Lipase-Catalyzed Ring-Opening Copolymerization of ε-Caprolactone and β-Lactam

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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 = 1.4×10^{-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 = 0.7×10^{-3} mol $\times$ 185.12 g/mol = 0.1296 gram

Yield (%) from experiment 1 = (0.0175/0.1296) $\times$ 100% = 13.5%

Yield (%) from experiment 2 = (0.0140/0.1296) $\times$ 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 = 0.7×10^{-3} mol $\times$ 185.12 g/mol = 0.1296 gram

Yield from experiment 1 (%) = (0.0625/0.1296) $\times$ 100% = 48%

Yield from experiment 2 (%) = (0.0519/0.1296) $\times$ 100% = 40%

Average yield (%) from duplicate experiments = (48% + 40%)/2 = 44%
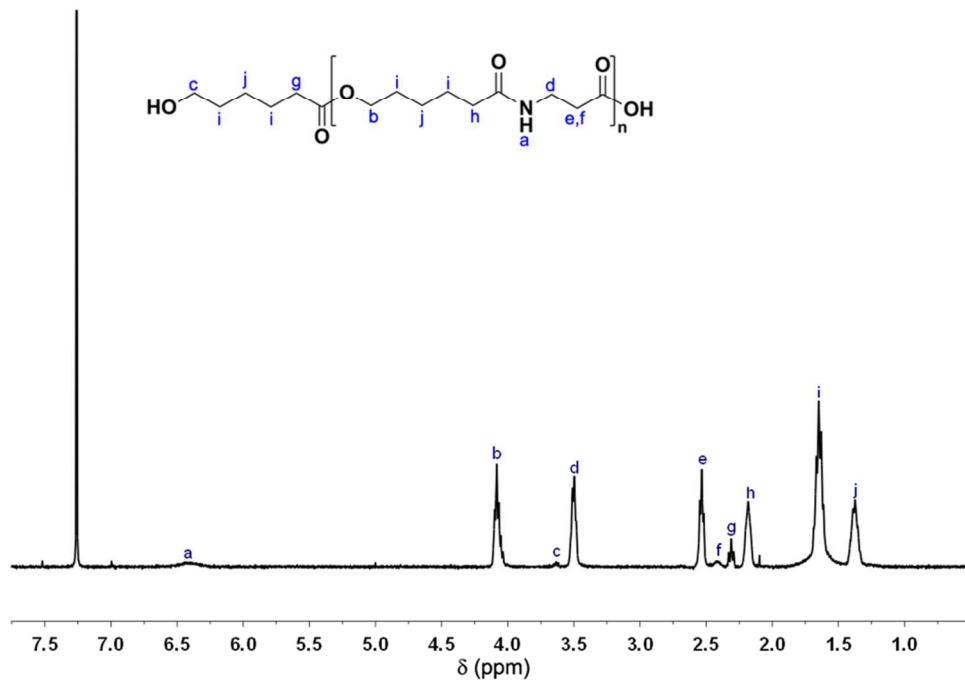
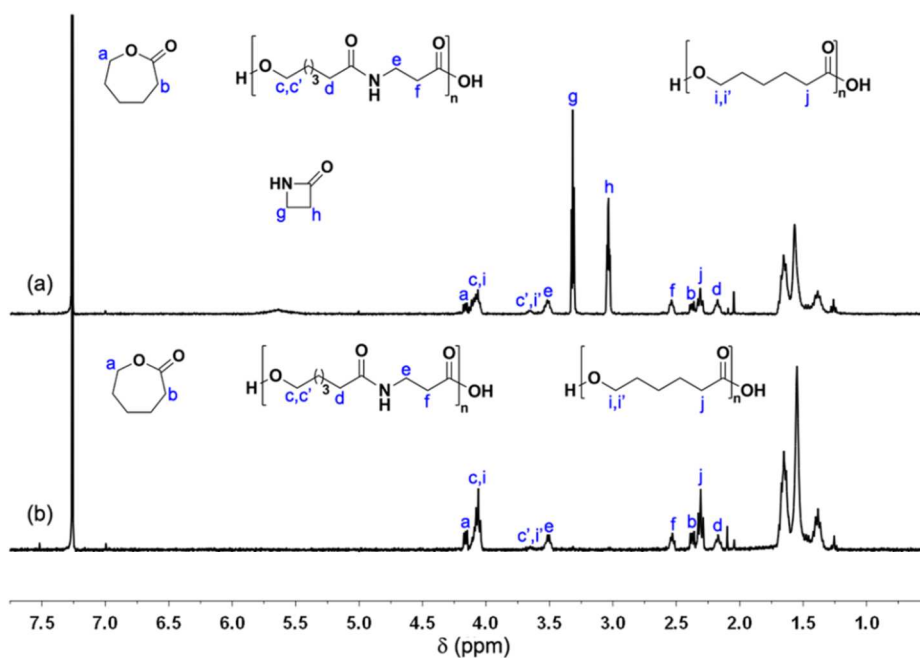**Figure S1**. ^{1}H NMR spectrum of poly(ε-CL-*co*-β-lactam) in CDCl$_3$

