

Supporting information

Toward Regulating Biodegradation in Stages of Polyurethane Copolymer with Bicontinuous Microphase Separation

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Experimental section

Synthesis of HO-PPDO_{41.15%}-c-PCL-OH. The predetermined amounts of PDO, ϵ -CL and BDO (as specified in the polymerization Table 1) were charged into a rigorously dried two-necked flask, then the reactor was immersed into a preheated oil bath ($T=140\text{ }^{\circ}\text{C}$), a predetermined amount of stannous octoate toluene solution (0.5 mol L^{-1} , the molar ratio of overall monomer and $\text{Sn}(\text{Oct})_2$ was 10000:1) was injected into the reactor to perform the reaction for 48h. After reaction, the reactor was cooled to room temperature. The crude product was purified by dissolving in CHCl_3 and then precipitated into excess of cold methanol, filtered, washed thrice with methanol to remove unreacted monomer, and dried in a vacuum oven at $40\text{ }^{\circ}\text{C}$ to a constant weight.

^1H NMR (400 MHz, CDCl_3 , RT) δ 4.26 (t, $J = 4.6\text{ Hz}$, 2H; $-\text{C}(\text{O})\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$; PDO), 4.15 (t, $J = 6.7\text{ Hz}$, 2H; $-\text{CH}_2\text{O}-$; CL*-PDO), 4.12 (s, 2H; $-\text{C}(\text{O})\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$; PDO), 4.05 (t, $J = 6.7\text{ Hz}$, 2H; $-\text{CH}_2\text{O}-$; CL), 3.77 (t, $J = 4.7\text{ Hz}$, 2H; $-\text{C}(\text{O})-\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$; PDO), 2.36 (t, $J = 7.5\text{ Hz}$, 2H; $-\text{C}(\text{O})\text{CH}_2-$; CL*-PDO), 2.29 (t, $J = 7.5\text{ Hz}$, 2H; $-\text{C}(\text{O})\text{CH}_2-$; CL), 1.65-1.60 (m, 4H; $-\text{C}(\text{O})\text{CH}_2\text{CH}_2-$ and $-\text{CH}_2\text{CH}_2\text{O}-$; CL), 1.40-1.30 (m, 2H; CH_2 ; CL).

^{13}C NMR (100 MHz, CDCl_3 , RT) δ 173.65, 173.6 and 173.5 ($-\text{C}(\text{O})-$; CL), 170.3 ($-\text{C}(\text{O})-$; PDO), 69.7 ($-\text{C}(\text{O})-\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$; PDO), 68.5 ($-\text{C}(\text{O})\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$; PDO), 64.8 ($-\text{CH}_2\text{O}-$; CL*-PDO), 64.3 ($-\text{CH}_2\text{O}-$; CL-CL), 63.4 ($-\text{C}(\text{O})\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$; PDO), 34.3, 34.2 and 34.1 ($-\text{C}(\text{O})\text{CH}_2-$; CL) 28.5, 28.4, 25.7, 25.6, 24.7 and 24.6 ($-\text{CH}_2$; CL).

Synthesis of HO-PCL-OH. The predetermined amounts of ϵ -CL and BDO were charged into a rigorously dried two-necked flask, then the reactor was immersed into a preheated oil bath ($T=130\text{ }^{\circ}\text{C}$), a predetermined amount of stannous octoate toluene solution (0.5 mol L^{-1} , the molar ratio of overall monomer and $\text{Sn}(\text{Oct})_2$ was 10000:1) was injected into the reactor to perform the reaction for 48h. After reaction, the reactor was cooled to room temperature. The crude product was purified by dissolving in CHCl_3 and then precipitated into excess of cold methanol, filtered, washed thrice with methanol to remove unreacted monomer, and dried in a vacuum oven at $40\text{ }^{\circ}\text{C}$ to a constant weight.¹

^1H NMR (400 MHz, Chloroform-*d*, RT) δ 4.05 (t, $J = 6.7$ Hz, 2H; $-\text{CH}_2\text{O}-$), 2.30 (t, $J = 7.5$ Hz, 2H; $-\text{C}(\text{O})\text{CH}_2-$), 1.67-1.60 (m, 4H; $-\text{C}(\text{O})\text{CH}_2\text{CH}_2-$ and $-\text{CH}_2\text{CH}_2\text{O}-$), 1.41-1.33 (m, 2H; CH_2).

