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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 \rightarrow 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 \times molar mass of repeating unit

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

Yield (%) = (actual yield/theoretical yield) \times 100%

Yield (%) from experiment 1 = $(0.1388/0.2592) \times 100\% = 53\%$

Yield (%) from experiment 2 = $(0.1228/0.2592) \times 100\% = 47\%$

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

$$\text{mol } \epsilon\text{-CL} = 0.7 \text{ mmol}$$

$$\text{mol } \beta\text{-lactam} = 2.1 \text{ mmol}$$

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

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

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

$$\text{Yield (\%)} \text{ from experiment 2} = (0.0140/0.1296) \times 100\% = 10.8\%$$

$$\text{Average yield (\%)} \text{ from duplicate experiments} = (13.5\% + 10.8\%)/2 = 12.1\%$$

b. For 3:1:

$$\text{mol } \epsilon\text{-CL} = 2.1 \text{ mmol}$$

$$\text{mol } \beta\text{-lactam} = 0.7 \text{ mmol}$$

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

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

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

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

$$\text{Average yield (\%)} \text{ from duplicate experiments} = (48\% + 40\%)/2 = 44\%$$

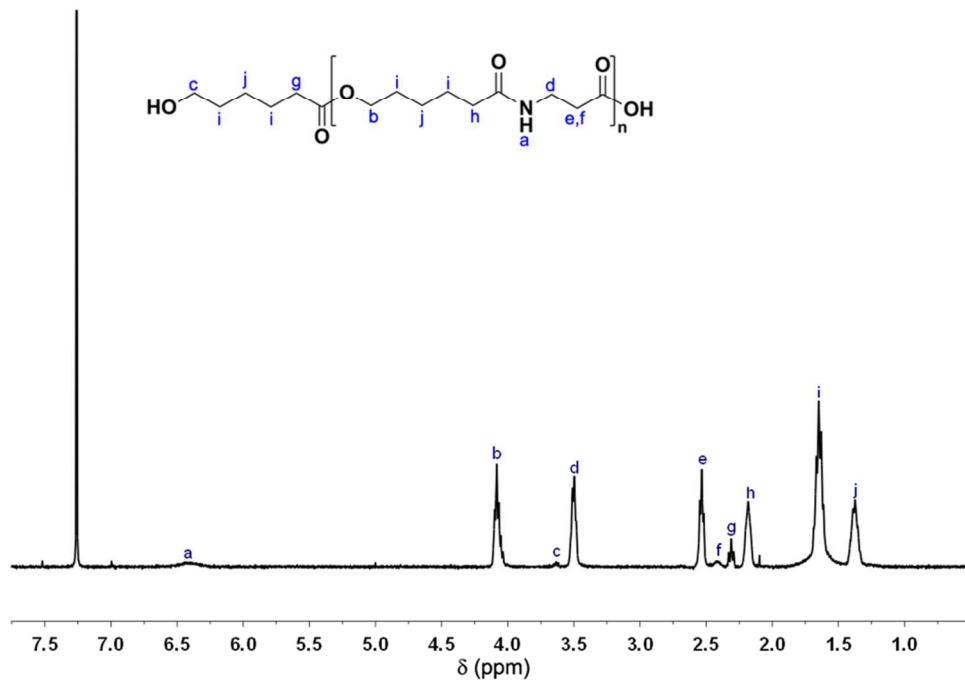


Figure S1. ^1H NMR spectrum of poly(ϵ -CL-co- β -lactam) in CDCl_3

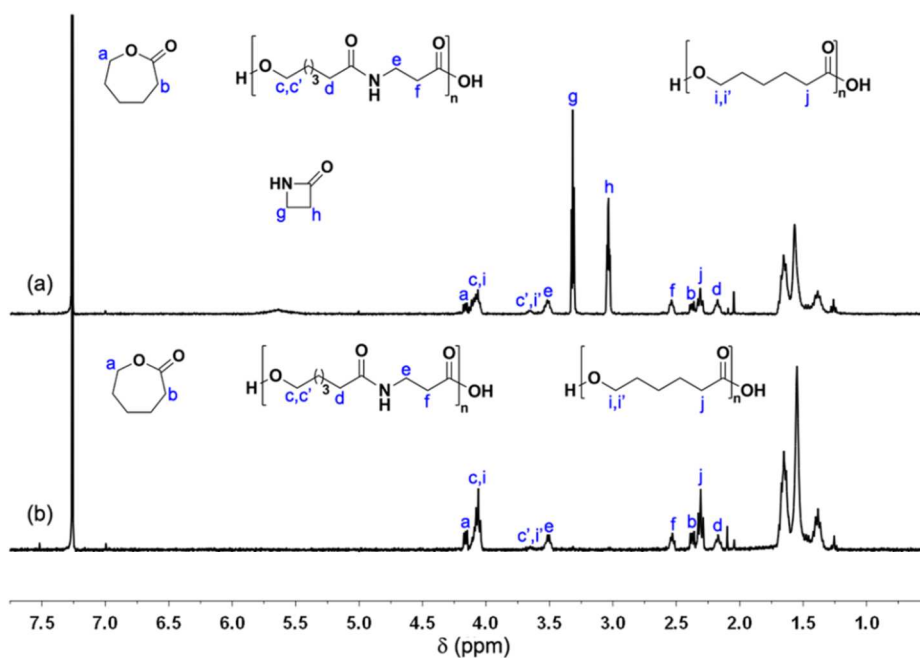


Figure S2. ^1H NMR of the evaporated ethyl acetate fraction from the ring opening polymerization of ϵ -CL and β -lactam in different feed ratios of ϵ -CL: β -lactam (a) 25:75 and (b) 75:25

