Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

8 Pages

11 Figures

2 Tables

1 video

Shape Memory Polymer (SMP) Scaffolds with Improved Self-Fitting Properties

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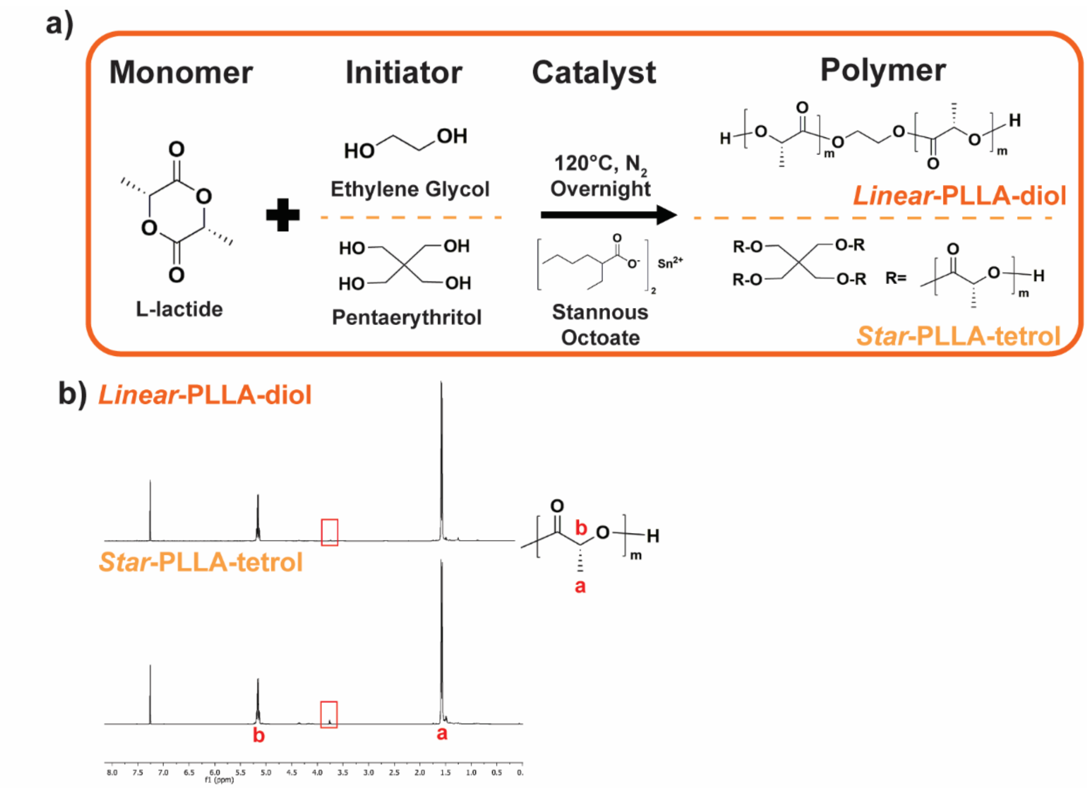
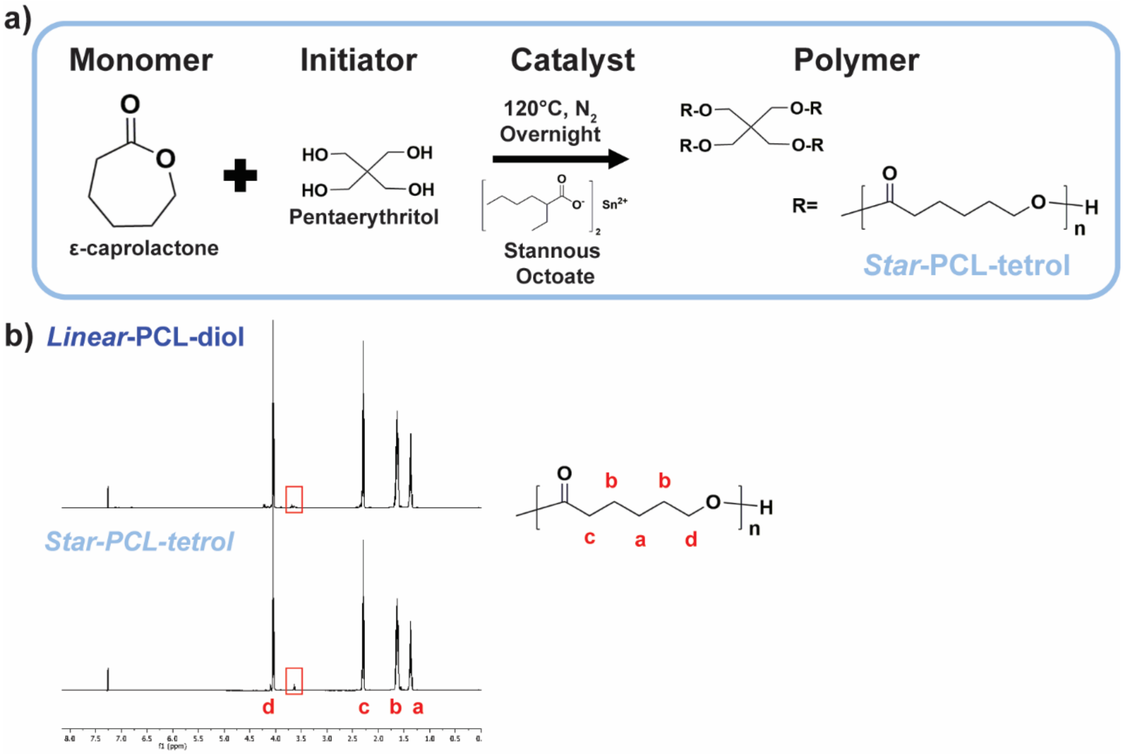


