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Supporting Information

Star-PCL Shape Memory Polymer (SMP) Scaffolds with Tunable Transition Temperatures for Enhanced Utility

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14 Pages

9 Figures

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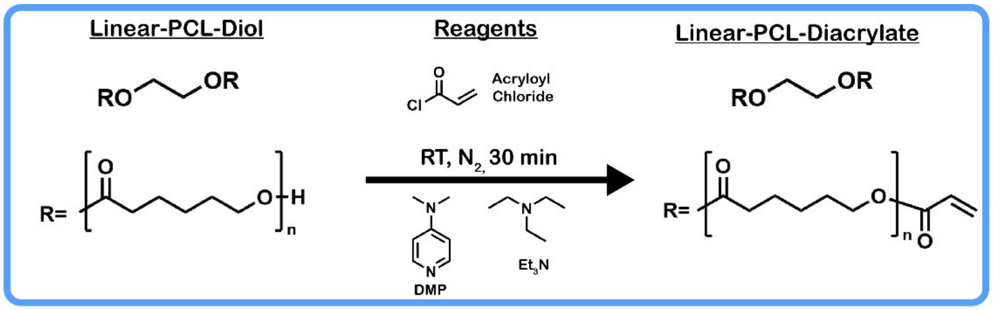
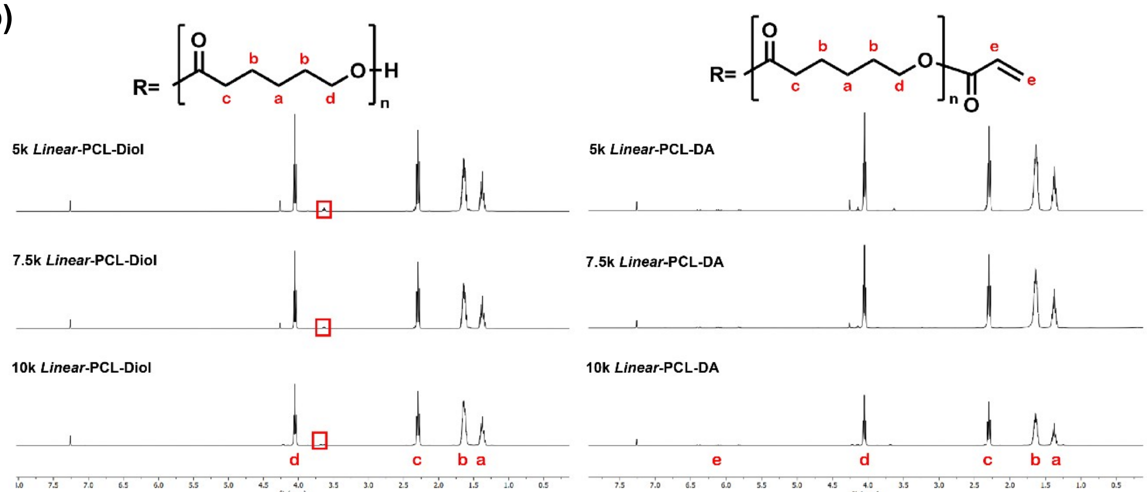
3 videos

(a)



(b)



(c)

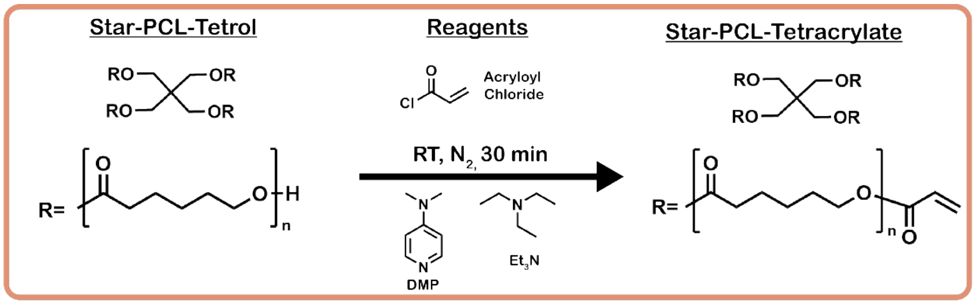
	DSC		NMR
	T_m	% Crystallinity	M_n (kg/mol)
10k *Linear*-PCL-diol	53.6 ± 0.18	48.8 ± 2.58	10.2
7.5k *Linear*-PCL-diol	53.2 ± 0.45	50.6 ± 0.08	7.4
5k *Linear*-PCL-diol	52.6 ± 1.63	53.2 ± 1.26	5.7

(d)

