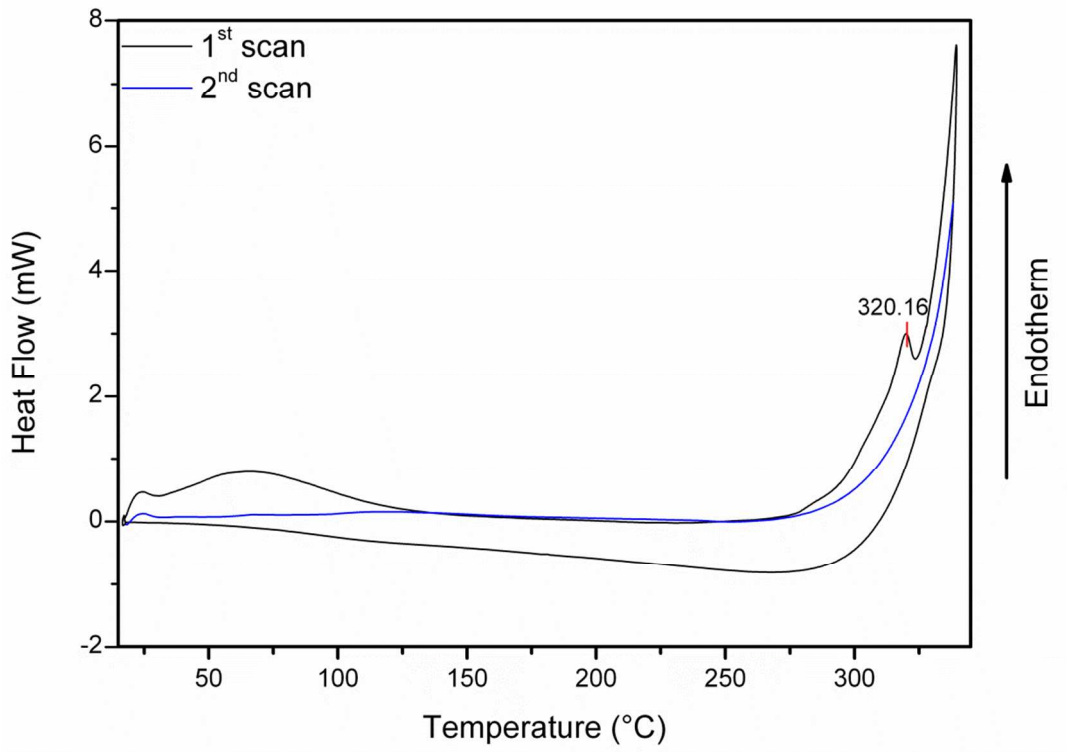



**Figure S12.** DSC curves of poly(β-lactam)