ACCSCIENCE PUBLISHING

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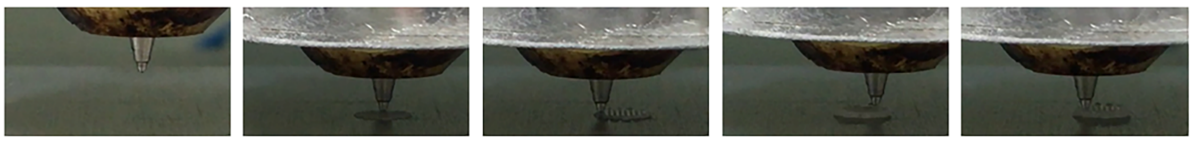
RESEARCH ARTICLE

Thermally tunable and biodegradable copolymer ink for 3D-printed implantable drug delivery depots

Supplementary file

A



B

Chamber Temp. (°C)		80				90				100				110				120			
Printing speed (mm/min)		50	100	200	400	50	100	200	400	50	100	200	400	50	100	200	400	50	100	200	400
CL0 Extrusion pressure (kPa)	100	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	200	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	300	X	X	X	X	Δ	Δ	Δ	Δ	Δ	O	O	Δ	Δ	Δ	O	O	Δ	Δ	O	Δ
	400	X	X	X	X	Δ	O	O	Δ	Δ	O	O	Δ	Δ	Δ	O	O	Δ	Δ	O	O
	500	X	X	X	X	O	O	O	O	O	O	O	O	Δ	O	O	O	Δ	O	O	O
CL1 Extrusion pressure (kPa)	100	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	200	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	Δ	X	X
	300	X	X	X	X	X	X	X	X	X	X	X	X	Δ	Δ	Δ	X	Δ	Δ	Δ	X
	400	X	X	X	X	X	O	O	X	X	Δ	O	X	Δ	Δ	O	Δ	Δ	Δ	O	X
	500	X	X	X	X	Δ	O	O	X	O	O	O	X	Δ	O	O	O	Δ	O	O	O
CL2 Extrusion pressure (kPa)	100	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	200	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	300	X	X	X	X	X	X	X	X	Δ	X	X	X	Δ	Δ	Δ	X	Δ	Δ	Δ	X
	400	X	X	X	X	X	Δ	O	Δ	Δ	Δ	O	X	Δ	Δ	O	Δ	Δ	Δ	O	X
	500	X	X	X	Δ	Δ	O	O	Δ	Δ	O	O	Δ	Δ	O	O	Δ	Δ	Δ	O	Δ
CL3 Extrusion pressure (kPa)	100	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	200	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	300	X	X	X	X	X	X	X	X	X	X	X	X	X	X	Δ	X	X	Δ	Δ	Δ
	400	X	Δ	O	Δ	Δ	Δ	O	X	Δ	Δ	Δ	Δ	X	X	O	Δ	Δ	Δ	O	Δ
	500	X	Δ	O	Δ	Δ	Δ	O	X	Δ	O	O	Δ	Δ	X	O	Δ	Δ	Δ	O	Δ
CL4 Extrusion pressure (kPa)	100	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	200	X	X	Δ	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	300	X	Δ	O	Δ	X	X	Δ	X	X	X	Δ	X	X	X	X	X	X	X	X	X
	400	Δ	Δ	O	Δ	Δ	Δ	O	Δ	X	Δ	O	Δ	X	Δ	Δ	X	X	Δ	Δ	X
	500	Δ	Δ	Δ	X	Δ	Δ	O	Δ	Δ	Δ	O	Δ	X	Δ	Δ	X	X	Δ	Δ	X