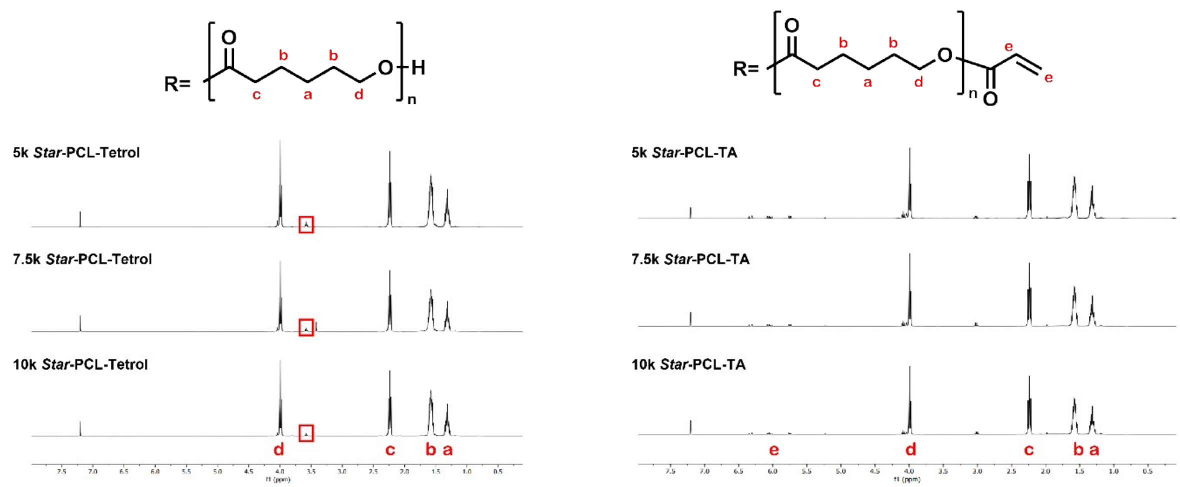
	DSC		NMR
	T_m	% Crystallinity	% Acrylation
10k *Linear*-PCL-DA	53.4 ± 0.13	45.9 ± 0.76	98%
7.5k *Linear*-PCL-DA	53.7 ± 0.16	48.6 ± 2.61	90%
5k *Linear*-PCL-DA	53.9 ± 0.52	48.5 ± 2.18	94%

Figure S1. **(a)** Synthetic scheme for the acrylation of *linear*-PCL-diol to produce *linear*-PCL-DA. **(b)** ^{1}H NMR spectra for *linear*-PCL-diols and *linear*-PCL-DAs of different M_ns. **(c)** Summary of *linear*-PCL-diols' thermal properties (from DSC), and M_n (from ^{1}H NMR). **(d)** Summary of the *linear*-PCL-DA macromers' thermal properties (from DSC), and % acrylation (from ^{1}H NMR).

(a)



(b)



(c)

	DSC		NMR
	T_m	% Crystallinity	M_n (kg/mol)
10k *Star*-PCL-tetrol	48.8 ± 1.44	42.2 ± 4.93	10.3
7.5k *Star*-PCL-tetrol	48.4 ± 0.42	43.9 ± 1.10	7.5
5k *Star*-PCL-tetrol	47.3 ± 1.10	43.9 ± 4.97	5.7

(d)

	DSC		NMR
	T_m	% Crystallinity	% Acrylation
10k *Star*-PCL-TA	49.0 ± 0.46	50.5 ± 2.77	89%
7.5k *Star*-PCL-TA	46.7 ± 0.57	44.4 ± 1.30	93%
5k *Star*-PCL-TA	43.5 ± 0.34	45.7 ± 0.58	96%

Figure S2. (a) Synthetic scheme for the acrylation of *star*-PCL-tetrol to produce *star*-PCL-TA. **(b)** ^{1}H NMR spectra for *star*-PCL-tetrols and *star*-PCL-TAs of different M_ns. **(c)** Summary of *star*-PCL-tetrols' thermal properties (from DSC), and M_n (from ^{1}H NMR). **(d)** Summary of *star*-PCL-TA macromers' thermal properties (from DSC) and % acrylation (from ^{1}H NMR).