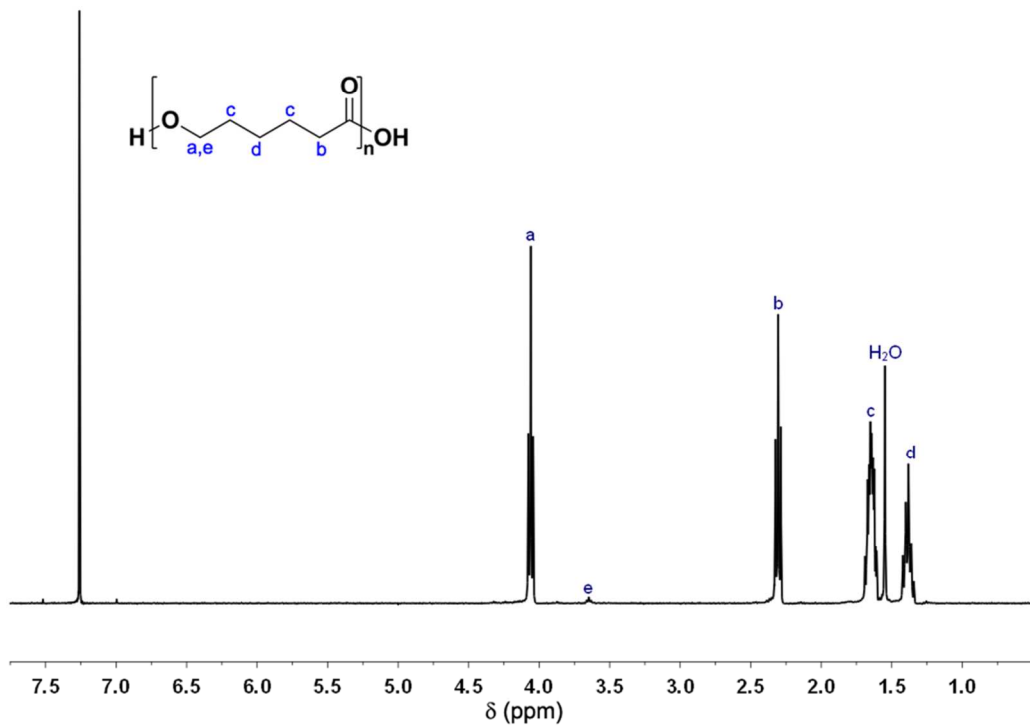


Figure S3. ^1H NMR spectrum of poly(ϵ -caprolactone) in CDCl_3

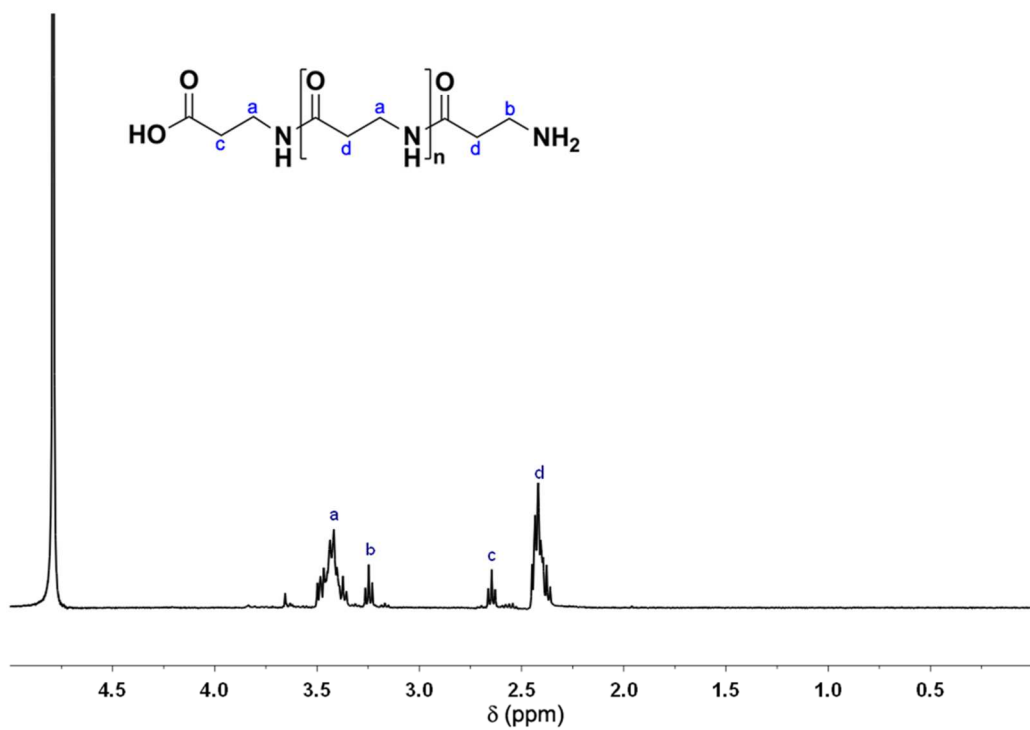


