

Supplementary Information

Radical Free Crosslinking of Direct-Write 3D Printed Hydrogels Through a Base Catalyzed Thiol-Michael Reaction

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General Experimental

0.1 M KP buffer preparation

Potassium phosphate dibasic (16.248 g, 0.119 mol) and potassium phosphate monobasic (0.888 g, 0.005 mol) was dissolved in deionized (DI) water (800 mL). The pH of the solution was adjusted to 8.01 using an aqueous sodium hydroxide solution (1 M), and the mixture was diluted to 1 L with DI water. pH was measured using a Mettler Toledo EL20-Basic Benchtop Education pH Meter (Columbus, OH, USA).

0.1 M PBS buffer preparation

Sodium chloride (80 g, 1.36 mol), potassium chloride (2 g, 0.027 mol), sodium phosphate dibasic (14.4 g, 0.106 mol), and potassium phosphate monobasic (2.4 g, 0.014 mol) were dissolved in DI water (800 mL). The solution was adjusted to pH 8.2 using an aqueous sodium hydroxide solution (1 M), and the mixture was diluted to 1 L with DI water.

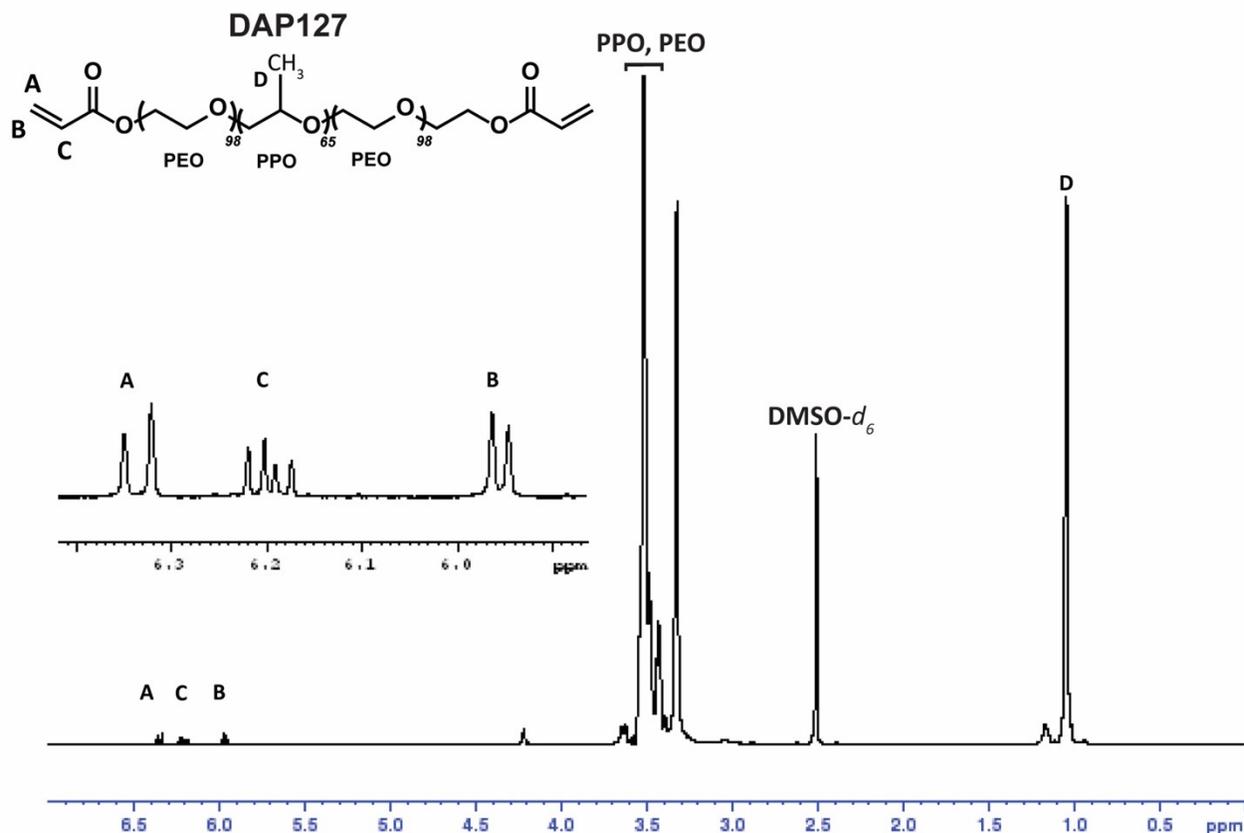


Figure S1. ¹H NMR spectrum of DAP127 (600 MHz, 293K, DMSO-*d*₆)