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
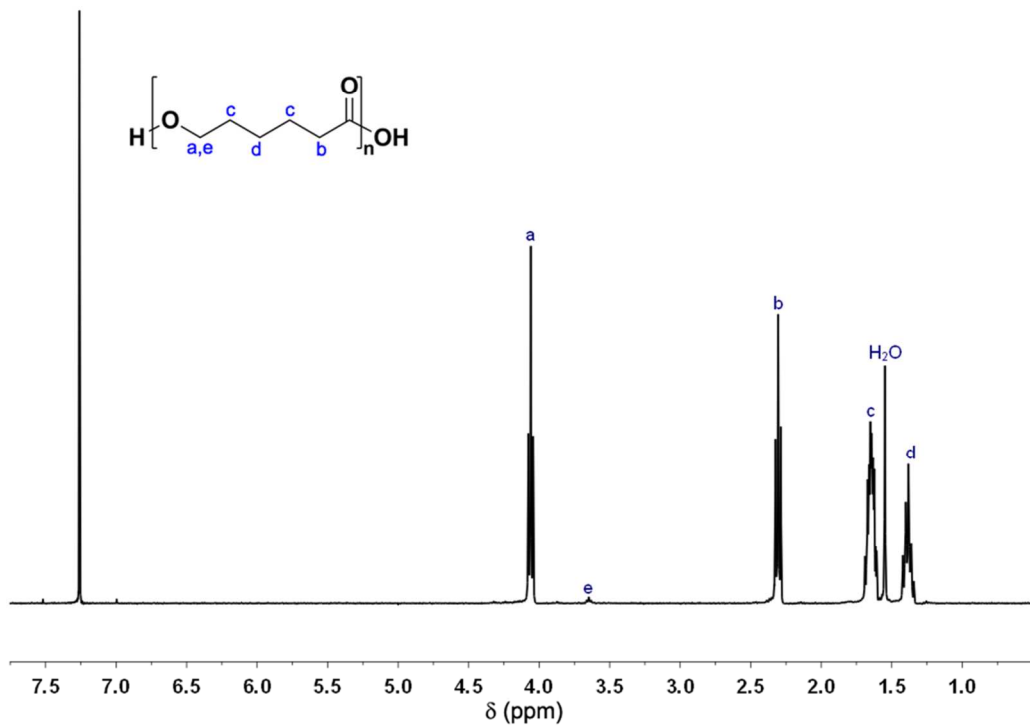
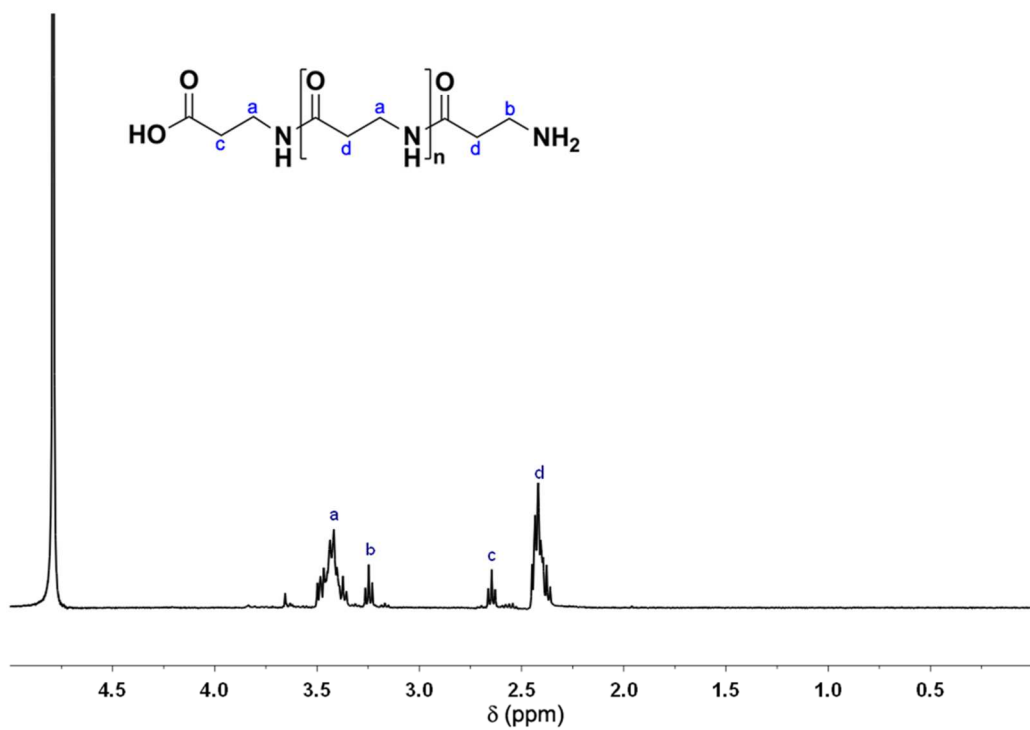**Figure S3.** ^{1}H NMR spectrum of poly(ε-caprolactone) in CDCl$_3$