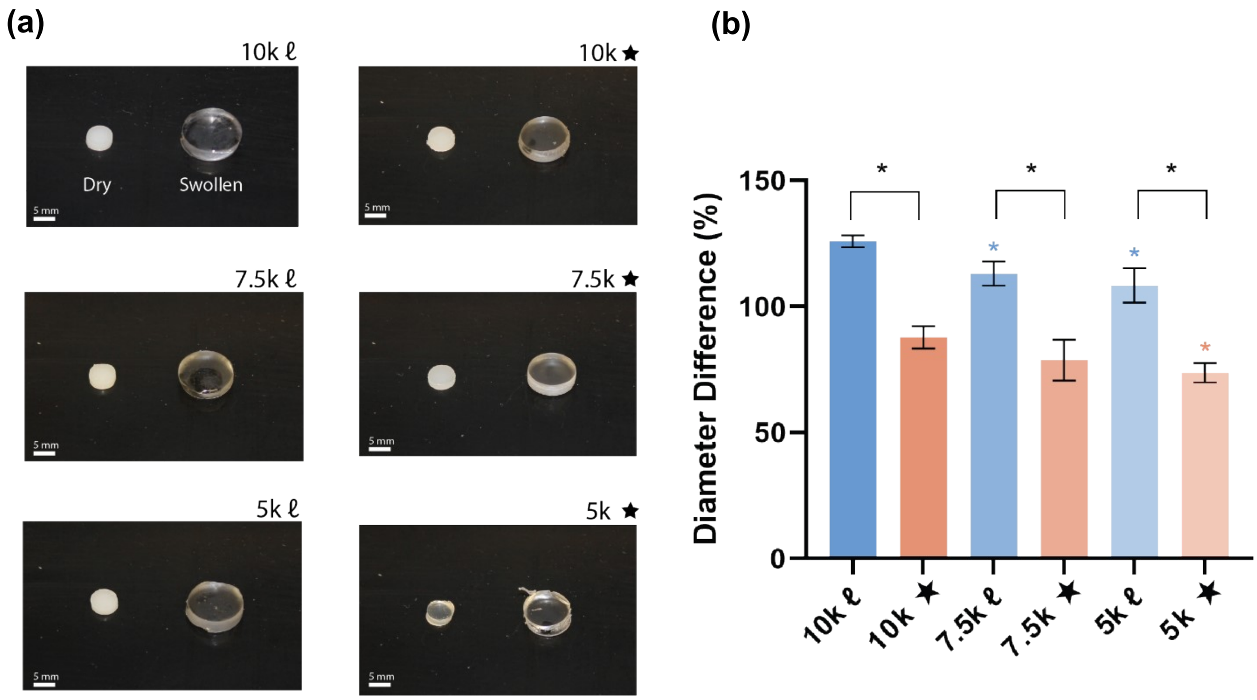


Figure S3. Crosslink density assessed via swelling tests of solid film discs. **(a)** For each macromer, image of resulting dry (left) and solvent-swollen (right) specimens. **(b)** Corresponding % diameter difference between a dry and solvent-swollen discs of a given composition. “Black *” $p < 0.05$ *linear*- versus *star*- films of same M_n. “Blue *” $p < 0.05$ versus 10kℓ. “Pink *” $p < 0.05$ versus 10k★.

Table S1. Crosslink density assessed via swelling tests of solid film discs.

	Diameter Difference (%)
10k ℓ	125.9 ± 2.34
10k ★	87.8 ± 4.39
7.5k ℓ	113.1 ± 4.83
7.5k ★	78.9 ± 8.12
5k ℓ	108.4 ± 6.89
5k ★	73.8 ± 3.92