^{13}C NMR (400 MHz, Chloroform-*d*, RT) δ 173.54 ($-\text{C}(\text{O})-$), 64.14($-\text{CH}_2\text{O}-$), 34.12($-\text{C}(\text{O})\text{CH}_2-$), 28.35, 25.53, 24.58($-\text{CH}_2$).

The number-average molecular weights of HO-PPDO_{41.15%}-*c*-PCL-OH (around 5000g/mol) and HO-PCL-OH (around 5400g/mol), which are very close to the theoretical value, are calculated from nuclear magnetic resonance (NMR) spectroscopy analysis via the following equation, respectively.

$$M_n(\text{HO-PPDO}_{41.15\%}\text{-c-PCL-OH}) = 102 \times I_{3.78} / I_{3.66} \times 2 + 114 \times I_{2.56} / I_{3.66} \times 2 + 90 \quad (1)$$

$$M_n(\text{HO-PCL-OH}) = 114 \times I_{2.56} / I_{3.66} \times 2 + 90 \quad (2)$$

where $I_{3.76}$ and $I_{3.66}$ are the peak integrations of the corresponding methylene protons of HO-PPDO-OH connected to ester bonds and hydroxyl groups, respectively; where $I_{2.56}$ and $I_{3.66}$ are the peak integrations of the corresponding methylene protons of HO-PCL-OH connected to ester bonds and hydroxyl groups, respectively; and 114, 102, and 90 are the molecular weights of caprolactone, PDO, and BDO, respectively.²

Copolymer randomness was evaluated by determining the sequence distribution in each copolymer. Therefore, the degree of randomness (R)³ of the copolymer chains can be calculated from the equation below:

$$R = 100/L_{\text{PDO}} + 100/L_{\text{CL}}$$

$$L_{\text{PDO}} = I_{\text{PDO-PDO}^*} / I_{\text{CL-PDO}^*} + 1$$

$$L_{\text{CL}} = I_{\text{CL-CL}^*} / I_{\text{PDO-CL}^*} + 1$$

where $I_{\text{PDO-PDO}^*}$ (4.35-4.40ppm) and $I_{\text{CL-PDO}^*}$ (4.25-4.30ppm) indicate the peak intensity of PDO-PDO* and CL-PDO* sequences of the copolymer calculated from ^1H NMR, and $I_{\text{CL-CL}^*}$ (2.25-2.33ppm) and $I_{\text{PDO-CL}^*}$ (2.33-2.39ppm) represent the peak intensity of CL-CL* and PDO-CL* sequences of the copolymer determined by ^1H NMR.

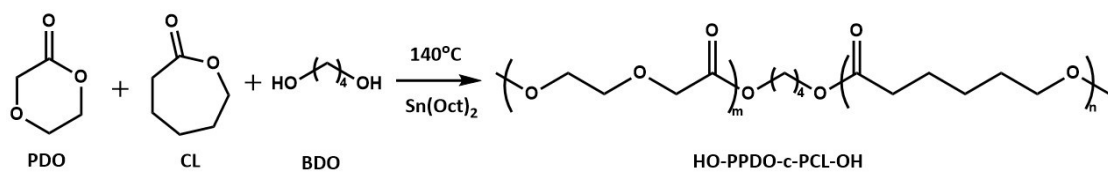


Table S1: Ring-opening polymerization results of prepolymer.