Figure S4. ^{1}H NMR spectrum of poly(β-lactam) in D$_2$O
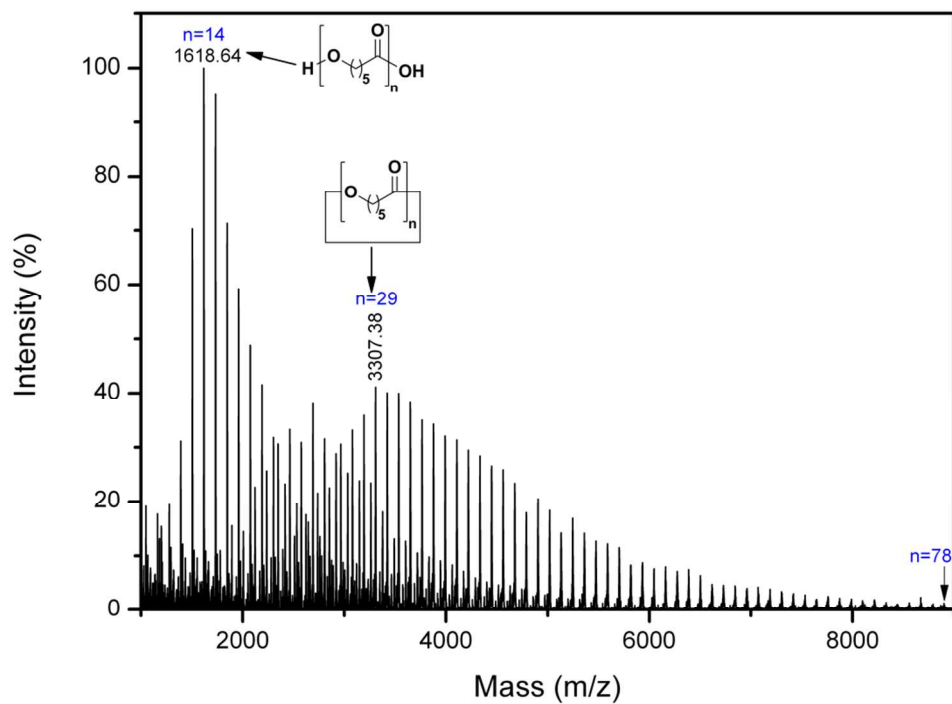
Figure S5. MALDI-ToF spectrum of poly(ε-caprolactone)
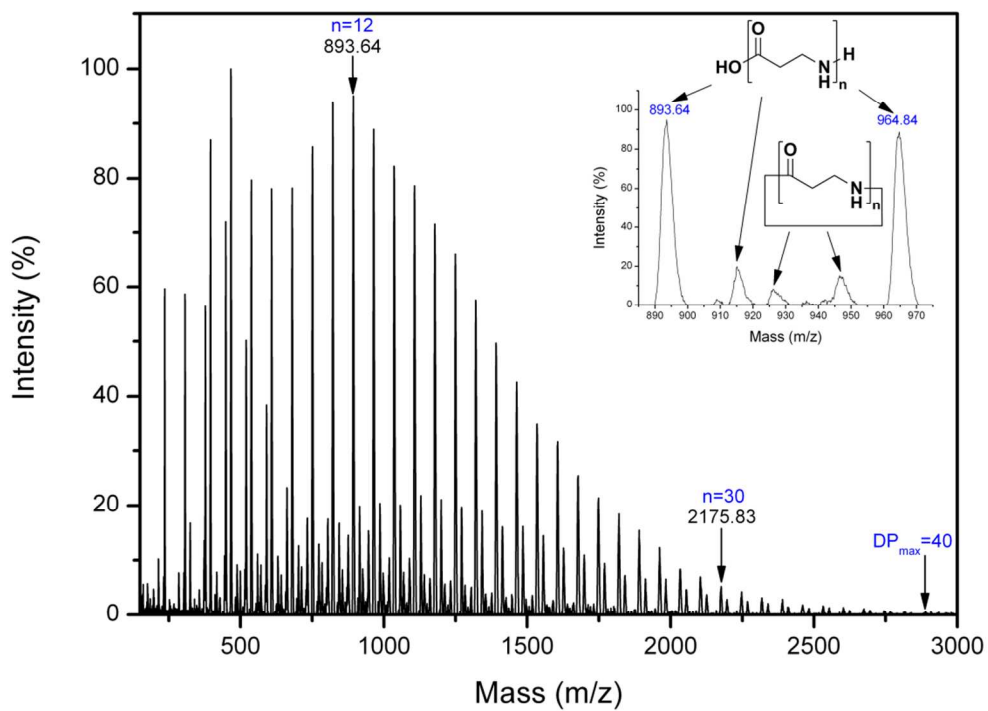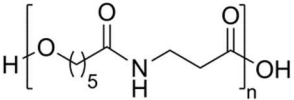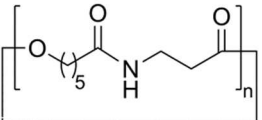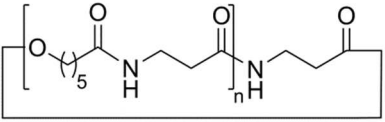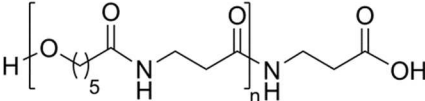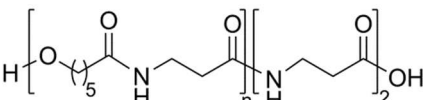
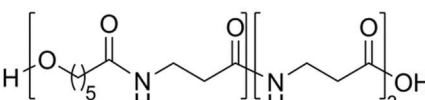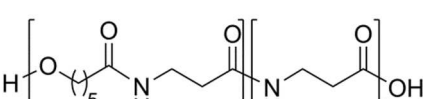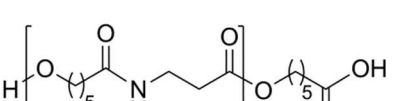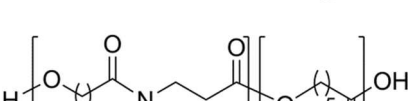**Figure S6.** MALDI-ToF spectrum of poly(β-lactam)

