Bridging Polymer Architecture, Printability, and Properties by Digital Light Processing of Block Copolycarbonates

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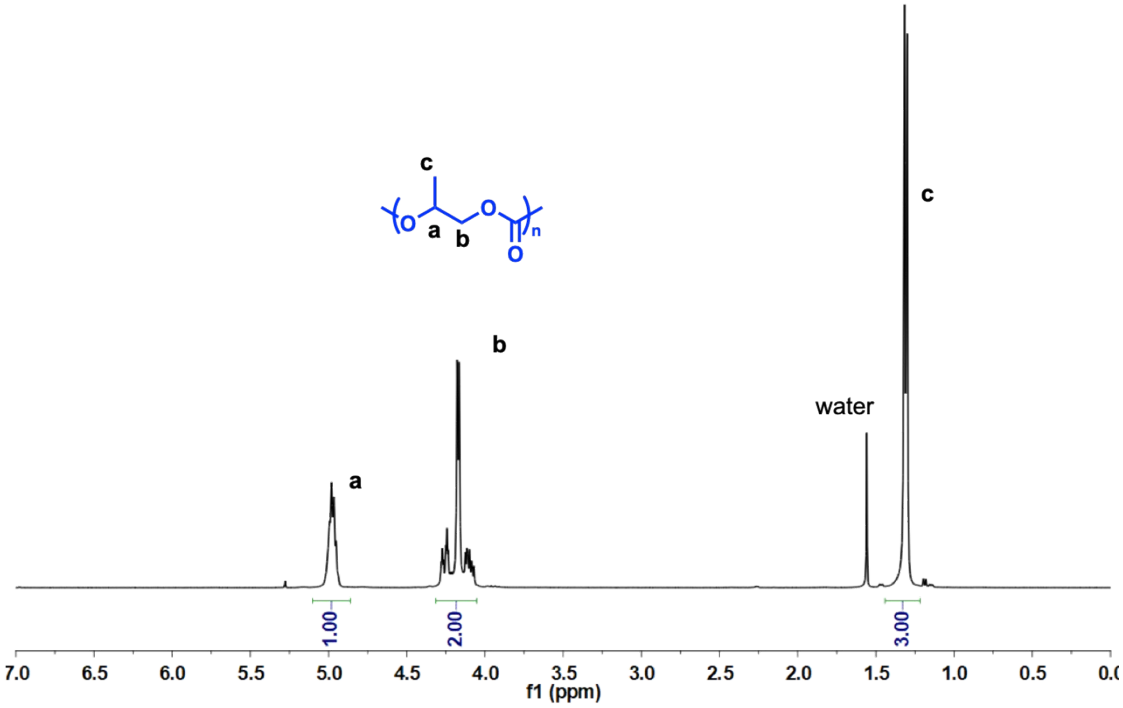


Figure S1. ^{1}H NMR spectrum of $P_{0\%A}$ in $CDCl_3$.