c)

	DSC			NMR
	T_g (°C)	T_m (°C)	% Crystallinity	M_n (kg/mol)
Linear-PLLA-diol	45.1 ± 0.90	155 ± 0.36	49.8 ± 0.56	15.6
Star-PLLA-tetrol	49.2 ± 0.54	152 ± 0.47	15.0 ± 1.9	14.7

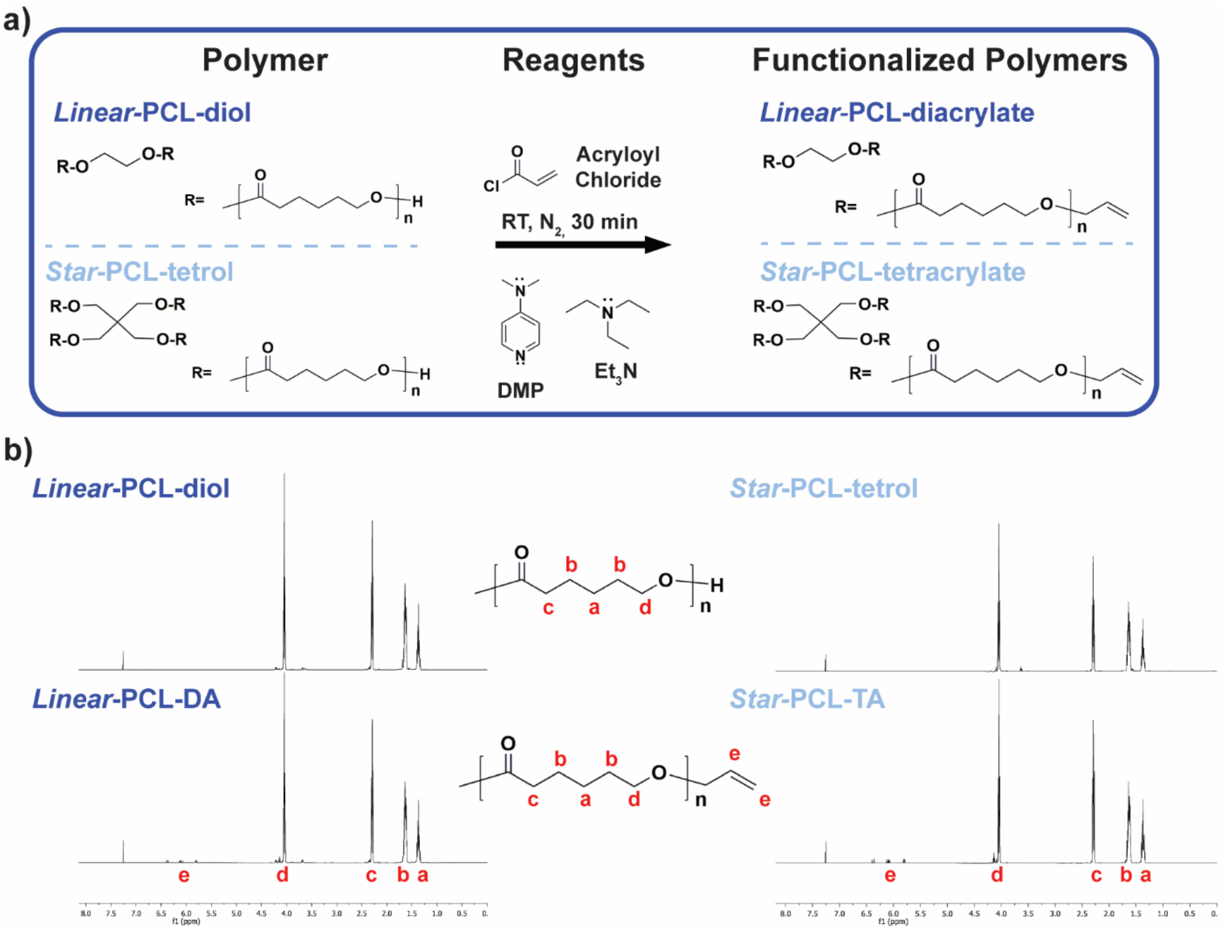
Figure S1. (a) Synthetic scheme for *linear*- and *star*-PLLA. (b) NMR spectra with red boxes to indicate the reference peaks representing the terminal C**H** used to calculate M_n. (c) Summary of thermal properties from DSC and M_n from NMR.