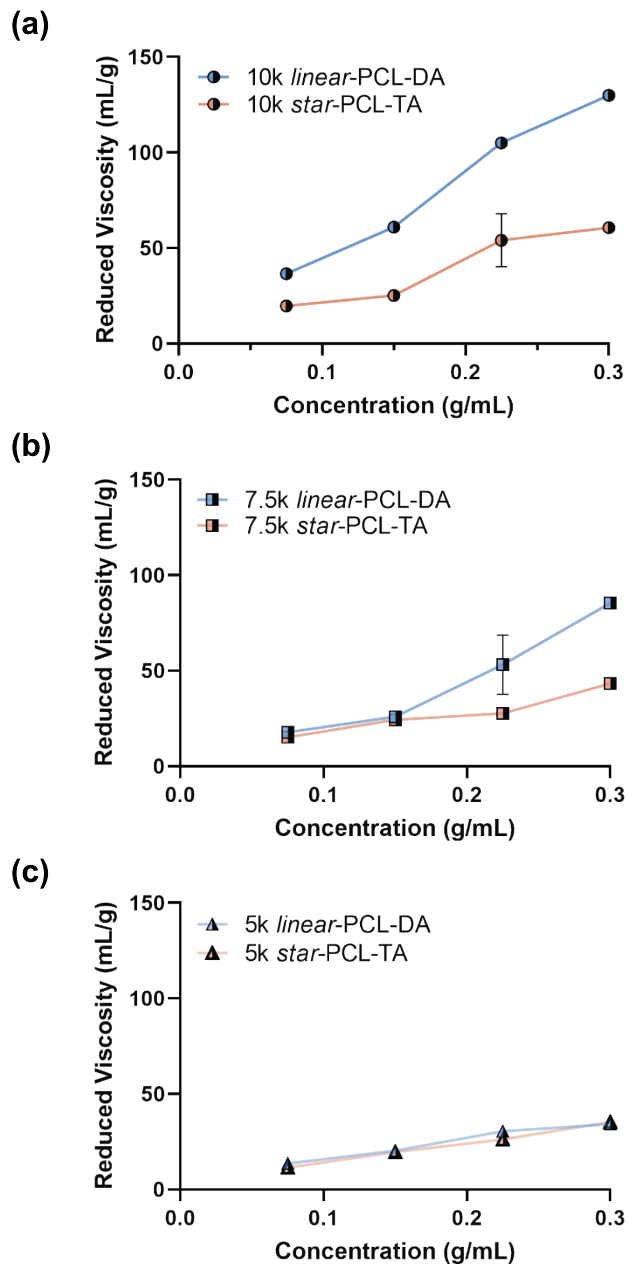


Figure S4. Reduced viscosity (η_{red}) of acrylated macromer solutions of varying M_ns: **(a)** 10 kg mol^{-1}, **(b)** 7.5 kg mol^{-1}, and **(c)** 5 kg mol^{-1}.

Table S2. Reduced viscosity (η_{red}) of acrylated macromer solutions of varying M_ns at designated concentrations.

	Reduced Viscosity (mL/g) at Concentration			
	0.075 g/mL	**0.150 g/mL**	**0.225 g/mL**	**0.300 g/mL**
10k ℓ	36.6 ± 0.71	60.9 ± 1.49	105.1 ± 2.84	129.9 ± 2.81
10k ★	19.7 ± 0.72	25.2 ± 0.37	54.1 ± 13.93	60.7 ± 1.48
7.5k ℓ	17.9 ± 0.19	25.9 ± 2.37	53.2 ± 15.57	85.5 ± 1.88
7.5k ★	15.2 ± 0.42	24.31 ± 0.55	27.6 ± 1.32	43.4 ±1.22
5k ℓ	13.6 ± 0.48	20.3 ± 0.31	30.4 ± 4.30	34.2 ± 0.70
5k ★	11.5 ± 0.08	19.5 ± 0.41	26.2 ± 0.21	35.3 ± 1.08