Table S1. Thiol-Michael hydrogel compositions at a constant DAP127 wt% of 25.67 with 3-arm (TMTMP) and 4-arm (PETMP) thiol crosslinkers.

	DAP (g)	H ₂ O (mL)	TMTMP (μL, equiv.)	PETMP (μL, equiv.)	Irgacure 754 (μL, equiv.)
DAP127-TMTMP ₁	7.7	22.3	200, 1	0	0
DAP127-TMTMP _{0.67}			134, 0.67	0	0
DAP127-TMTMP _{0.33}			66, 0.33	0	0
DAP127-PETMP _{0.5}			0	117, 0.50	0
DAP127			0	0	3.8, 0.02

Table S2. Direct-write 3D printing parameters used to print dogbones with dimensions according to ISO standard 37-4 and compression disks with dimensions (outer diameter-*d* height-*h*) 10 mm × 8.0 mm

Parameter	
Nozzle size (mm)	0.9
Head temperature (°C)	25
Bed temperature (°C)	25
Layer height (mm)	0.4
Shell thickness (mm)	0.9
Initial layer thickness (mm)	0.3
Initial layer line width (%)	100
Print speed (mm/s)	3.5
Travel speed (mm/s)	20
Bottom layer speed (mm/s)	10

Table S3. Curing conditions used for testing crosslinking of DAP127-TMTMP_{0.67}.

Curing Condition	pH	Concentration (M)	Gelation
Incubation (37 °C)	--	--	No
KP Buffer	8.0	0.1	No
KP Buffer	8.0	0.05	No
PBS	8.2	0.1	Yes
PBS	8.2	0.05	No

Table S4. Dimensional stability calculated as % size increase of DAP127-PETMP_{0.5} gels after curing in 0.1M PBS buffer for 24 h.

DAP127-PETMP_{0.5}	Length (mm)	% Size increase
As printed	35.14 ± 0.34	--
After curing	36.49 ± 0.18	3.84