Prepolymer	PDO (mol)	CL (mol)	[M]/[Cat.]/[I]	Conv.-PDO ^a (%)	Conv.-CL ^a (%)	M_n ^b (Da)	\mathcal{D}^b
HO-PPDO _{41%} -C-PCL-OH	0.5	0.5	1:10000:40	73.2	81.1	5031	1.31
HO-PCL-OH	0	1.0	1:10000:40	--	79.3	5392	1.37

^aMonomer conversion measured by ¹H NMR of the quenched solution. ^bNumber-average molecular weight (M_n) and dispersity index ($\mathcal{D}=M_w/M_n$), determined by gel permeation chromatography (GPC) at 30°C in CHCl₃.



Fig S1. The photographs of the original HO-PPDO_{41.15%}-c-PCL-OH (left) and HO-PCL-OH (right).

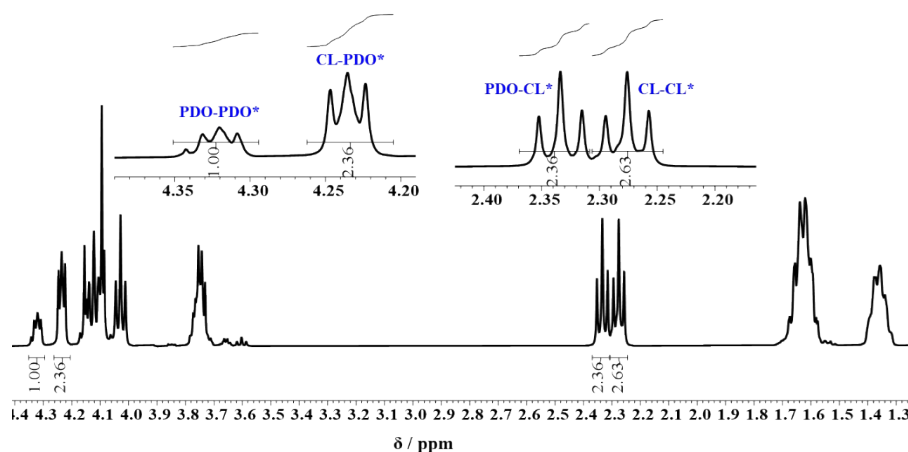


Fig S2. The ¹H NMR spectra of HO-P(DO_{41.15%}-c-CL)-OH.

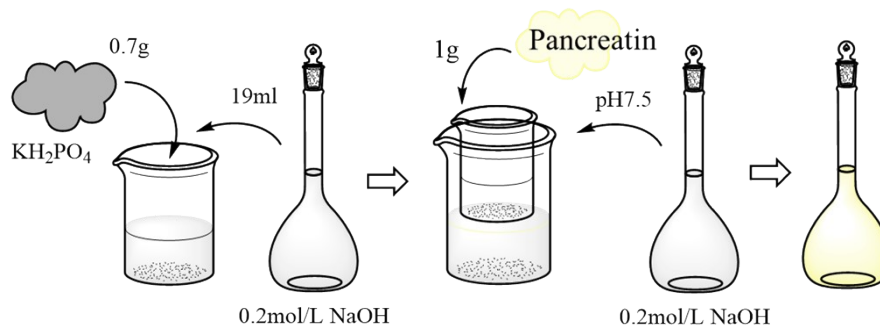


Fig S3: The schematic diagram of preparing Artificial pancreatic juice.

Table S2: Chemical Composition and Molecular Characteristics of PCL-b-CrP-U.

Samples	P^1 (g)	P^2 (g)	PDO (%)	PCL (%)	M_n^b (Da)	\mathcal{D}^b
PCL-U	0	30.00	0	100	68582	1.53
PCL-b-CrP ₁₀ -U	12.12	20.00	9.25	90.75	59431	1.46
PCL-b-CrP ₂₀ -U	19.91	10.00	21.15	78.85	60371	1.40
PCL-b-CrP ₂₅ -U	48.84	20.00	25.34	74.66	53590	1.52

¹Prepolymer: HO-P(DO_{41.15%}-c-CL)-OH; ²Prepolymer: HO-PCL-OH; ^bNumber-average molecular weight (M_n) and dispersity index ($\mathcal{D}=M_w/M_n$), determined by gel permeation chromatography (GPC) at 30°C in CHCl₃.