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⁺ : ▪ (grey) Na⁺ : ■ (black)		18
H⁺ : ●		0
H⁺ : ⊗		71
H⁺ : ◆		89
H⁺ : ▼		160
H⁺ : ✳		231.1
H⁺ : ♥		302.2
H⁺ : ♠		132.1
H⁺ : ▲		246.1

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

Symbol adduct	Structures	Mass of end group (amu)
H⁺ : ◼ (gray) Na⁺ : ◼ (black)		18
H⁺ : ⬤		0
H⁺ : ⊗		71
H⁺ : ◆ (gray) Na⁺ : ◆ (black)		89
H⁺ : ▼ (gray) Na⁺ : ▼ (black)		160
H⁺ : ✳ (gray) Na⁺ : ✳ (black)		231.1
H⁺ : ♥		302.2
H⁺ : ♠		132.1
H⁺ : ▲		246.1

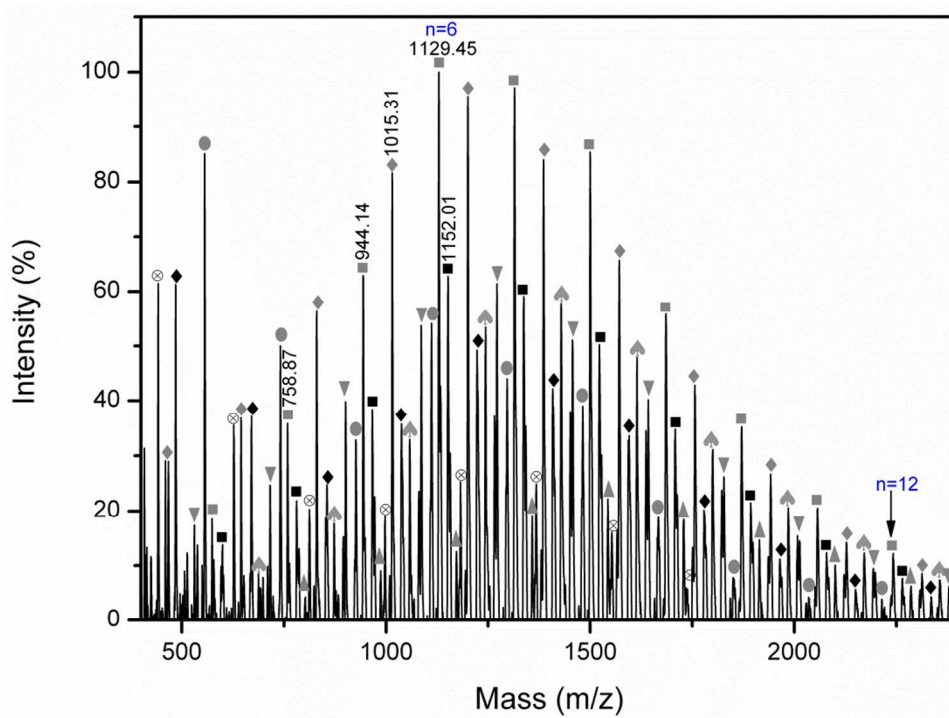**Figure S7.** MALDI-ToF spectrum of the side product dissolved in formic acid

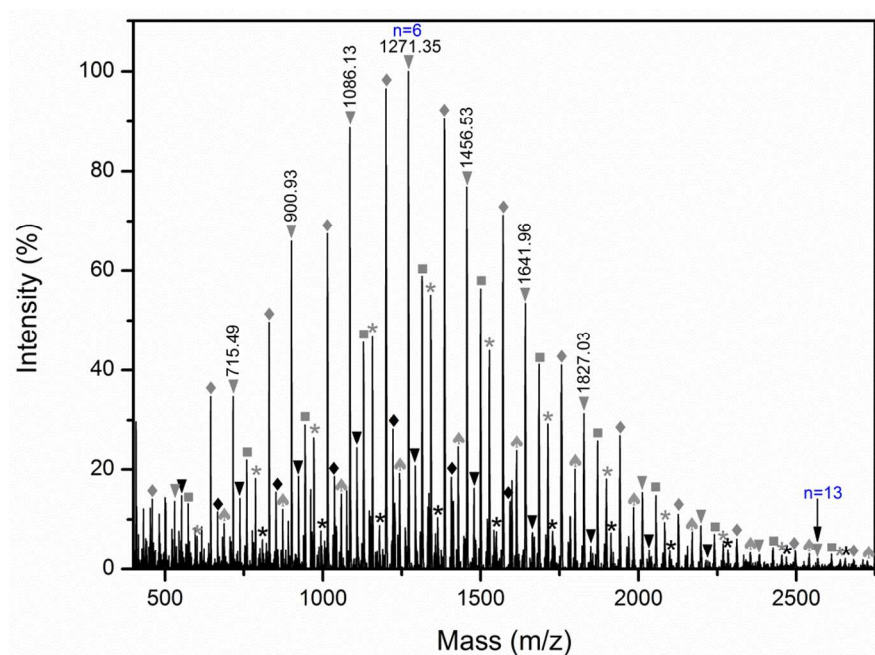**Figure S8.** MALDI-ToF spectrum of poly(ε-CL-*co*-β-lactam) with addition of NaTFA