c)

	DSC			NMR
	T_g (°C)	T_m (°C)	% Crystallinity	M_n (kg/mol)
Linear-PCL-diol	-65.1 ± 0.82	52.7 ± 0.16	47.7 ± 1.3	10.3
Star-PCL-tetrol	-63.2 ± 1.2	50.0 ± 0.37	44.8 ± 1.6	10.9

Figure S2. (a) Synthetic scheme for *star*-PCL-tetrol. [Note: *linear*-PCL-diol was purchased.] (b) NMR spectra with red boxes to indicate the reference peaks representing terminal C**H₂** used to calculate M_n. (c) Summary of thermal properties from DSC and M_n from NMR.



c)

	NMR % acrylation
Linear-PCL-DA	93.4
Star-PCL-TA	87.4

Figures S3. (a) Synthetic scheme for acrylation of *linear*-PCL-diol and *star*-PCL-tetrol. NMR spectra for (b) *linear*-PCL-DA and (c) *star*-PCL-TA. (d) Summary of NMR % acrylation calculations.

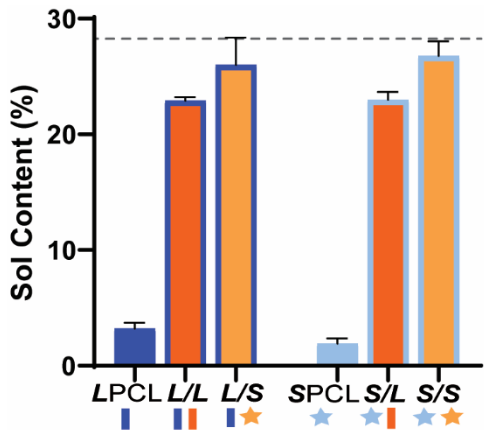


Figure S4. Sol content values of scaffolds demonstrating adequate cross-linking with an upper limit of ~29% mass loss [~2-4% for ***L****PCL* and ***S****PCL* controls + ~25% thermoplastic PLLA] for semi-IPN compositions.