Table S3: The FT-IR spectrum of PCL-b-CrP-U samples mainly shows the peak attribution table.

Samples	-NH (stretching bands)	C=O	-C- NH-	-CH ₂	-CH ₃	-NH (bending vibrations)	C-O-C
PCL-U	3324	1721	1469	2942	2865	1530	--
PCL-b-CrP ₁₀ -U	3323	1721	1469	2942	2865	1535	1240/11 88/1104
PCL-b-CrP ₂₀ -U	3323	1722	1462	2942	2865	1535	1240/11 88/1104
PCL-b-CrP ₂₅ -U	3323	1722	1460	2941	2865	1535	1240/11 88/1104

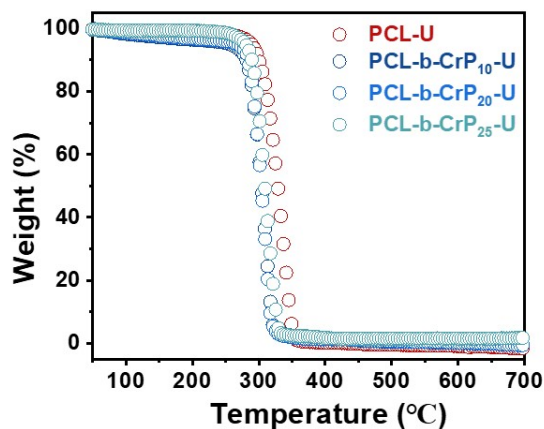


Fig S4. The TGA curves of PCL-b-CrP-U samples.

Table S4. The data of TGA curves of PCL-b-CrP-U samples.

Samples	$T_{5\%}$ (°C)	T_{max} (°C)
PCL-U	288.8	337.4
PCL-b-CrP ₁₀ -U	255.9	322.4
PCL-b-CrP ₂₀ -U	267.0	309.8
PCL-b-CrP ₂₅ -U	289.5	306.8

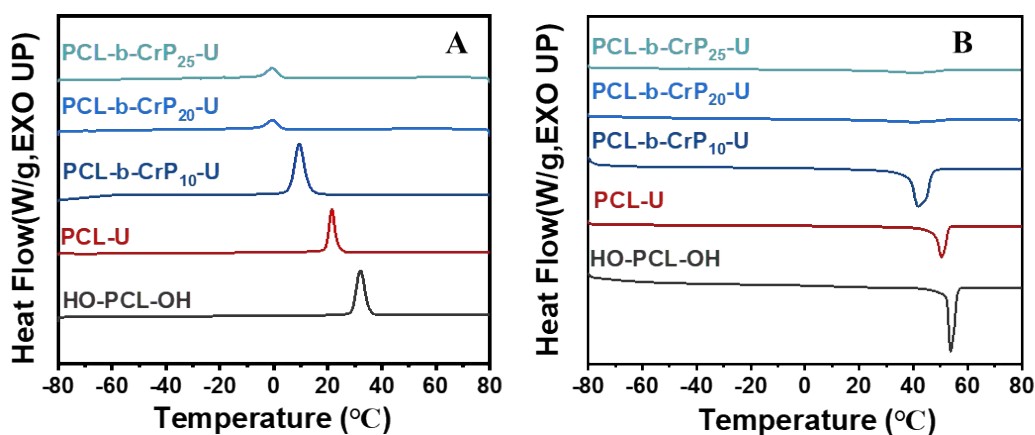


Fig S5. The DSC of PCL-b-CrP-U. (A): to the cooling scans; (B): the second heating scan.

Table S5. Thermal Characterization of PCL-b-CrP-U.