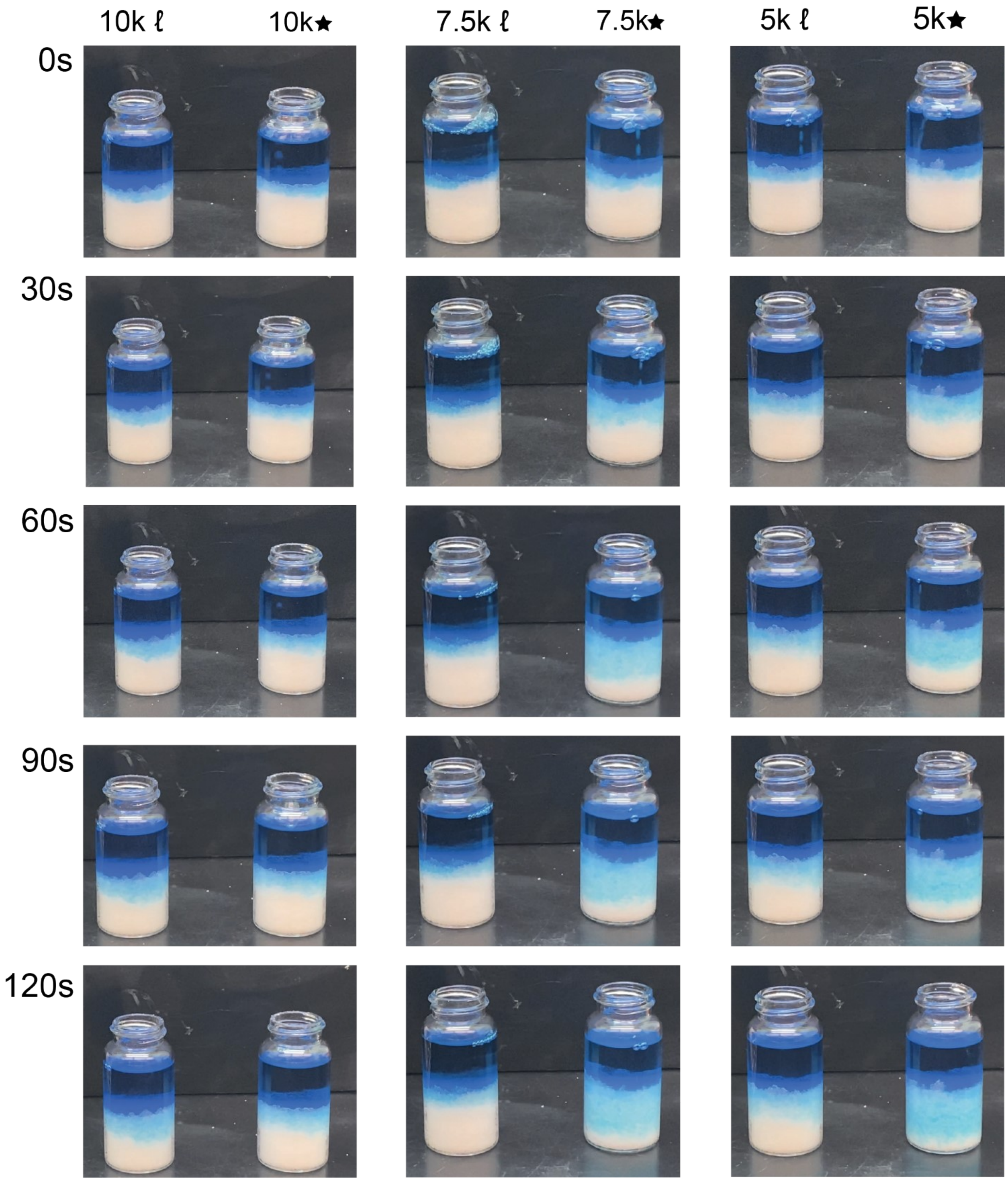


Figure S5. Dye-containing macromer solution diffusion through a salt mold. Accompanied videos provided.

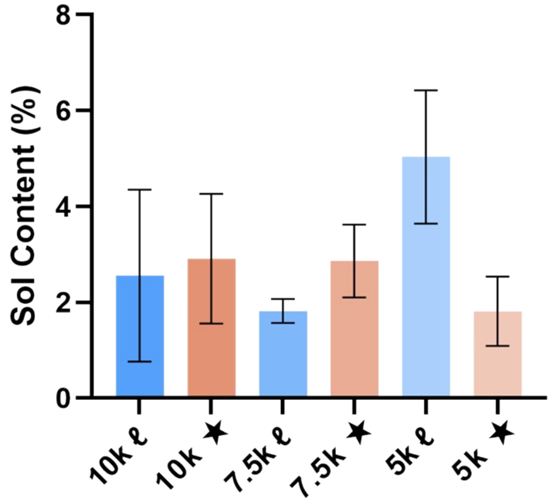


Figure S6. Sol content (%) of scaffolds.

Table S3. Sol content (%) of scaffolds.

	Sol Content (%)
10k ℓ	2.6 ± 1.80
10k ★	2.9 ± 1.35
7.5k ℓ	1.8 ± 0.25
7.5k ★	2.9 ± 0.76
5k ℓ	5.0 ± 1.39
5k ★	1.8 ± 0.72