Figure S4. ^1H NMR spectrum of poly(β -lactam) in D_2O

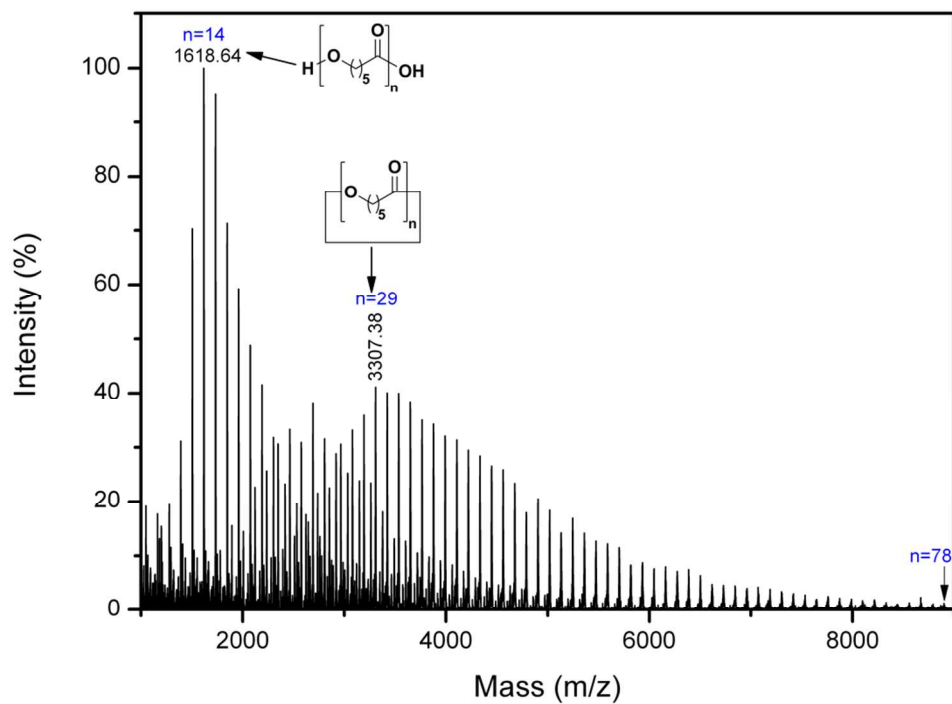


Figure S5. MALDI-ToF spectrum of poly(ϵ -caprolactone)