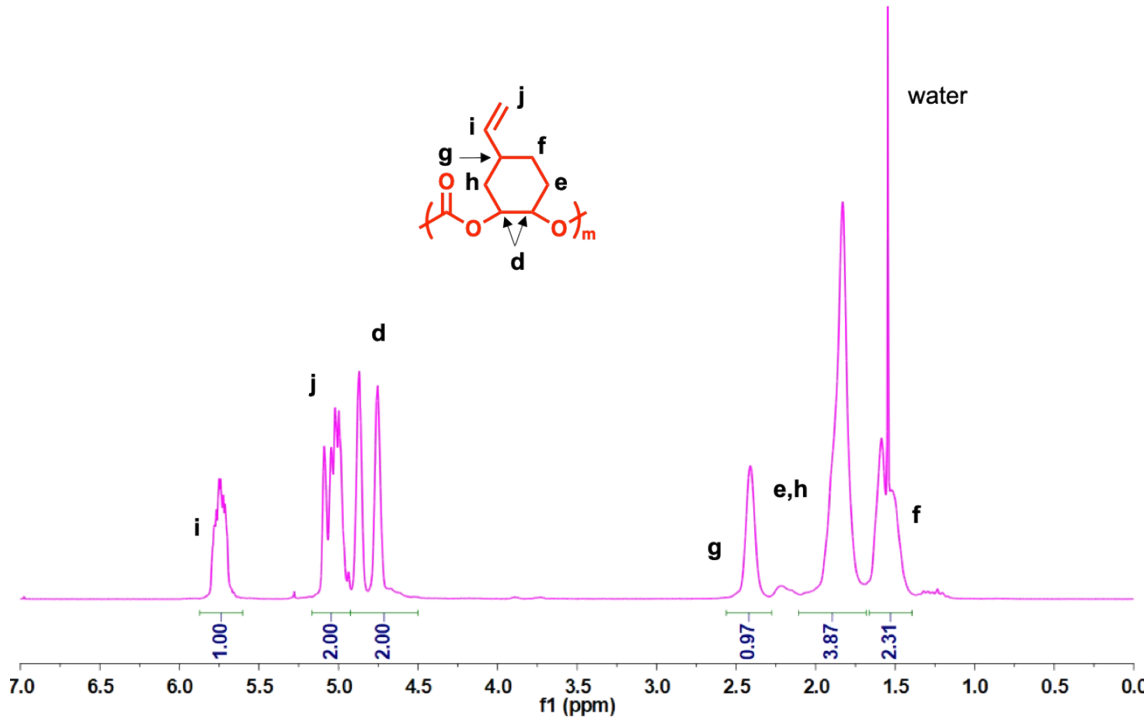


Figure S2. ^{1}H NMR spectrum of $P_{100\%A}$ in $CDCl_3$.

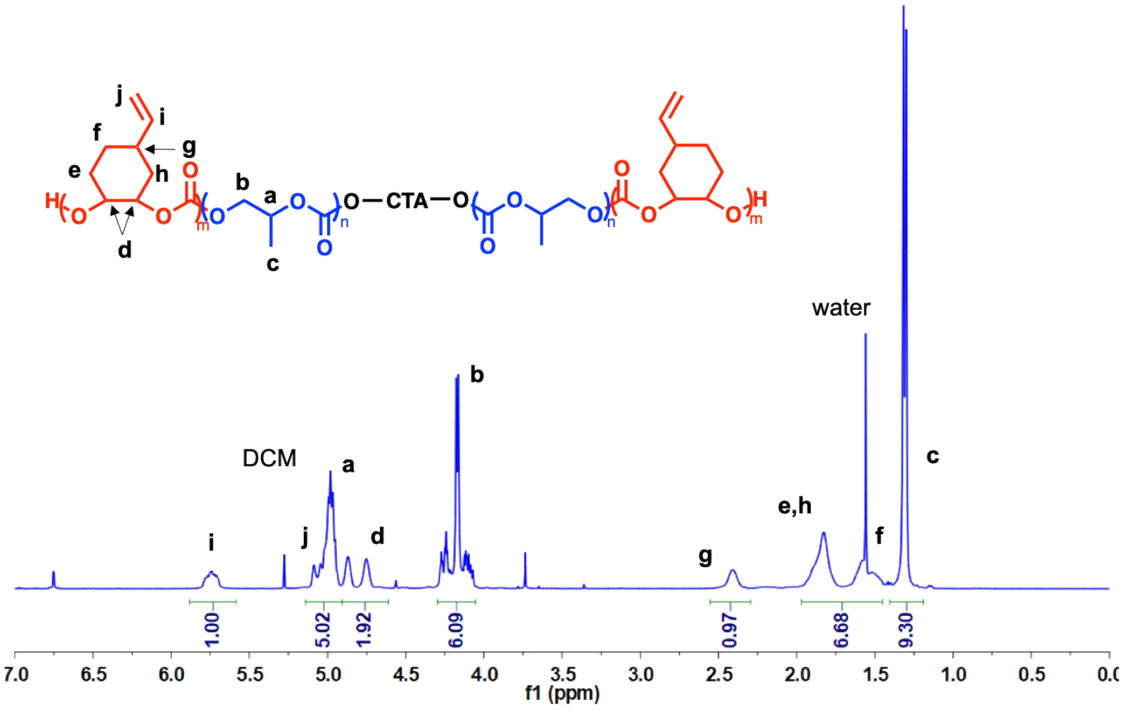


Figure S3. ^{1}H NMR spectrum of $BCP_{25\%A}$ in $CDCl_3$.