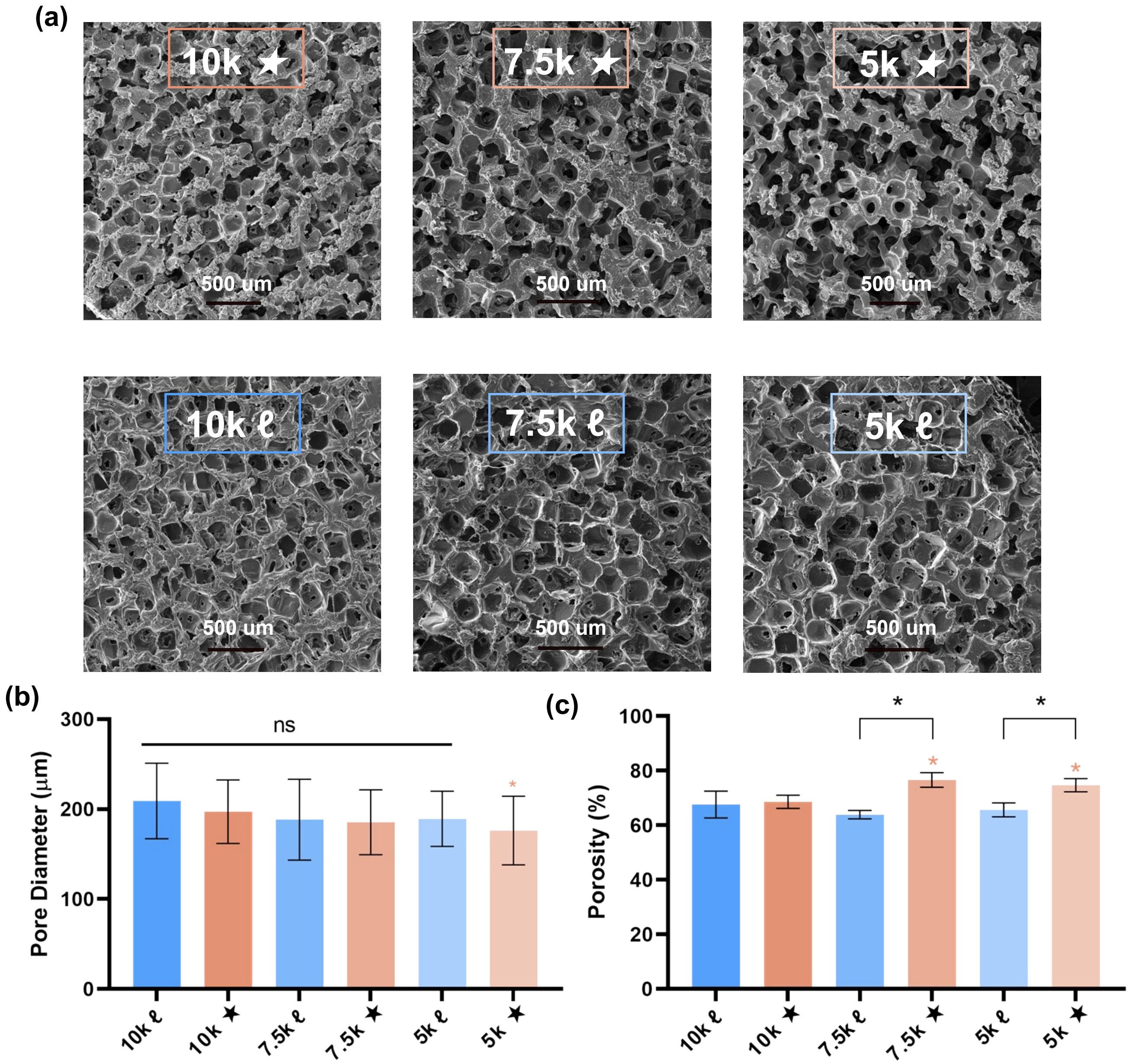


Figure S7. **(a)** SEM images of the scaffold cross-sections. **(b)** Scaffold pore diameters. **(c)** % Porosity of scaffolds. "Black *" $p < 0.05$ comparing *linear*- and *star*- scaffolds of same M_n. "Blue *" $p < 0.05$ versus 10kℓ. "Pink *" $p < 0.05$ versus 10k★.

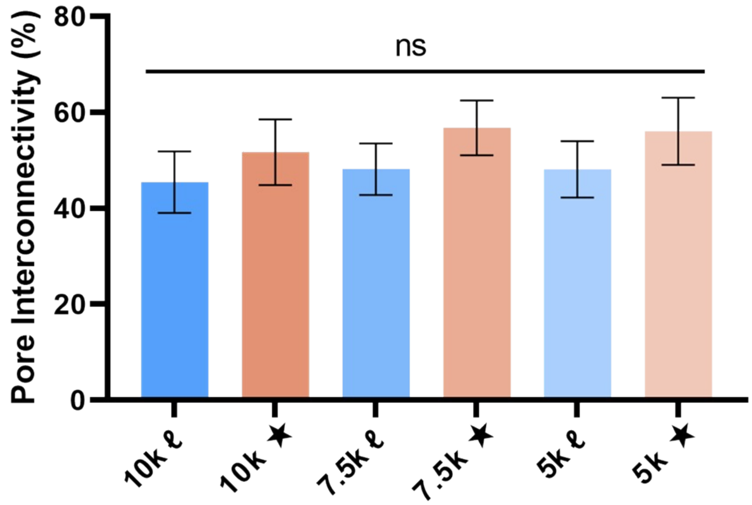


Figure S8. Scaffold pore interconnectivity.

Table S4. Scaffold pore size, % porosity, and % pore interconnectivity.

	Pore Size (µm)	**Porosity (%)**	**Pore Interconnectivity (%)**
10k ℓ	209.1 ± 42.00	67.6 ± 4.93	45.4 ± 6.40
10k ★	197.2 ± 35.21	68.6 ± 2.43	51.7 ± 6.85
7.5k ℓ	188.4 ± 44.89	63.9 ± 1.53	48.1 ± 5.36
7.5k ★	185.4 ± 36.03	76.6 ± 2.67	56.7 ± 5.69
5k ℓ	189.2 ± 30.60	65.7 ± 2.58	48.1 ± 5.84
5k ★	176.2 ± 38.20	74.7 ± 2.43	56.0 ± 6.98

Table S5. T_m and % crystallinity of scaffolds.