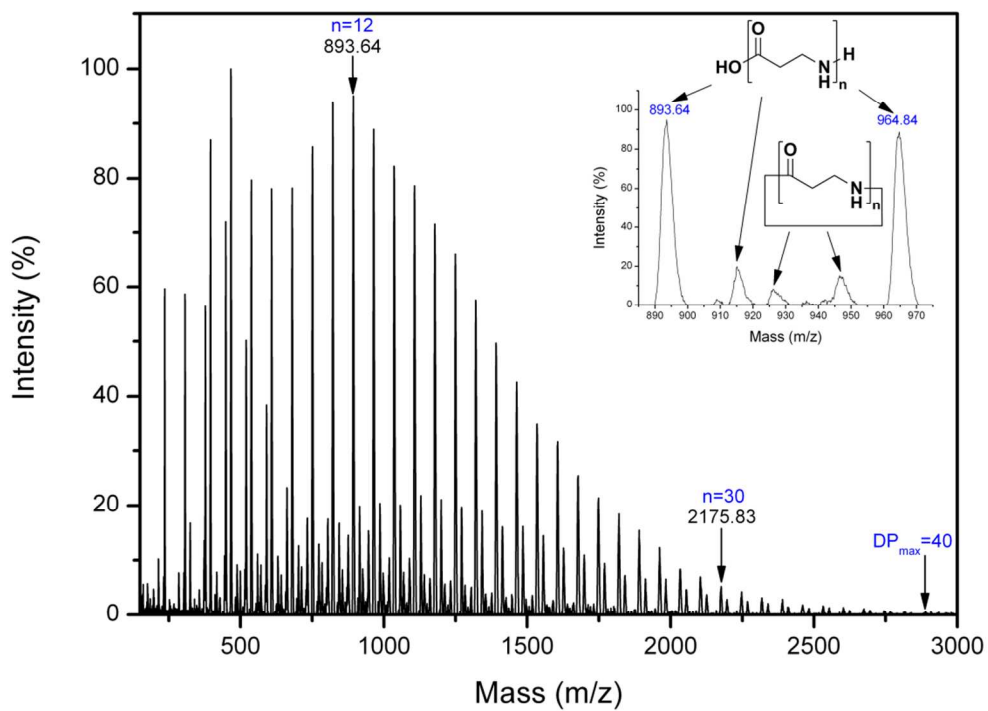
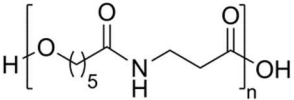
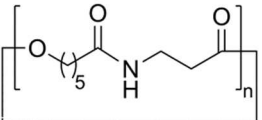
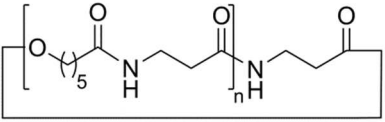
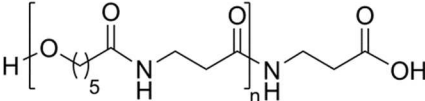
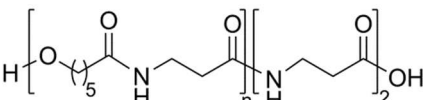
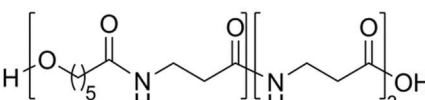
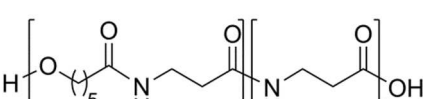
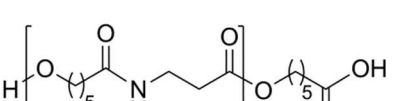
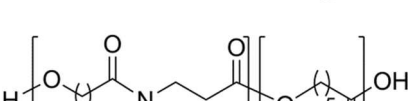


Figure S6. MALDI-ToF spectrum of poly(β -lactam)

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 ⁺ : ■ 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 ⁺ : ■ Na ⁺ : ■		18
H ⁺ : ●		0
H ⁺ : ⊗		71
H ⁺ : ◆ Na ⁺ : ◆		89
H ⁺ : ▼ Na ⁺ : ▼		160
H ⁺ : * Na ⁺ : *		231.1
H ⁺ : ♥		302.2
H ⁺ : ♠		132.1
H ⁺ : ▲		246.1