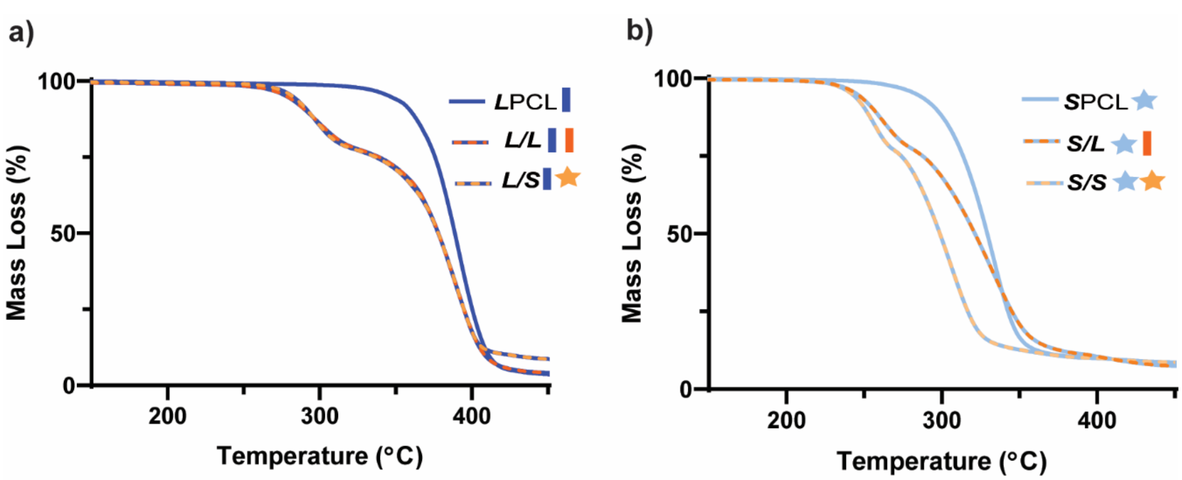


Figure S5. TGA of scaffolds verifying ~25% thermoplastic in PCL/PLLA semi-IPNs (a) for *linear*-PCL-DA based compositions, and (b) for *star*-PCL-TA based compositions.

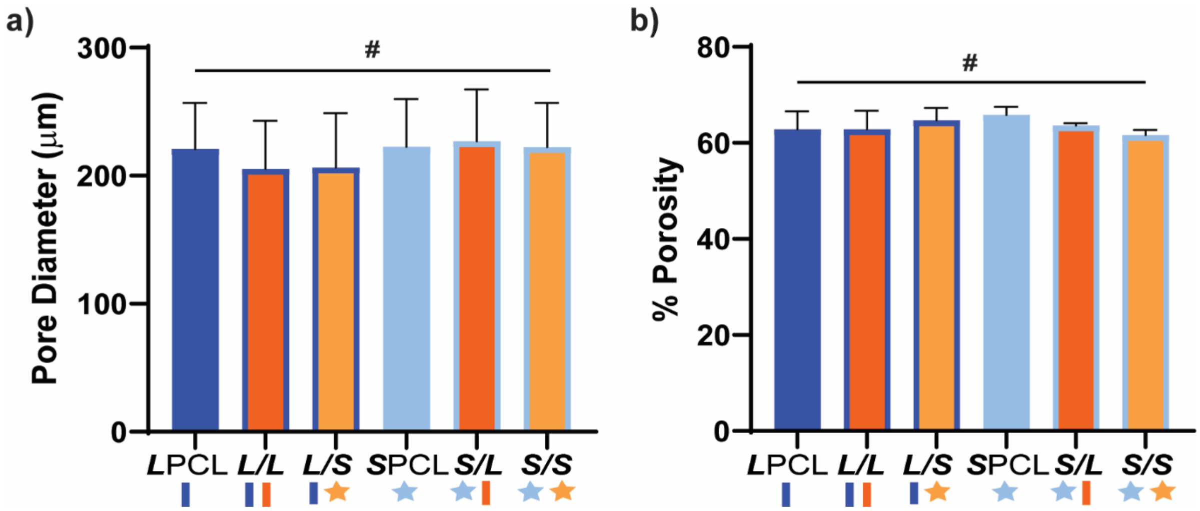


Figure S6. (a) Pore size was maintained at ~220 μm for all scaffolds, and (b) all scaffolds exhibited similar ~60% porosity ($^{\#}p > 0.05$).