Samples	T_g^c (°C)	T_m^a (°C)	ΔH_m^a (J/g)	T_c^b (°C)	ΔH_c^b (J/g)	T_m^c (°C)	ΔH_m^c (J/g)	$\chi_{c,PCL}^c$ (%)
PCL-U	-60.80	55.43	66.75	21.43	55.90	53.74	79.96	39.72
PCL-b-CrP ₁₀ -U	-58.88	50.56	71.74	9.24	53.14	50.31	55.22	38.98
PCL-b-CrP ₂₀ -U	-53.17	55.96	14.15	-0.58	22.20	41.85	49.65	19.59
PCL-b-CrP ₂₅ -U	-54.14	45.56	9.158	-0.84	24.28	40.57	21.96	19.32

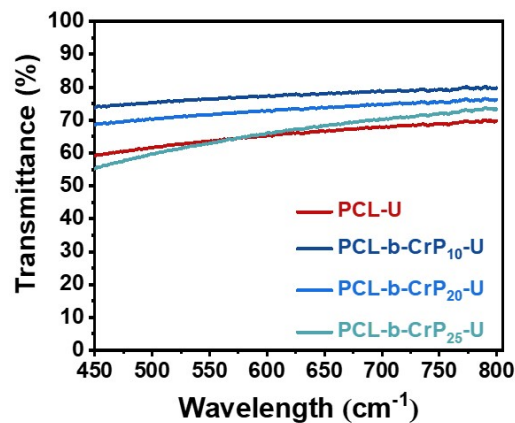
^arecorded according to the first heating scans of the DSC curves; ^brecorded according to the cooling scans; ^crecorded according to the second heating curve.

Table S6. Mechanical performances of PCL-b-CrP-U samples.

Samples	Elasticity Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (HA)
PCL-U	257.1±18.0	40.6±2.1	3646±78	69
PCL-b-CrP ₁₀ -U	220.9±22.1	23.0±1.9	2761±62	62
PCL-b-CrP ₂₀ -U	40.2±2.2	7.6±1.1	1520±17	49
PCL-b-CrP ₂₅ -U	39.5±4.4	7.5±0.8	1401±23	47

Table S7. Summary of cyclic tensile test of PCL-b-CrP₂₀-U and PCL-b-CrP₂₅-U in the first loading-unloading cycle.

Samples	Strain (%)	Hysteresis		Elastic recovery
		Value (MJ/m ³)	Ratio (%)	ratio (%)
PCL-b-CrP ₂₀ -U	30	64.257	64.81	70.00
PCL-b-CrP ₂₀ -U	50	136.027	67.30	66.01
PCL-b-CrP ₂₅ -U	30	56.215	59.51	71.7
PCL-b-CrP ₂₅ -U	50	126.965	63.27	67.3

**Fig S6.** The transmittance of PCL-b-CrP-U film after storage for one months at visible wavenumber.

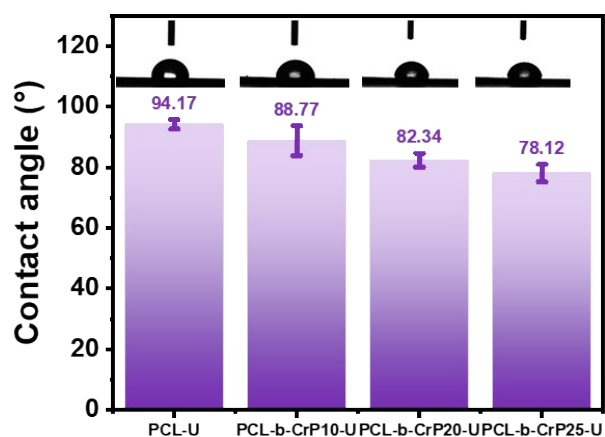


Fig S7. The contact angle measurements for PCL-b-CrP-U samples.

Table S8: The Change data of mechanical properties of PCL-U samples after degradation for 10 weeks.

Degradation time (week)	Elasticity Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
0	257.6±12.2	41.0±1.9	364±87
1	245.1±9.6	40.4±2.3	3497±117
2	240.1±18.7	39.1±2.1	3396±287
3	207.8±21.1	39.9±3.4	3380±253
4	199.1±20.9	38.4±2.4	3297±159
5	216.7±19.9	38.5±3.1	3181±279
6	179.2±7.8	35.6±5.8	3204±199
7	172.1±11.1	35.3±5.1	3134±102
8	178.5±13.2	32.5±4.9	3160±99
9	175.9±15.1	35.7±5.7	3054±176
10	172.2±10.2	34.2±5.9	3016±232

Table S9: The Change data of mechanical properties of PCL-b-CrP₁₀-U samples after degradation for 10 weeks.