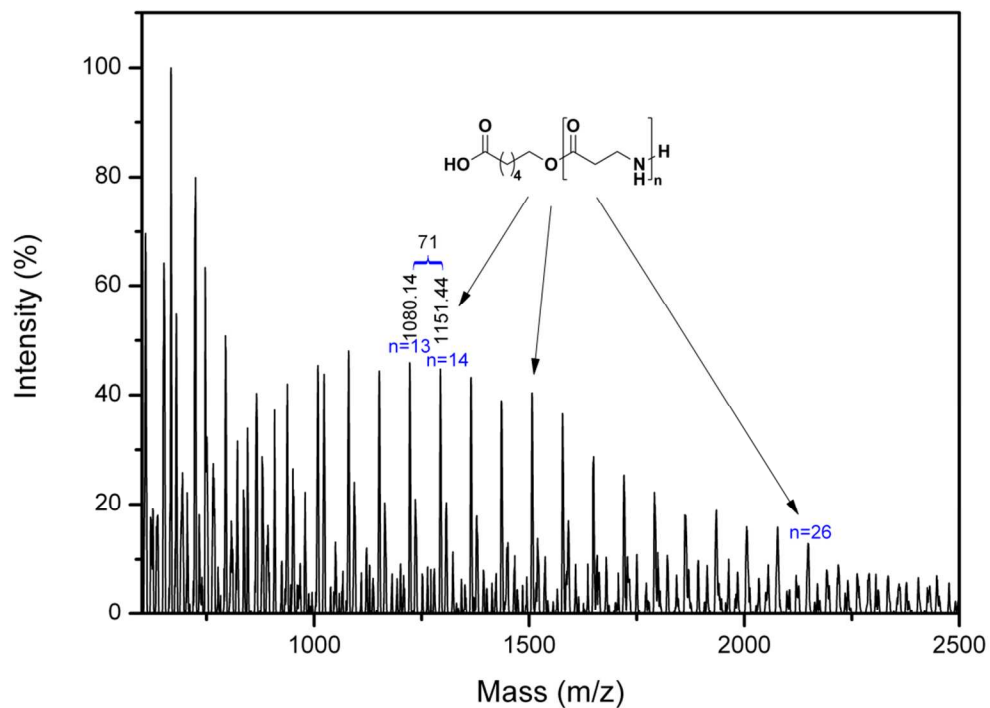


Figure S7. MALDI-ToF spectrum of the side product dissolved in formic acid

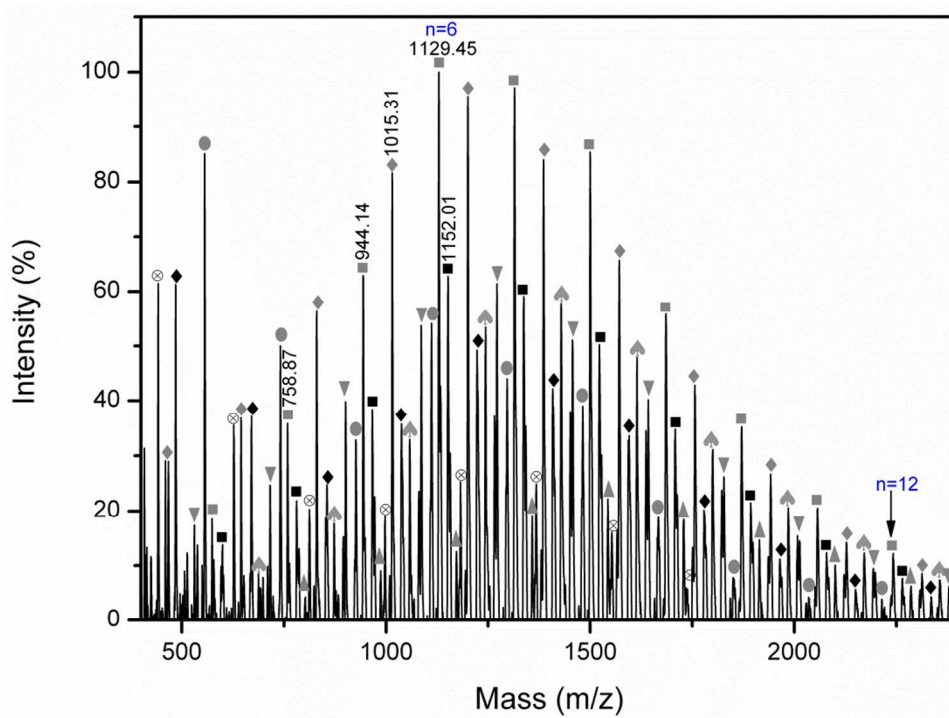


Figure S8. MALDI-ToF spectrum of poly(ϵ -CL-*co*- β -lactam) with addition of NaTFA