Table S1. Thermal properties of scaffolds.

	PCL			PLLA		
	T_m onset (°C)	T_m midpoint (°C)	% Crystallinity	T_m onset (°C)	T_m midpoint (°C)	% Crystallinity
***L**PCL*	50.5 ± 0.41	56.1 ± 0.56	42.7 ± 1.7	--	--	--
L/L	50.5 ± 0.61	56.6 ± 0.21	42.0 ± 1.9	153.9 ± 1.8	164.0 ± 1.5	37.6 ± 7.3
L/S	51.1 ± 0.27	56.3 ± 0.25	42.5 ± 2.0	152.2 ± 0.84	157.5 ± 0.44	19.5 ± 1.8
***S**PCL*	42.6 ± 0.20	49.2 ± 0.02	30.4 ± 3.5	--	--	--
S/L	41.0 ± 0.83	50.0 ± 0.12	33.5 ± 1.6	155.2 ± 0.56	160.0 ± 0.19	23.0 ± 7.1
S/S	39.7 ± 2.0	50.3 ± 0.20	39.2 ± 4.3	147.9 ± 2.2	156.5 ± 0.13	24.7 ± 5.8

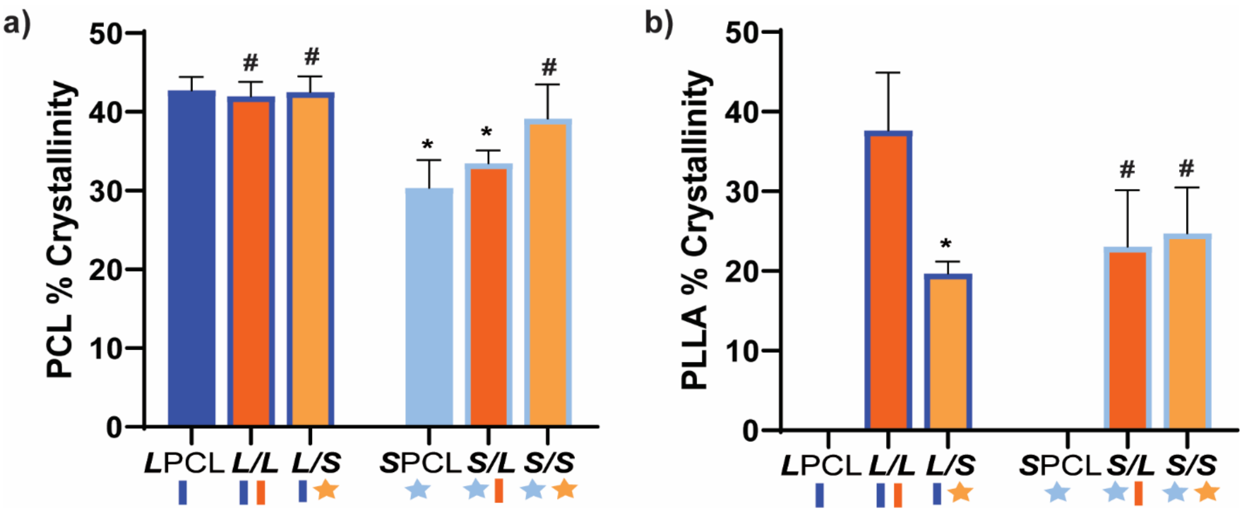


Figure S7. Scaffold (a) PCL % crystallinity; *$p < 0.05$ and $^{\#}p > 0.05$ versus ***LPCL*** and (b) PLLA % crystallinity; *$p < 0.05$ and $^{\#}p > 0.05$ versus ***L/L***.