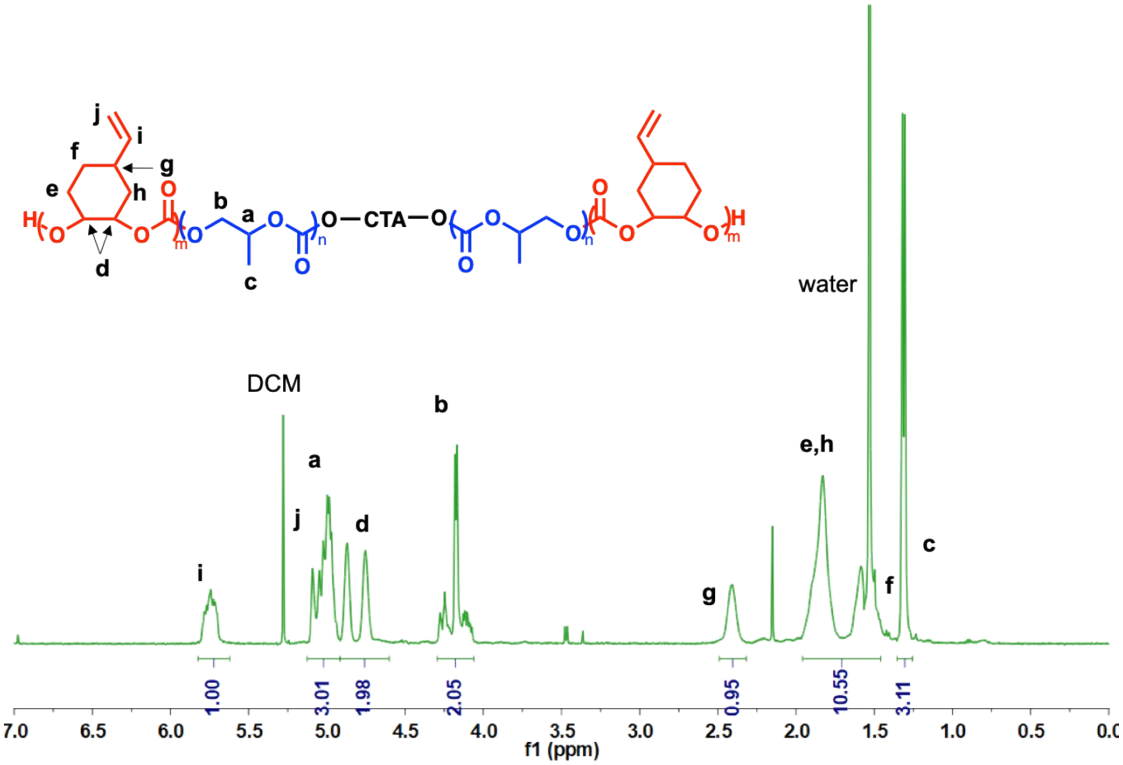


Figure S4. ^{1}H NMR spectrum of $BCP_{49\%A}$ in $CDCl_3$.