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
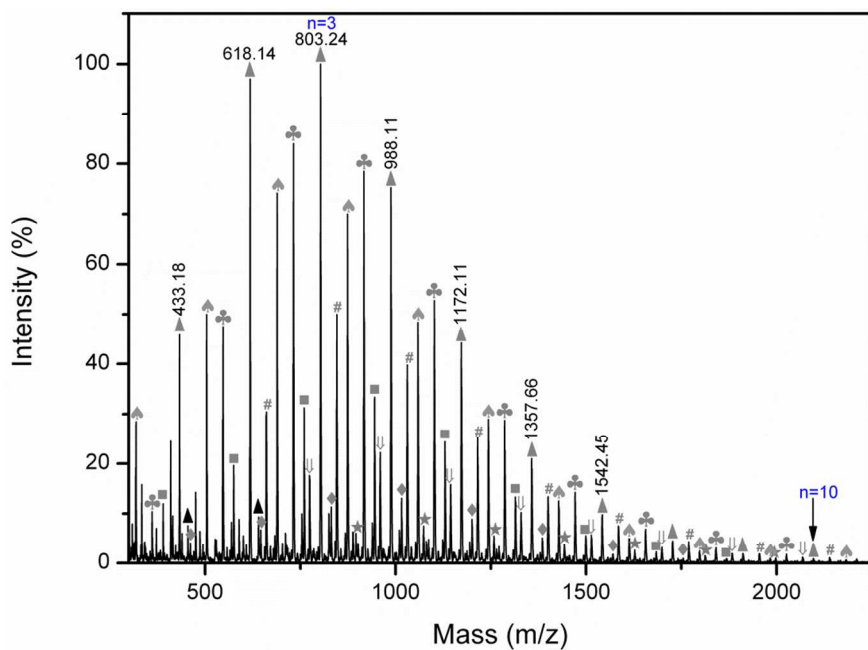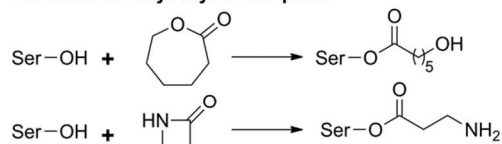