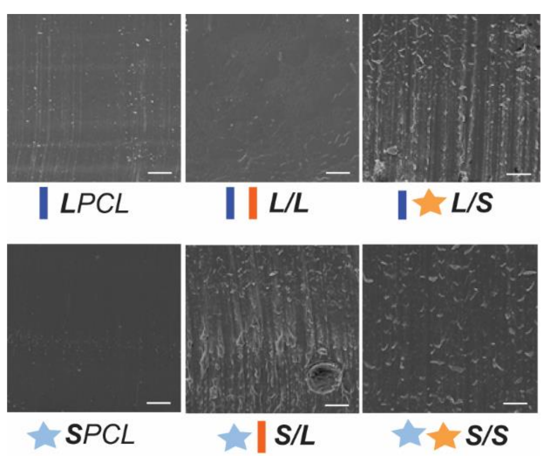


Figure S8. SEM images of solid film cross-sections of analogous compositions to scaffolds to examine relative miscibility or phase separation. Scale bars = 50 μm.

Table S2. Mechanical properties of scaffolds.

	Modulus (MPa)	Compressive Strength (MPa)	Toughness (mJ)
***L*PCL**	9.65 ± 2.8	21.6 ± 4.0	238 ± 74
L/L	23.8 ± 3.6	28.0 ± 5.2	275 ± 66
L/S	17.4 ± 4.2	34.3 ± 6.0	325 ± 61
***S*PCL**	3.57 ± 0.58	15.0 ± 3.2	115 ± 25
S/L	11.9 ± 2.3	24.5 ± 7.7	184 ± 45
S/S	11.3 ± 2.4	15.3 ± 6.8	138 ± 58

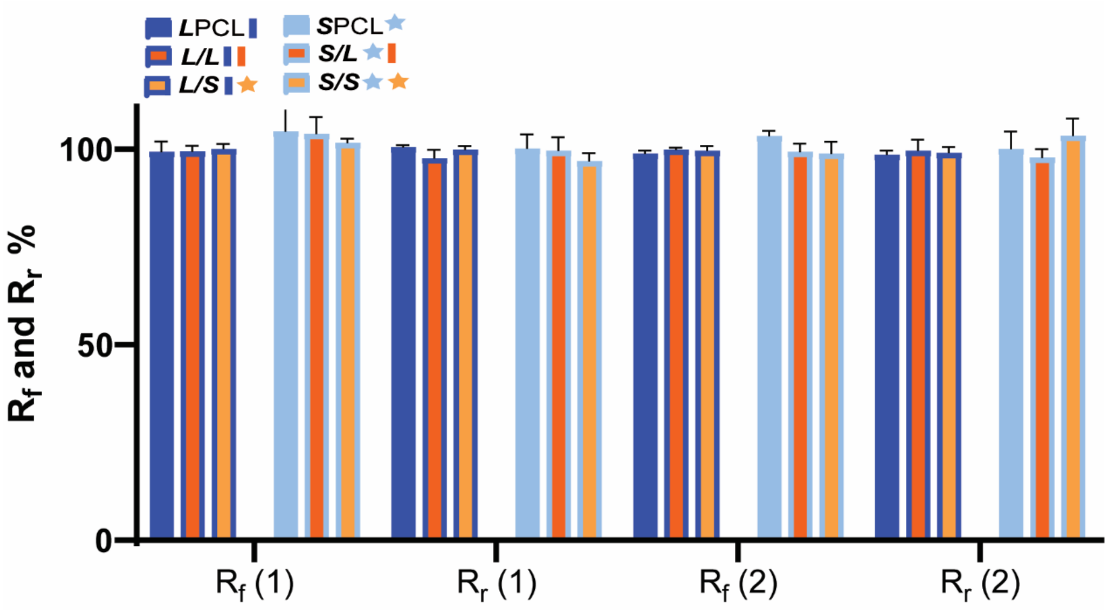


Figure S9. Quantitative shape fixity (R_f) and shape recovery (R_r) over 2 cycles; $^{\#}p > 0.05$.