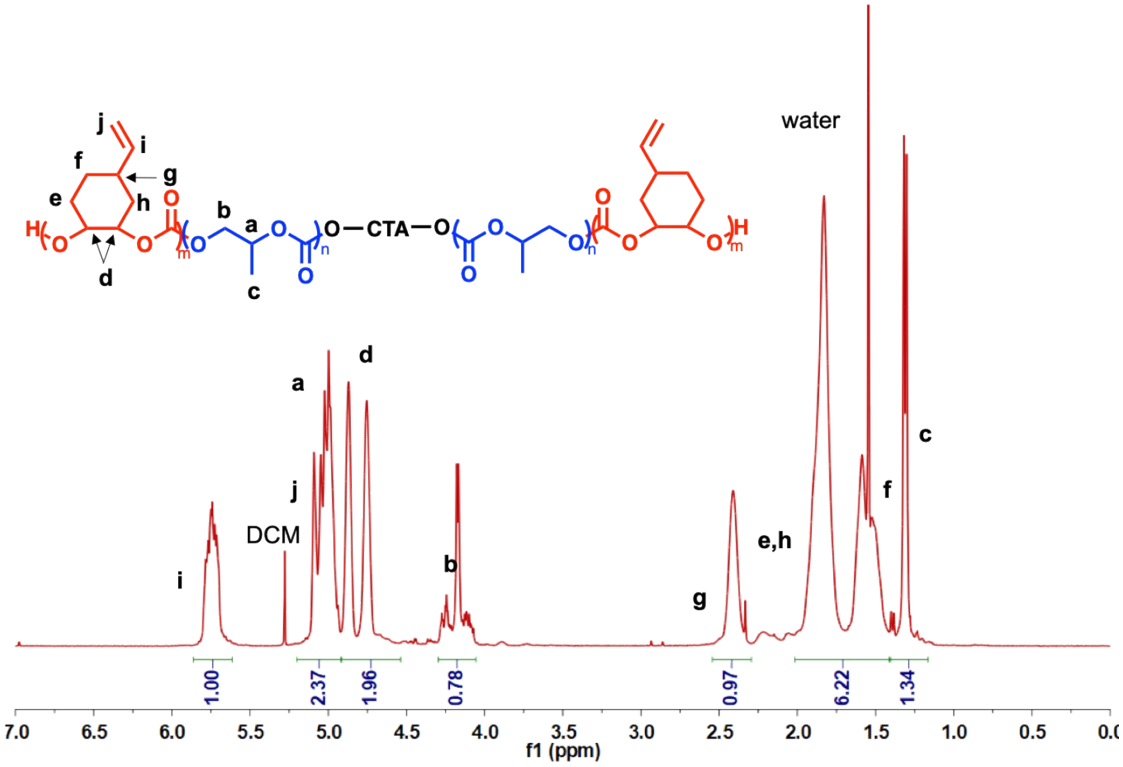


Figure S5. ^{1}H NMR spectrum of $BCP_{72\%A}$ in $CDCl_3$.

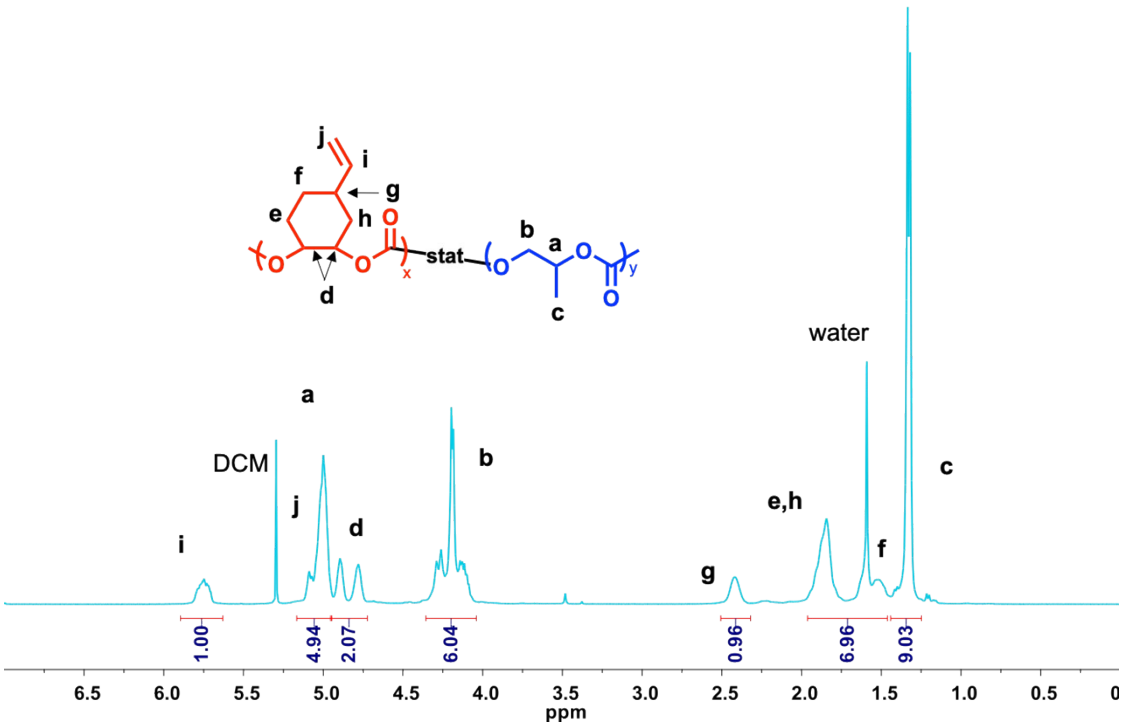


Figure S6. ^{1}H NMR spectrum of $Stat_{24\%A}$ in $CDCl_3$.