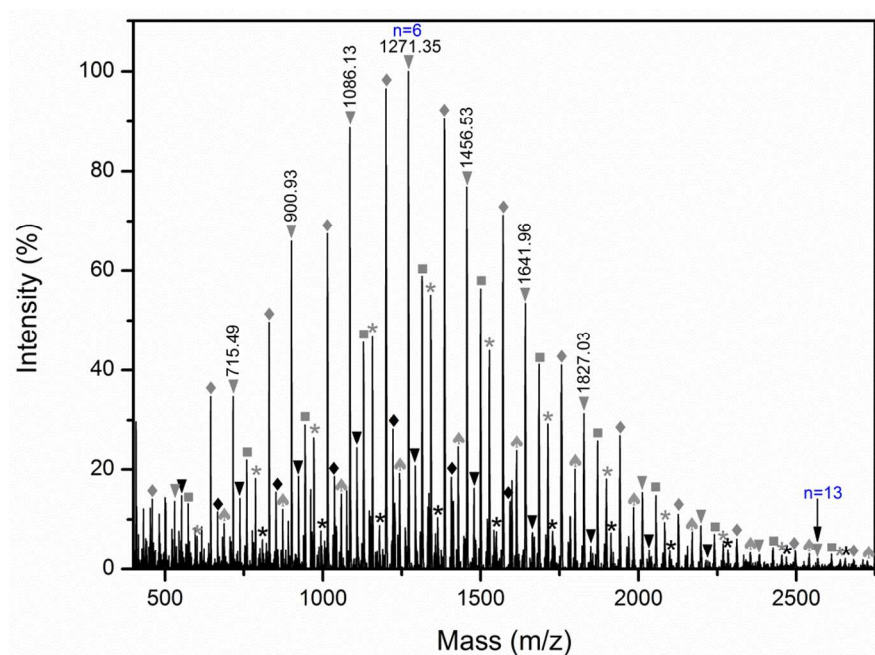


Figure S9. MALDI-ToF spectrum of poly(ϵ -CL-co- β -lactam) from the reaction with feed ratio 75:25 of β -lactam: ϵ -CL