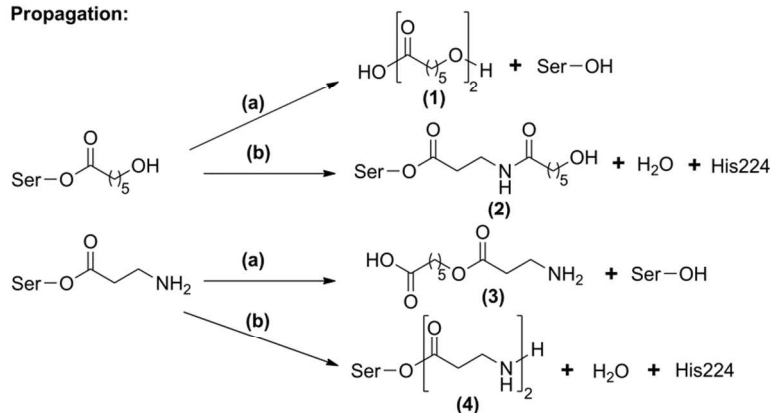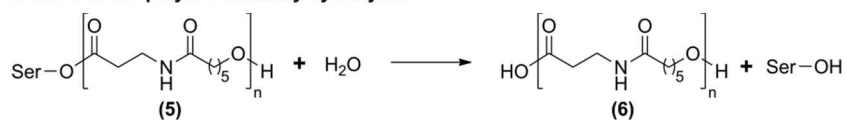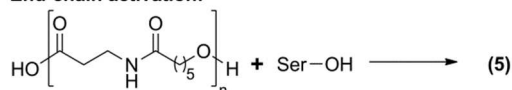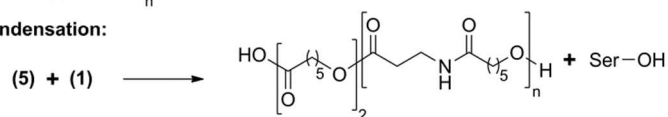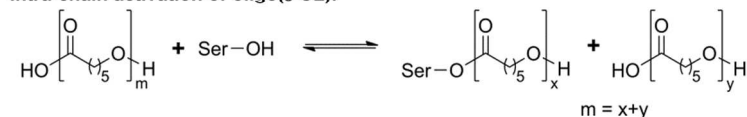**Figure S10.** MALDI-ToF spectrum of poly(ε-CL-*co*-β-lactam) from the reaction with feed ratio 25:75 of β-lactam:ε-CL

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$^+$: ▼ Na$^+$: ▼		160
H$^+$: ♠		132.1
H$^+$: ▲ Na$^+$: ▲		246.1
H$^+$: ♣		360.2
H$^+$: #		474.2
H$^+$: ⇓		588.3
H$^+$: ★		702.4
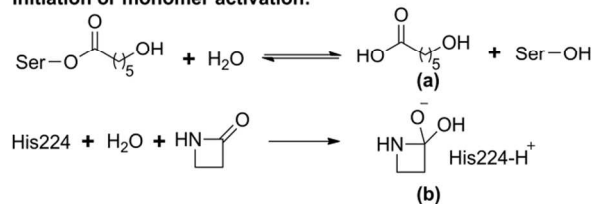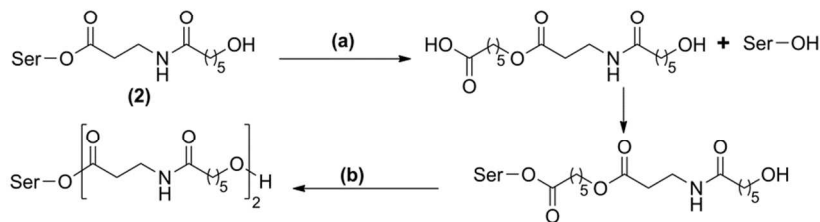
Scheme S1. Proposed reaction mechanism of CAL-B-catalyzed formation of poly(ε-CL-*co*-β-lactam).