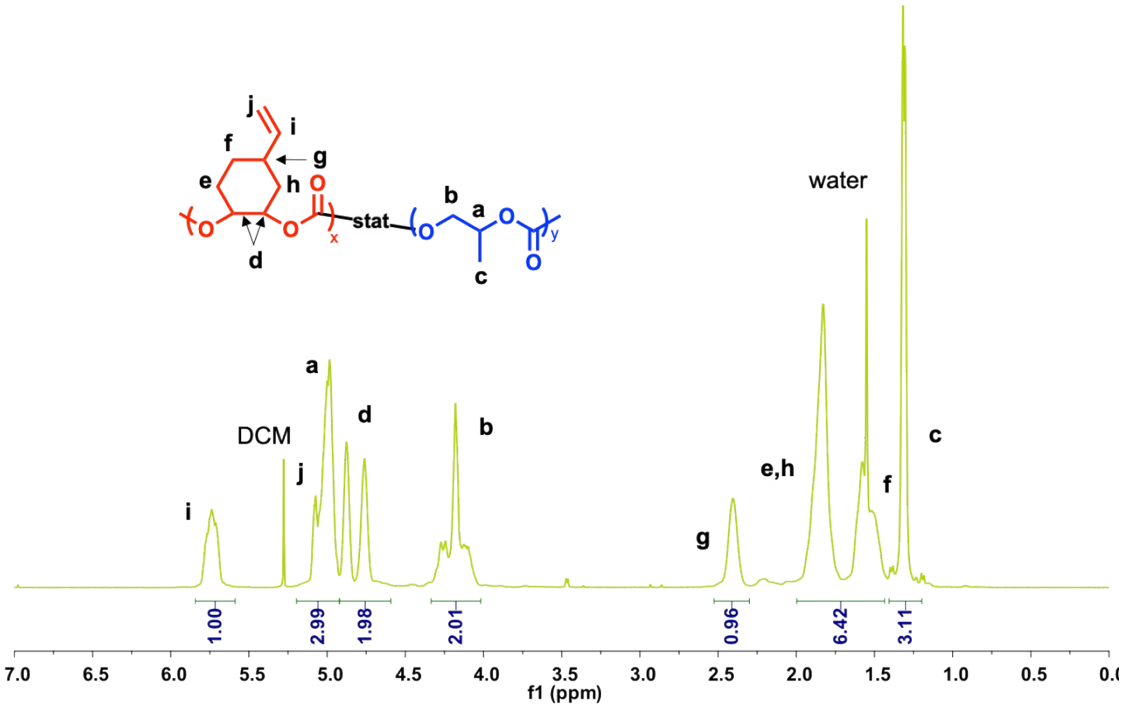
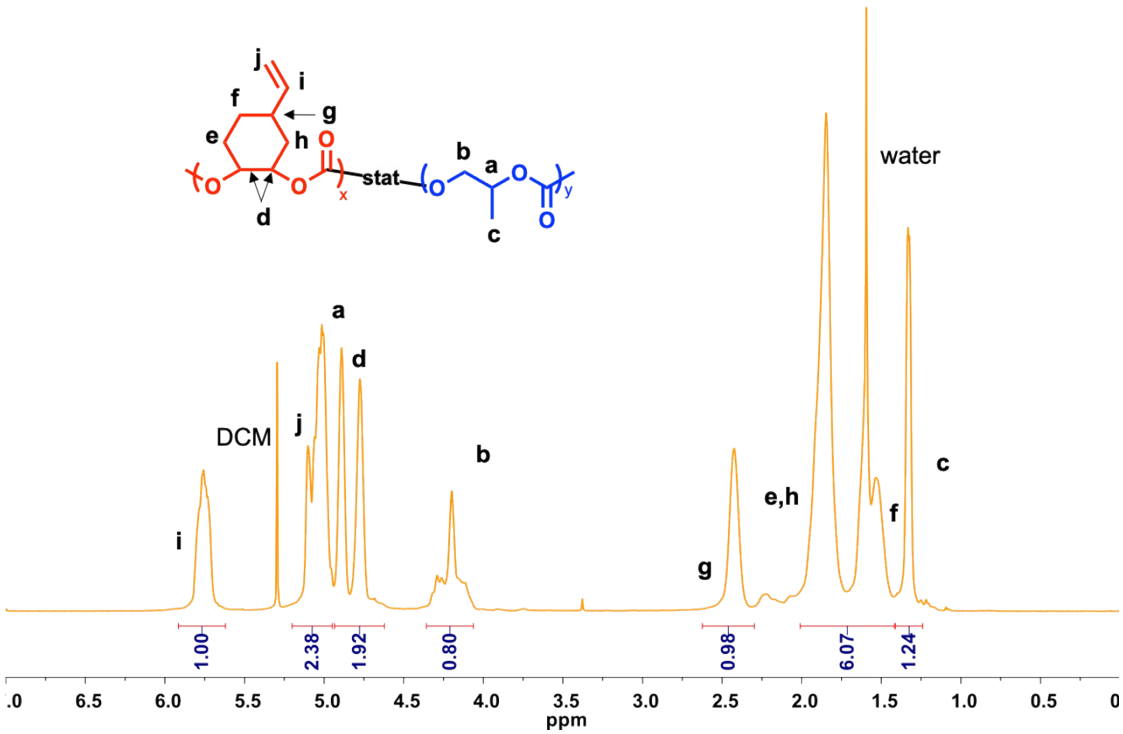


Figure S7. ^{1}H NMR spectrum of $Stat_{50\%A}$ in $CDCl_3$.