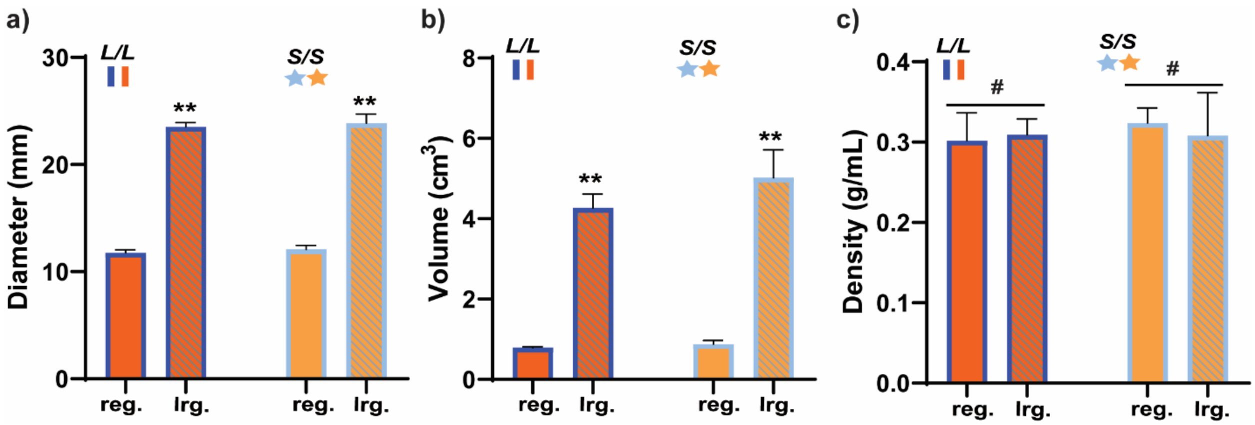
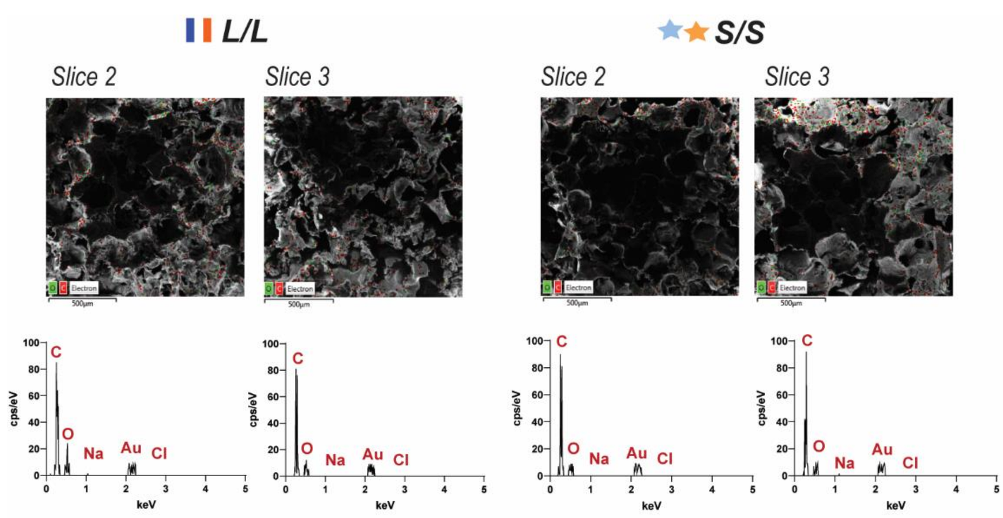


Figure S10. The scaled-up, “larger”, scaffolds (“lrg.”) compared to “regular” scaffolds (“reg.”) having: (a) 2X the diameter, (b) 5X the volume, and (c) constant density (**p <0.01, # p >0.05 versus reg).



Element	Wt. %
C	50.6 ± 2.0
O	31.0 ± 1.8
Au	18.4 ± 2.2

Element	Wt. %
C	49.3 ± 2.2
O	33.8 ± 2.1
Au	17.0 ± 2.5

Element	Wt. %
C	48.1 ± 2.1
O	32.6 ± 1.9
Au	19.3 ± 2.4

Element	Wt. %
C	49.3 ± 2.1
O	31.3 ± 1.9
Au	19.5 ± 2.4

Figure S11. “Larger” scaffold slices were subjected to SEM EDS elemental mapping to confirm full porogen (NaCl) leaching. As shown, Na and Cl were both not detected, indicating that scaffolds were free from residual porogens.

Video S1. Diffusion of ***L/L*** and ***S/S*** semi-IPN macromer solutions through salt templates.