C

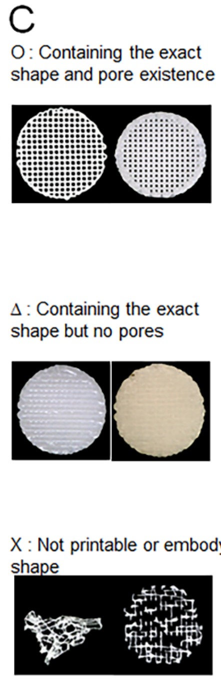


Figure S1. Evaluation of printability of CL polymer inks under various fused deposition modeling 3D printing conditions. (A) Representative images showing the extrusion behavior of CL polymer inks from the heated nozzle during the printing process. (B) Summary matrix illustrating the printability outcomes of CL polymer inks (CL0–CL4) under different chamber temperatures (80–120 °C), printing speed (50–400 mm/min), and extrusion pressures (100–500 kPa). Printability was scored as follows: [○] for successful printing with accurate shape and well-defined pores; [Δ] for accurate shape but no visible pores; and [x] for printing failure or distorted structures. Green-highlighted cells denote optimal printing conditions for each polymer ink. (C) Visual reference guide corresponding to the symbols used in the matrix: [○] indicates depots with preserved structure and porosity; [Δ] denotes structurally intact depots lacking defined pores; and [x] represents failed or deformed prints. Abbreviation: CL, poly(ε-caprolactone-ran-lactide).