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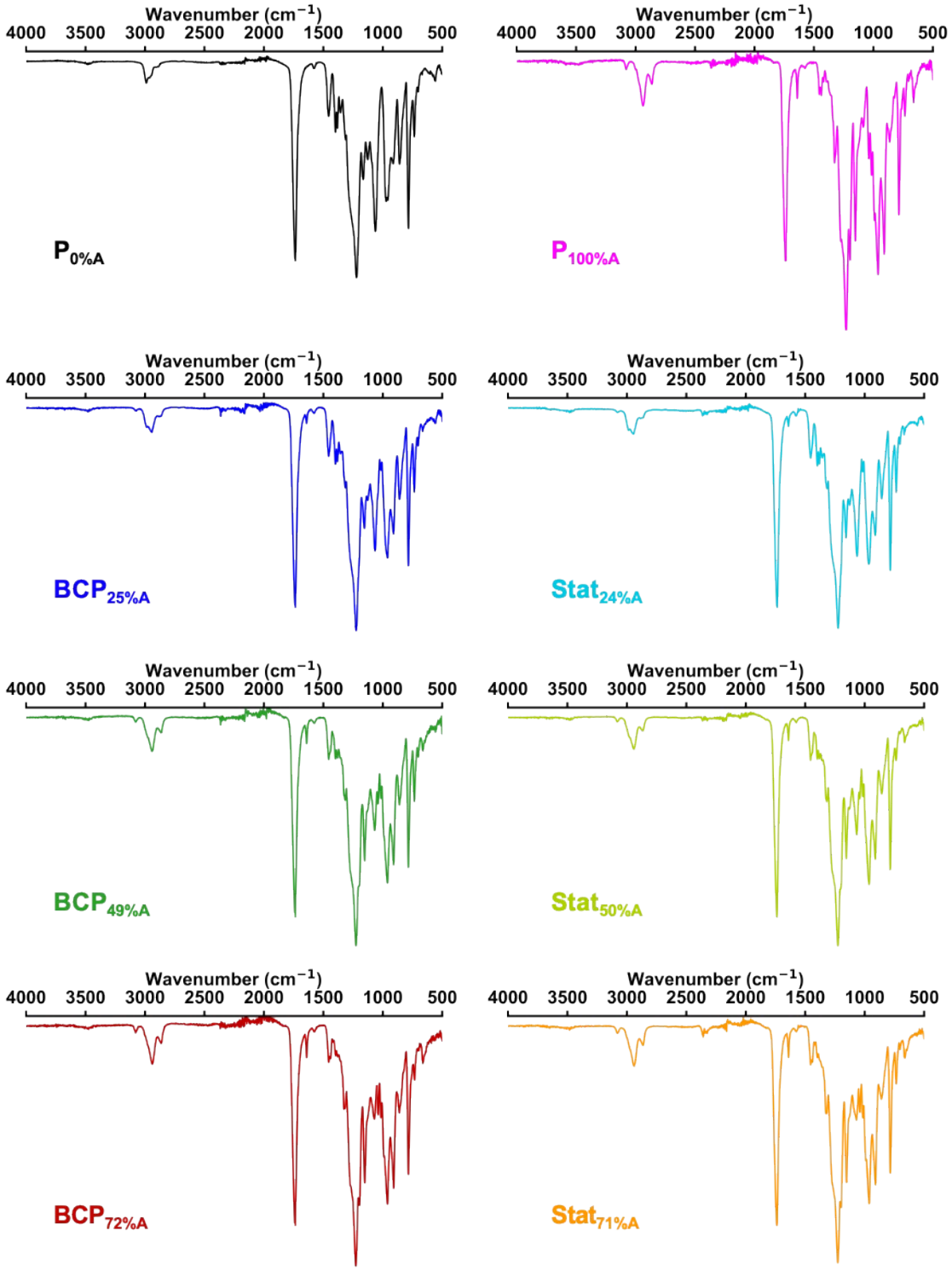


Figure S9. FTIR for each polymer. All spectra are normalized to the signal at 1720 cm^{-1} corresponding to the C=O stretch.