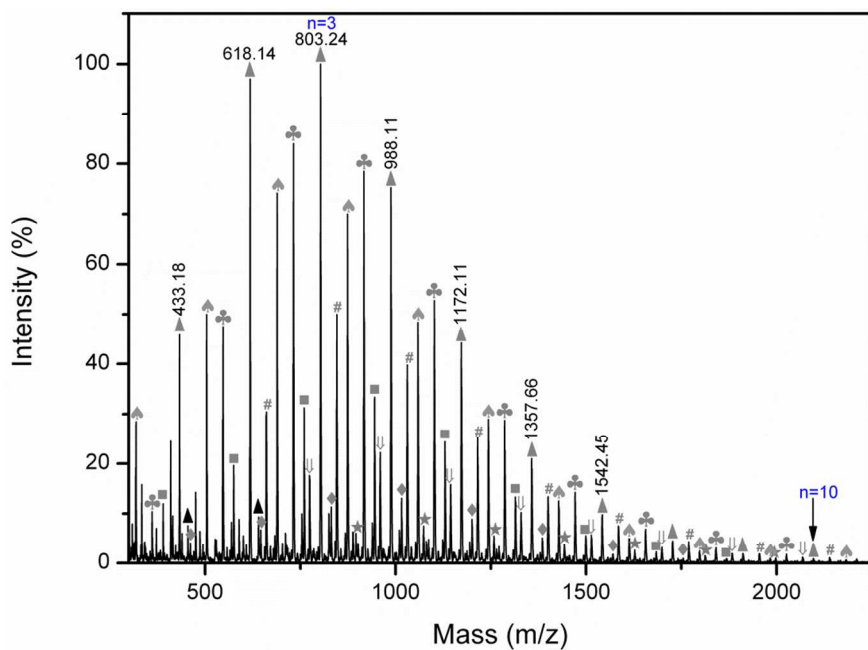
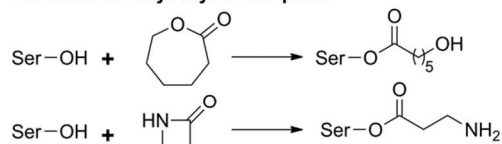
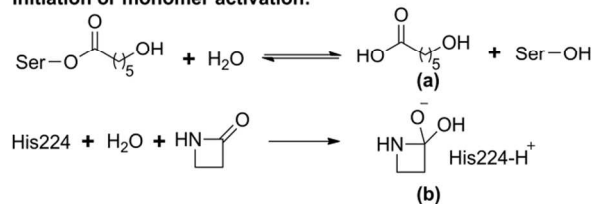
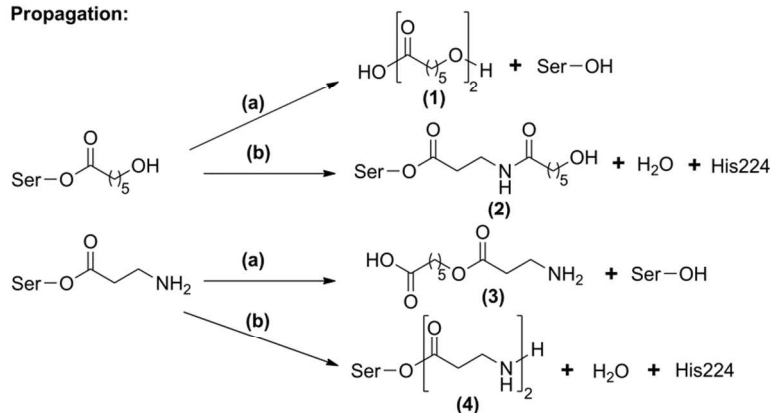
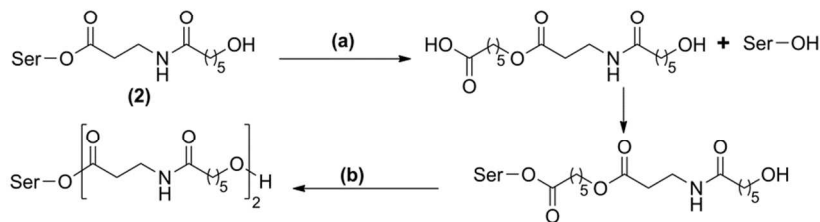
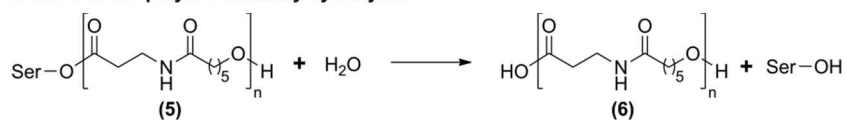
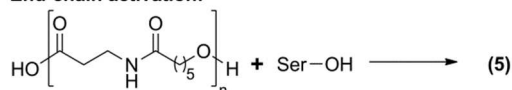
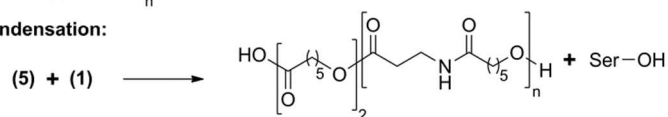
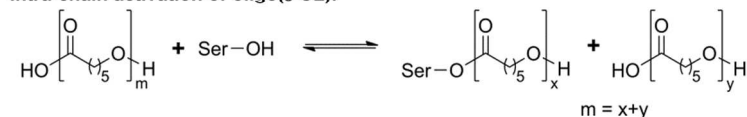


Figure S10. MALDI-ToF spectrum of poly(ϵ -CL-co- β -lactam) from the reaction with feed ratio 25:75 of β -lactam: ϵ -CL

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 ⁺ : ▼ Na ⁺ : ▼		160
H ⁺ : ♠		132.1
H ⁺ : ▲ Na ⁺ : ▲		246.1
H ⁺ : ♣		360.2
H ⁺ : #		474.2
H ⁺ : ↓↓		588.3
H ⁺ : ★		702.4

Formation of acyl-enzyme complex:**Initiation or monomer activation:****Propagation:****Formation of alternating copolymer:****Release of the polymer chain by hydrolysis:****End-chain activation:****Polycondensation:****Intra-chain activation of oligo(ϵ -CL):**