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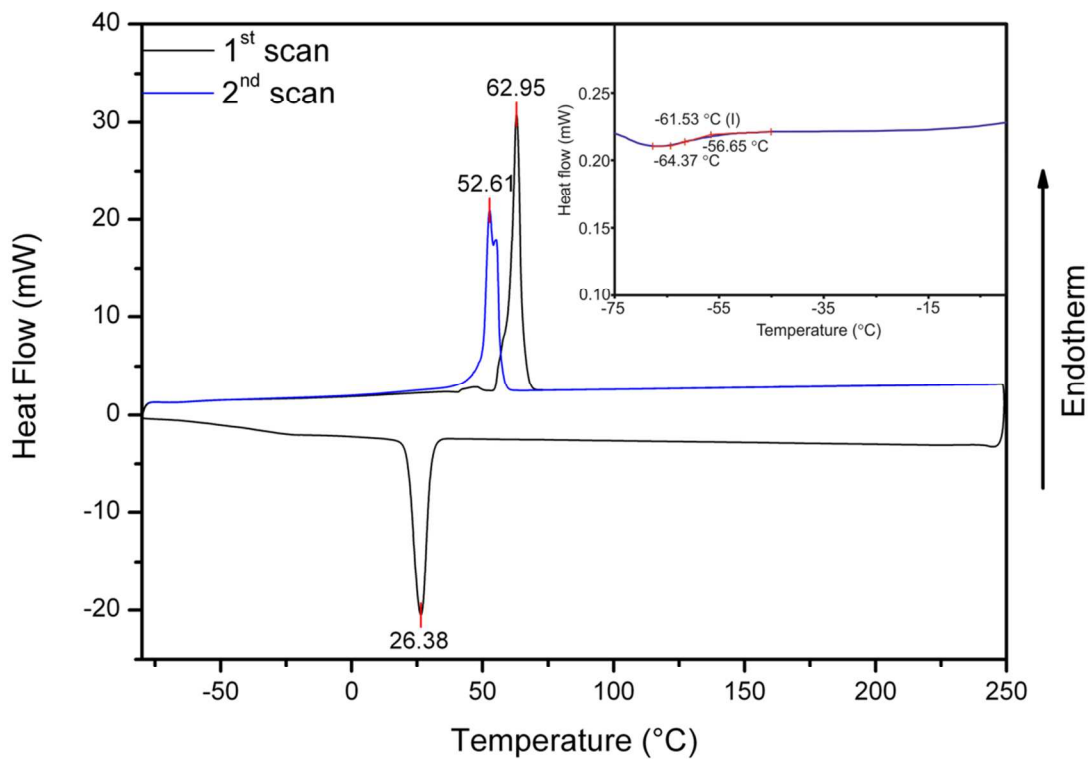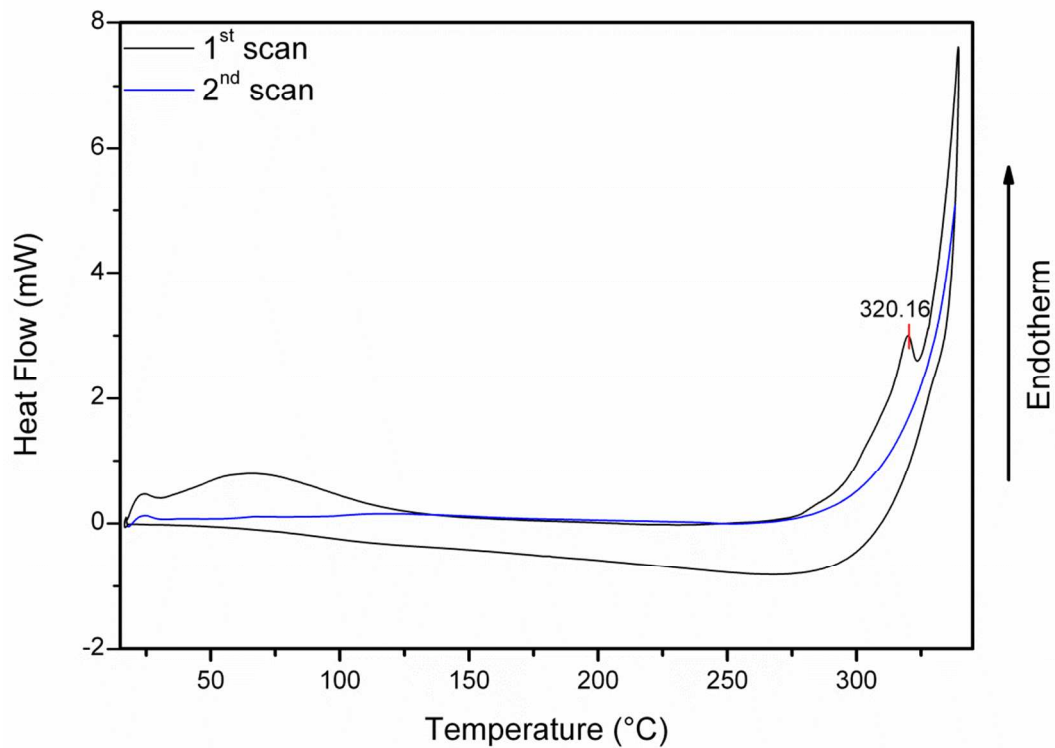

Figure S12. DSC curves of poly(β-lactam)