	$T_{m,onset}$ (°C)	$T_{m,}$(°C) ["midpoint"]	Crystallinity (%)
10k ℓ	51.3 ± 0.13	56.7 ± 0.11	46.5 ± 1.09
10k ★	39.6 ± 2.25	46.2 ± 1.53	26.7 ± 2.07
7.5k ℓ	48.6 ± 1.15	52.2 ± 0.93	37.1 ± 0.35
7.5k ★	34.3 ± 4.04	40.4 ± 2.12	22.4 ± 5.55
5k ℓ	45.9 ± 0.27	51.4 ± 0.11	35.3 ± 1.23
5k ★	17.8 ± 0.52	29.1 ± 0.42	18.7 ± 0.30

Table S6. Scaffold shape fixity (R_f) and shape recovery (R_r) for cycle 1 and cycle 2.

	$R_{f\ cycle\ 1}$ (%)	$R_{r\ cycle\ 1}$ (%)	$R_{f\ cycle\ 2}$ (%)	$R_{r\ cycle\ 2}$ (%)
10k ℓ	99.3 ± 7.77	108.6 ± 6.28	103.5 ± 3.62	97.0 ± 1.90
10k ★	103.6 ± 3.43	103.5 ± 3.79	101.5 ± 4.75	96.4 ± 1.02
7.5k ℓ	104.0 ± 4.17	100.8 ± 0.70	102.3 ± 2.62	101.3 ± 3.46
7.5k ★	98.3 ± 3.46	97.3 ± 3.27	102.7 ± 5.52	101.8 ± 5.05
5k ℓ	97.6 ± 1.72	99.9 ± 0.58	95.3 ± 3.12	99.7 ± 1.64
5k ★	107.3 ± 4.02	98.8 ± 2.46	108.5 ± 3.43	99.9 ± 2.09

Table S7. Radial pressure exerted by scaffold at its T_m.

	Radial Pressure (kPa)
10k ℓ	107 ± 32
10k ★	273 ± 56
7.5k ℓ	122 ± 58
7.5k ★	156 ± 85
5k ℓ	77 ± 21
5k ★	165 ± 61

Table S8. Scaffold mass loss (%) during accelerated degradation study (0.1 M NaOH, 37 °C).

	Composition					
Time (day)	10kℓ	10k★	7.5kℓ	7.5k★	5kℓ	5k★
1	2.4 ± 3.24	0.5 ± 1.01	3.1 ± 3.16	12.0 ± 2.12	1.9 ± 0.80	0.3 ± 1.11
2	2.5 ± 1.52	4.0 ± 1.79	1.1 ± 0.97	9.2 ± 6.06	2.6 ± 2.10	10.9 ± 10.90
3	0.9 ± 1.25	3.4 ± 2.25	3.3 ± 0.99	7.8 ± 1.90	3.7 ± 2.24	25.3 ± 7.93
4	1.7 ± 1.19	5.4 ± 2.46	4.8 ± 1.63	14.0 ± 4.50	9.2 ± 6.39	36.8 ± 8.89
5	4.4 ± 1.34	6.6 ± 1.47	7.1 ± 1.57	33.5 ± 8.87	1.0 ± 2.03	57.0 ± 34.29
6	5.7 ± 0.99	11.3 ± 2.99	9.7 ± 4.67	45.3 ± 17.79	7.7 ± 2.60	84.6 ± 18.98
7	5.8 ± 2.88	16.6 ± 6.08	16.3 ± 2.34	50.5 ± 14.71	9.2 ± 2.29	97.9 ± 1.91
8	27.8 ± 11.99	16.9 ± 5.65	17.0 ± 2.49	65.8 ± 31.67	9.7 ± 1.52	98.6 ± 1.73
9	35.8 ± 10.22	29.8 ± 6.56	22.6 ± 7.04	96.7 ± 5.77	17.2 ± 13.30	100.0 ± 0.00
10	58.2 ± 28.05	35.2 ± 12.84	42.9 ± 10.20	97.6 ± 2.68	27.0 ± 18.06	100.0 ± 0.00
12	72.3 ± 11.29	69.1 ± 15.52	81.3 ± 32.40	100.0 ± 0.00	13.6 ± 5.26	100.0 ± 0.00
15	81.2 ± 22.58	100.0 ± 0.00	100.0 ± 0.00	100.0 ± 0.00	58.7 ± 5.83	100.0 ± 0.00