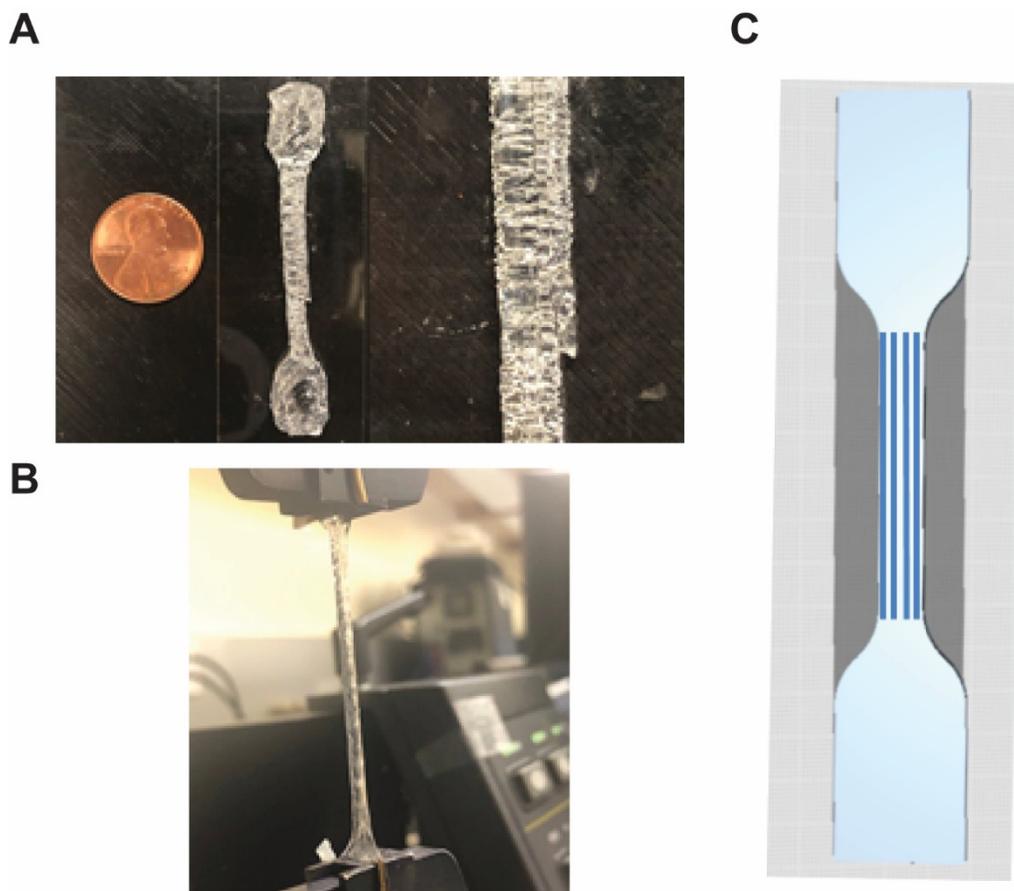
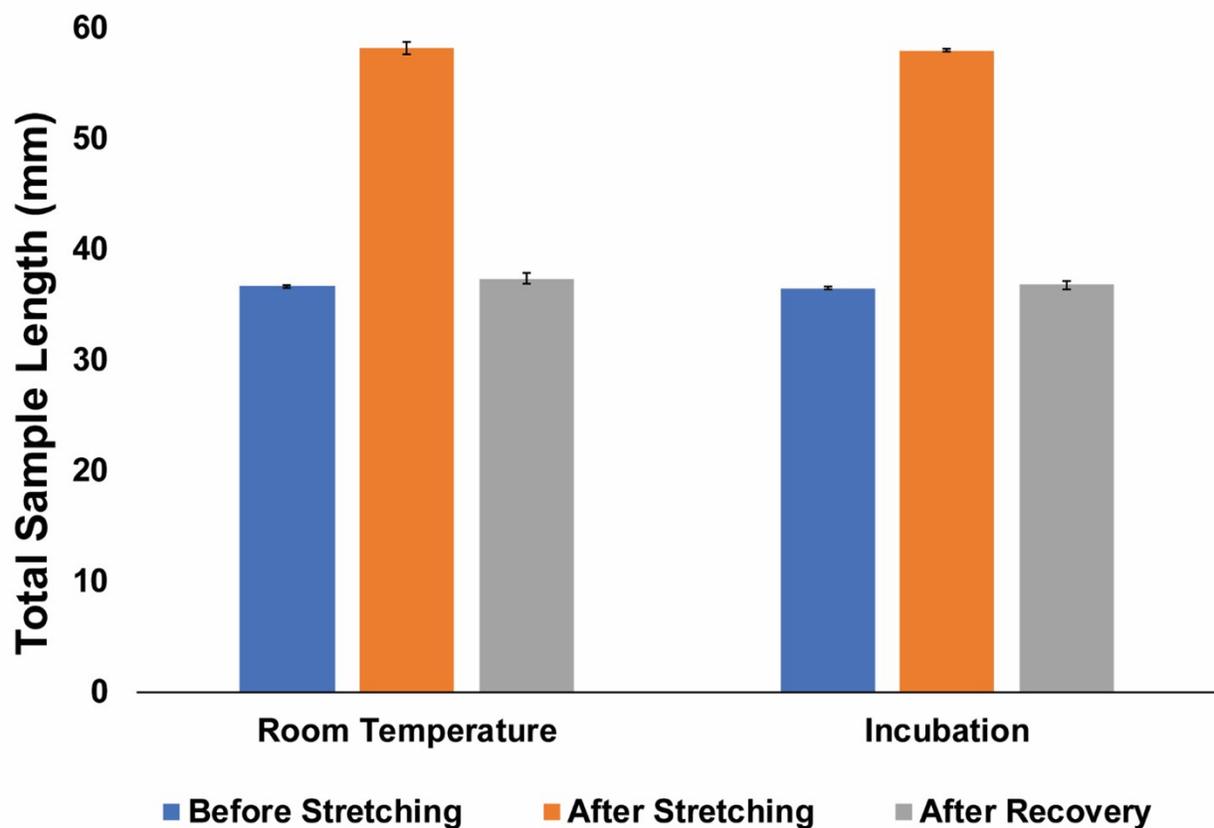
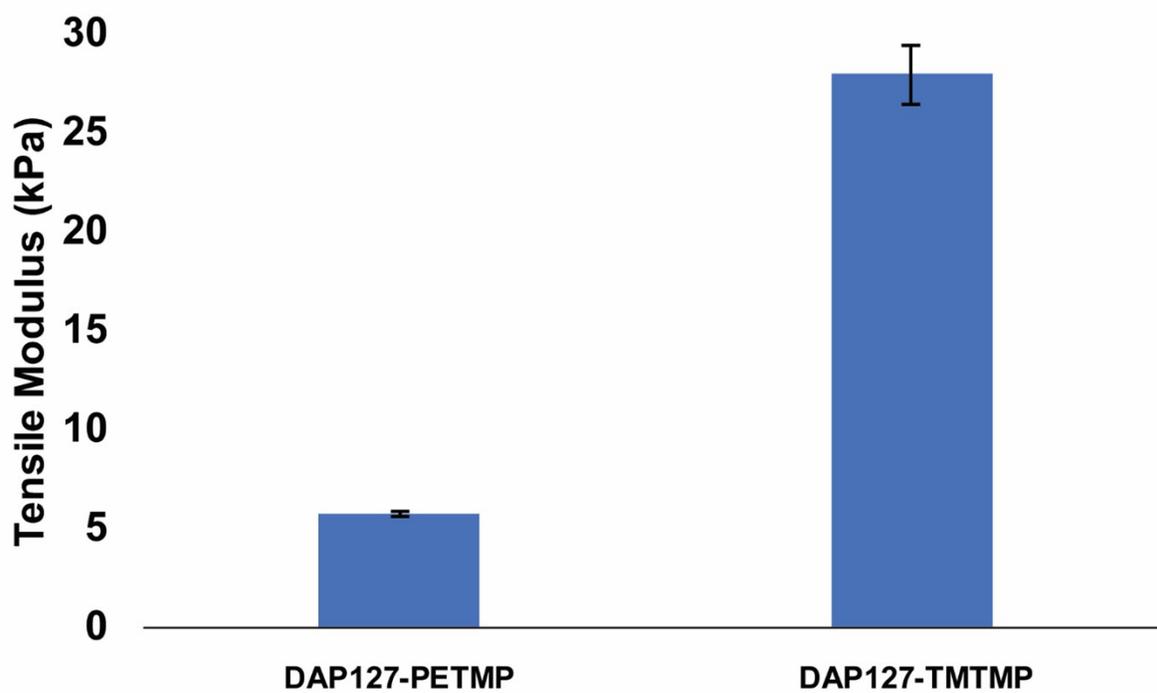


Figure S2. Optical images illustrating surface defects of **A**, DAP127-TMTMP_{0.1} after stretching and **B**, DAP127-PETMP_{0.5} during tensile testing, and **C**, STL file of dogbone with illustration of the print direction along the gauge region.



	Before Stretching (mm)	After Stretching (mm)	After Recovery (mm)	Size Increase (%)
Room Temperature	36.62 ± 0.14	58.11 ± 0.54	37.32 ± 0.46	1.92 ± 1.48
Incubation	36.47 ± 0.09	57.94 ± 0.16	36.74 ± 0.41	0.95 ± 0.66

Figure S3. Graph and values of total sample lengths before and after stretching, and after recovery at room temperature and incubation at 37 °C.



	DAP127-PETMP	DAP127-TMTMP
Tensile Modulus	5.76 ± 0.13	28 ± 1.50

Figure S4. Graph and values of tensile modulus of DAP127-PETMP and DAP127-TMTMP.