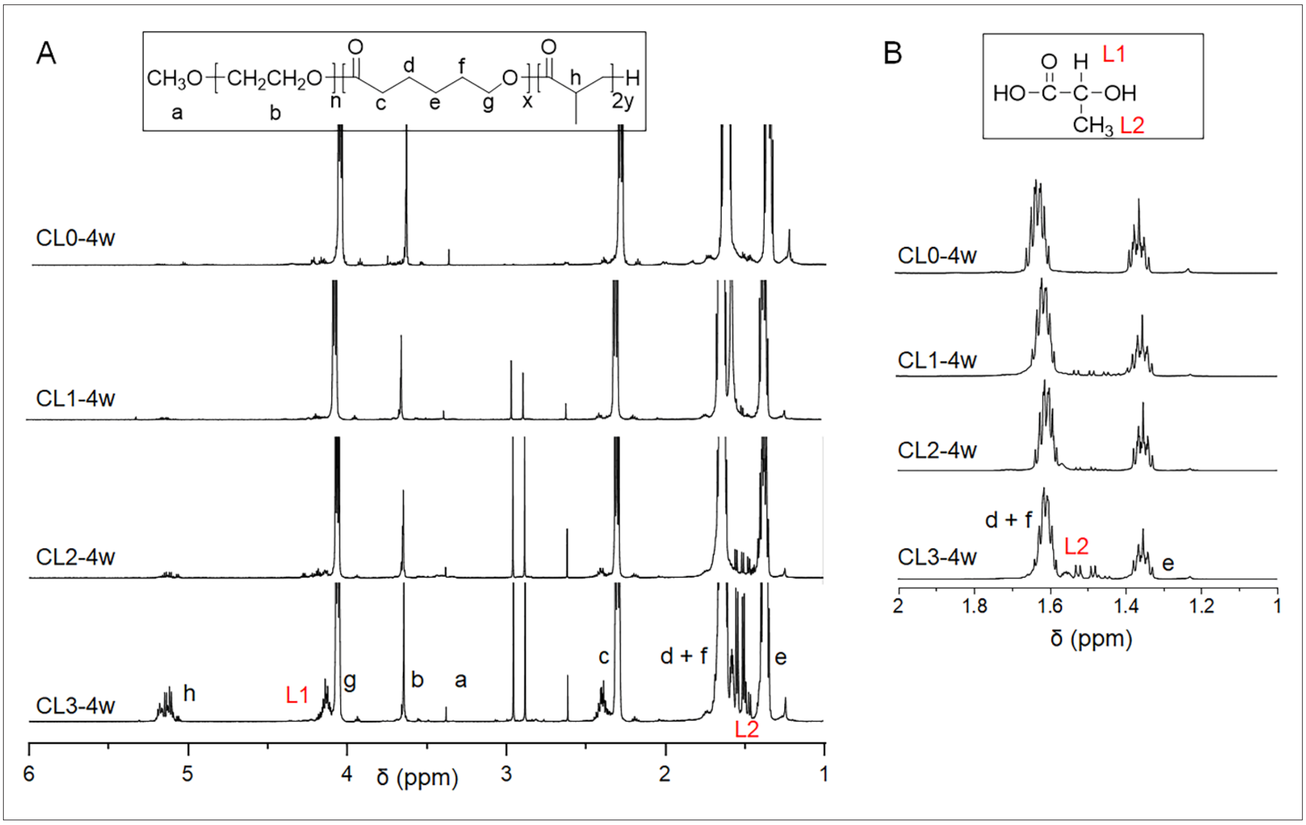


Figure S2. Hydrolytic degradation analysis of CL0, CL1, CL2, and CL3 bioinks via proton nuclear magnetic resonance spectroscopy (^{1}H NMR) spectroscopy after incubation in distilled water at 37 °C. (A) Full ^{1}H NMR spectra of the incubated samples, showing the overall chemical structure of each formulation. (B) Magnified view of the L2 region (1.0–2.0 ppm highlighting the methyl proton signals of lactide units to assess hydrolytic cleavage and degradation behavior over time).

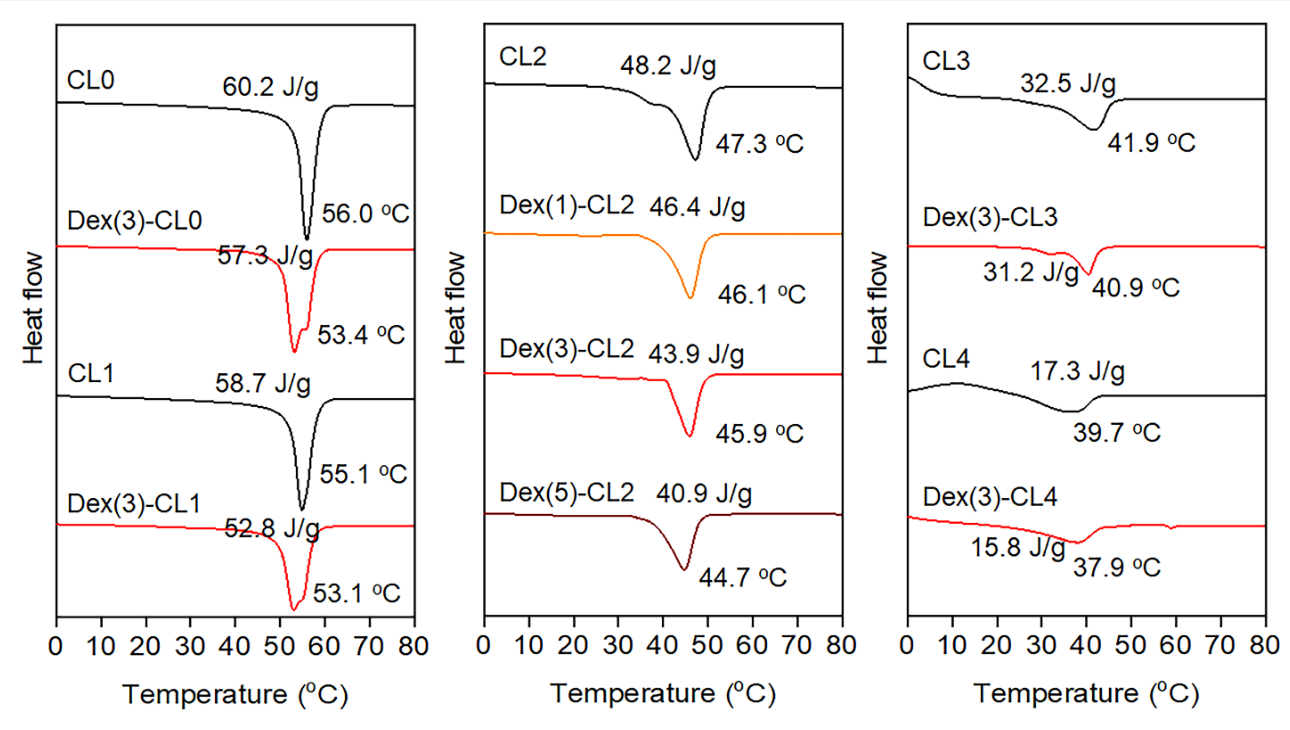


Figure S3. Differential scanning calorimetry curves of CL0, CL1, CL2, and CL3 bioinks and Dex-CL. Abbreviations: CL, poly(ε-caprolactone-ran-lactide); Dex-CL, dexamethasone-loaded CL.