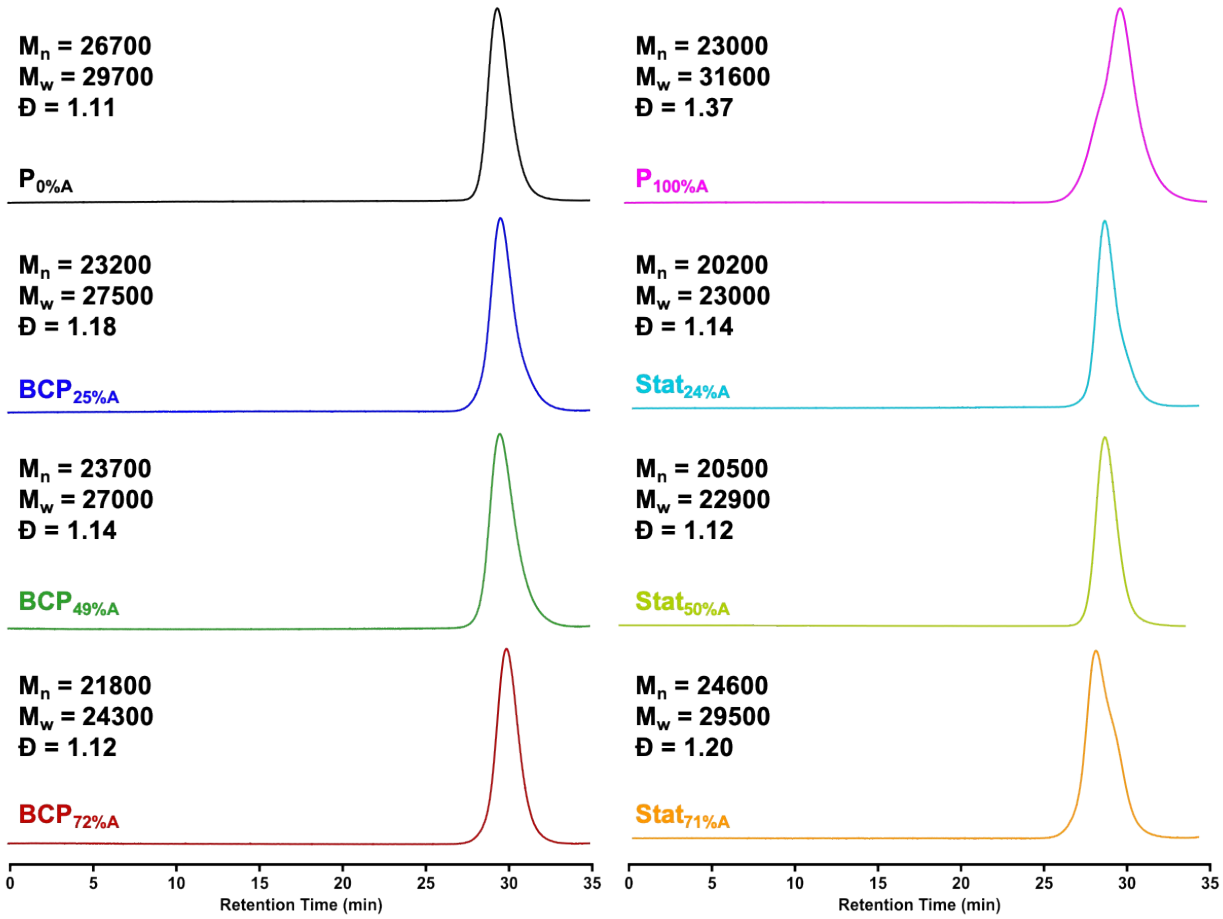


Figure S10. SEC traces for each polymer, normalized to intensity of 1.

Table S1. Polymer composition of BCP, Stat, and Homo aPCs used for DLP.

Polymer	[a]PC:VCHC	[b]M_n (kDa)	[b]Đ	[c]N_{PO}	[c]N_{VCHO}	[c]N
$P_{0\%A}$	1.00 : 0	26.7	1.11	262	0	262
$P_{100\%A}$	0.00 : 1	23.0	1.37	0	137	137
$BCP_{25\%A}$	3.05 : 1	23.2	1.18	147	49	196
$BCP_{49\%A}$	1.03 : 1	23.7	1.14	90	86	176
$BCP_{72\%A}$	0.39 : 1	21.8	1.12	41	105	146
$Stat_{24\%A}$	3.223: 1	20.2	1.14	130	41	171
$Stat_{50\%A}$	1.01 : 1	20.5	1.12	76	76	152
$Stat_{71\%A}$	0.40 : 1	24.6	1.20	48	117	165

[a] Determined by ^{1}H NMR integration. [b] Determined by SEC in THF against PS standards. [c] Number of repeat units of each monomer based on M_n and molar ratio.