Degradation time (week)	Elasticity Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
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0	220.4±6.7	23.0±1.2	2761±63
1	215.6±5.9	18.9±1.1	1233±101
2	218.1±7.1	16.5±1.7	643±74
3	214.3±5.2	15.4±1.4	627±89
4	204.4±5.3	15.0±0.9	397±57
5	202.3±4.9	14.8±1.7	337±149
6	200.9±6.1	15.9±2.1	321±79
7	206.8±7.6	15.5±2.7	312±113
8	197.4±9.9	15.2±3.1	216±98
9	199.0±8.9	13.9±3.2	150±101
10	206.1±9.1	9.9±2.7	120±81

Table S10: The Change data of mechanical properties of PCL-b-CrP₂₀-U samples after degradation for 10weeks.

Degradation time (week)	Elasticity Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
0	43.6±1.6	7.6±0.8	1520±65
1	42.7±3.4	6.0±0.5	661±147
2	49.8±2.1	7.1±0.7	588±211
3	52.1±3.3	6.0±0.5	552±173
4	38.9±1.8	5.7±0.3	449±119
5	39.3±2.6	6.6±0.6	331±111
6	40.7±1.9	6.1±1.1	257±133
7	41.1±2.0	6.7±0.9	250±97
8	39.4±2.1	6.0±0.8	130±146
9	30.9±3.9	4.6±1.2	71±41
10	30.7±3.1	3.5±1.4	16±7

Table S11: The Change data of mechanical properties of PCL-b-CrP₂₅-U samples after

degradation for 10 weeks.

Degradation time (week)	Elasticity Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
0	39.6±5.4	7.5±1.1	1401±89
1	37.4±4.7	5.9±0.7	702±136
2	33.9±5.1	5.5±0.4	625±117
3	31.2±2.2	4.8±0.3	487±193
4	32.6±1.9	4.6±0.8	312±159
5	33.1±4.1	4.8±0.6	101±67
6	32.4±3.7	4.4±0.9	84±61
7	26.8±2.6	1.5±0.7	9±5

Table S12: The changes of PCL mass fraction(ϕ_{PCL}) during degradation of PCL-b-CrP₁₀-U、PCL-b-CrP₂₀-U、PCL-b-CrP₂₅-U.

samples	ϕ_{PCL} (%)			
	Degradation time (week)			
	0	3	6	10
PCL-U	100	100	100	100
PCL-b-CrP ₁₀ -U	91.64	92.01	92.30	92.69
PCL-b-CrP ₂₀ -U	80.65	81.13	81.33	81.73
PCL-b-CrP ₂₅ -U	78.38	82.54	82.71	83.03

$$\chi_{c, PCL}(\%) = \frac{\Delta H_m PCL}{\Delta H_{0,PCL} \times (\phi PCL)} \times 100\%$$

where H_m is the experimental melting enthalpy and w is the weight fraction of the corresponding component in the blend. $\Delta H_{0,PCL}=139J/g$ for PCL were used according to reported enthalpy of melting of 100% crystalline PCL.

Table S13: The changes of PPDO and PCL content during degradation of PCL-b-CrP₁₀-U、PCL-b-CrP₂₀-U、PCL-b-CrP₂₅-U.

samples	PPDO content (%)				PCL content (%)			
	Degradation time (week)				Degradation time (week)			
	0	3	6	10	0	3	6	10
PCL-U	--	--	--	--	100	100	100	100
PCL-b-CrP ₁₀ -U	9.25	8.85	8.53	8.10	90.75	91.15	91.47	91.90
PCL-b-CrP ₂₀ -U	21.15	20.63	20.41	19.98	78.85	79.37	79.58	80.01
PCL-b-CrP ₂₅ -U	25.34	19.11	18.94	18.59	74.66	80.89	81.06	81.41

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