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

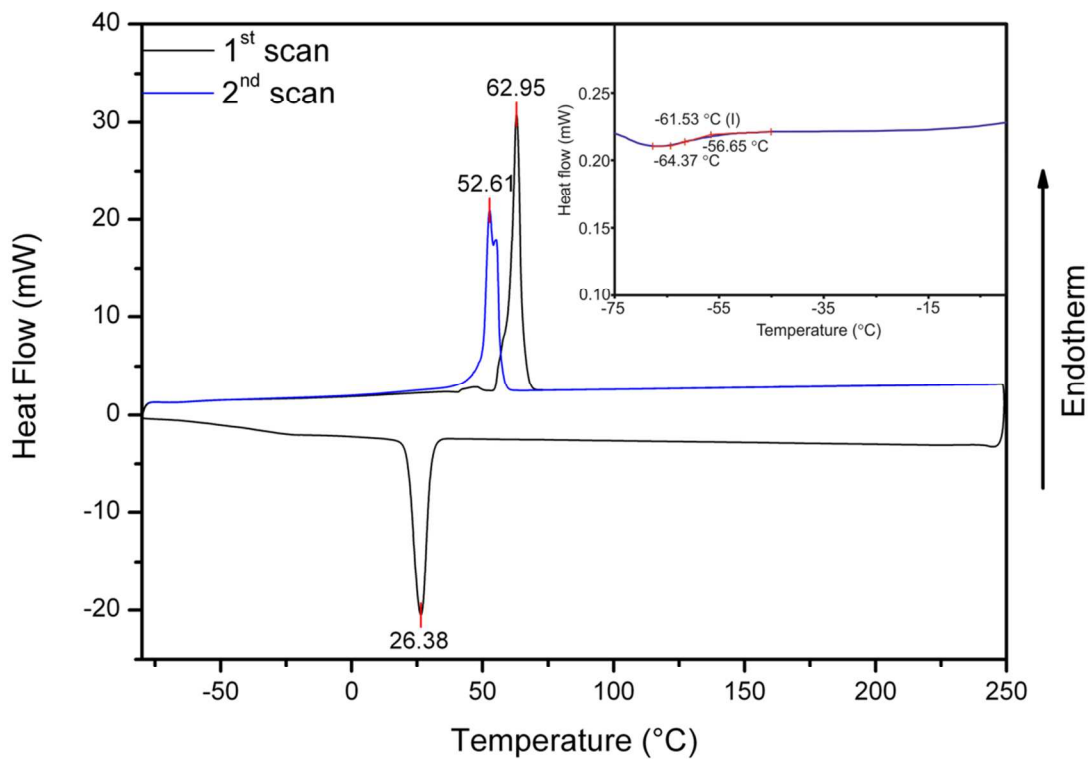


Figure S11. DSC curves of poly(ϵ -caprolactone)

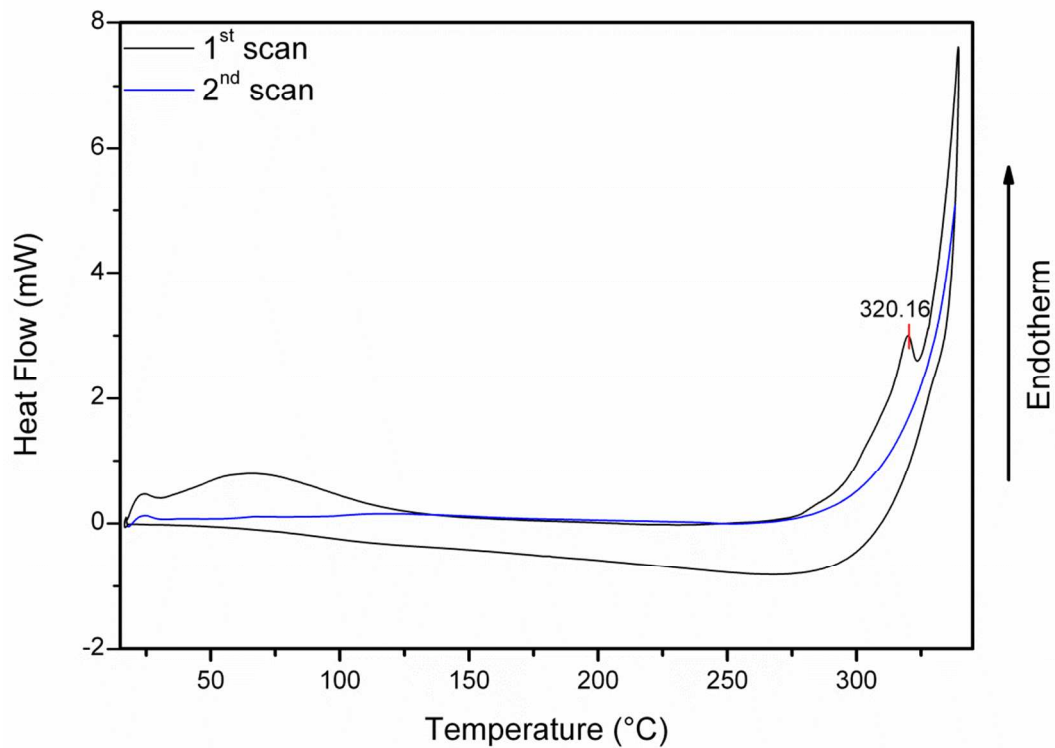


Figure S12. DSC curves of poly(β -lactam)