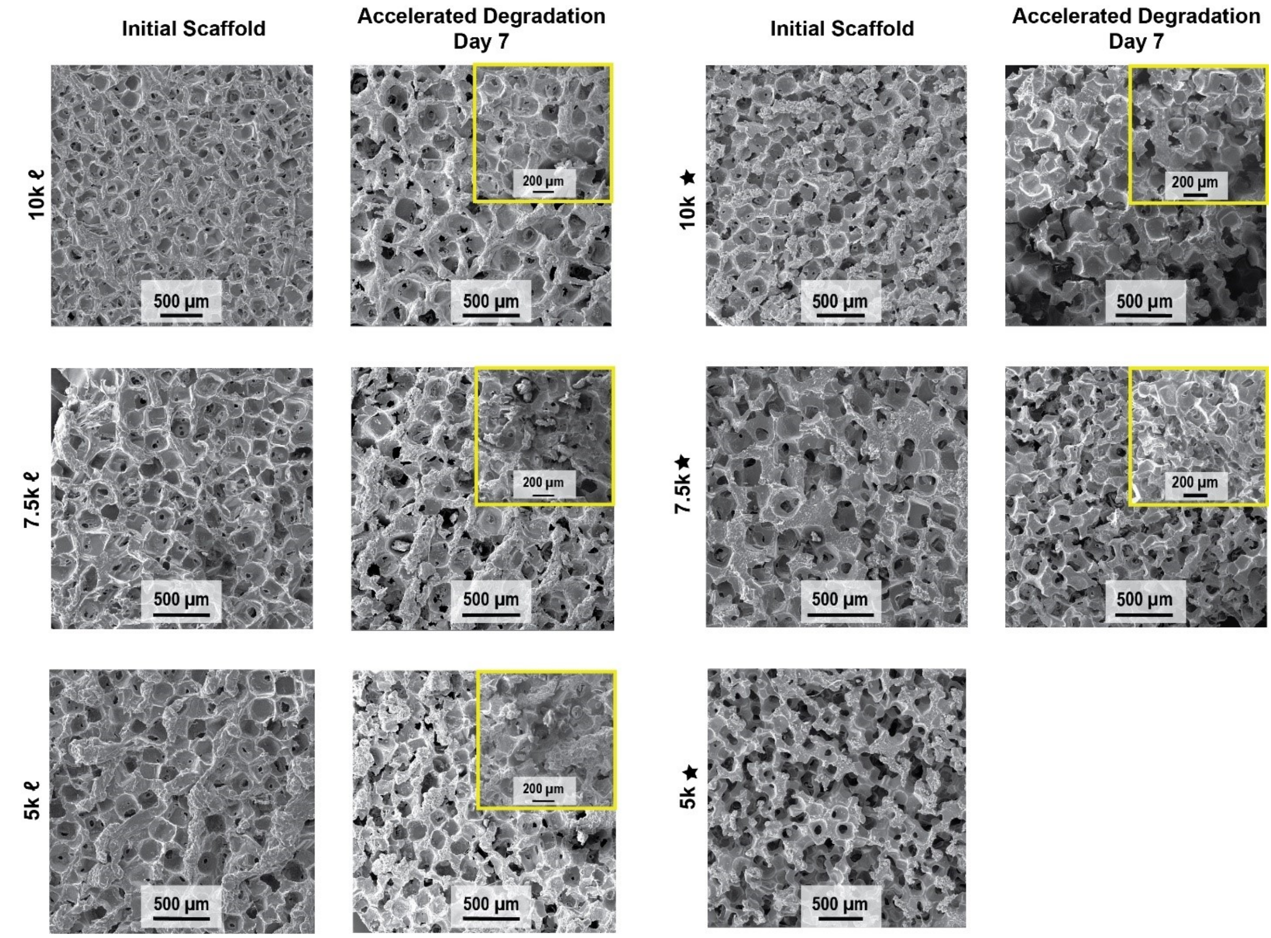


Figure S9. SEM images of initial scaffolds and scaffolds after 7 days in 0.1M NaOH (37 °C).

Table S9. Scaffold compressive mechanical properties.

	Compressive Modulus (MPa)	**Compressive Strength (MPa)**	**Compressive Toughness (MJ m^{-3})**
10k ℓ	7.10 ± 2.20	32.73 ± 1.93	5.24 ± 0.68
10k ★	2.02 ± 0.68	10.55 ± 3.57	1.84 ± 0.46
7.5k ℓ	5.54 ± 1.96	31.97 ± 4.56	4.35 ± 0.98
7.5k ★	1.30 ± 0.65	7.30 ± 4.04	1.23 ± 0.62
5k ℓ	4.65 ± 1.62	27.74 ± 11.23	4.29 ± 1.16
5k ★	0.69 ± 0.18	5.37 ± 2.52	0.86 ± 0.32