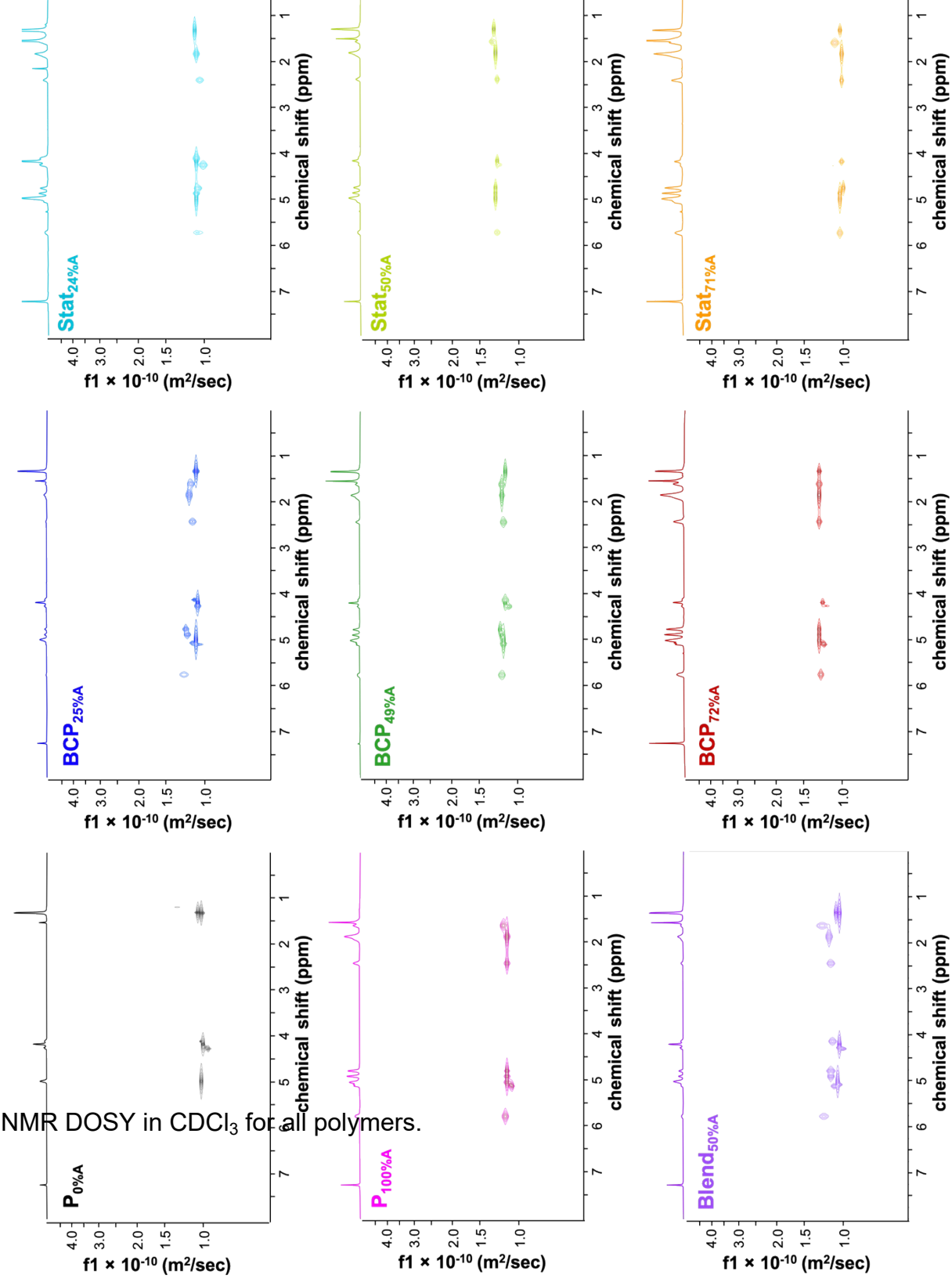


Figure S11. ^{1}H NMR DOSY in $CDCl_3$ for all polymers.

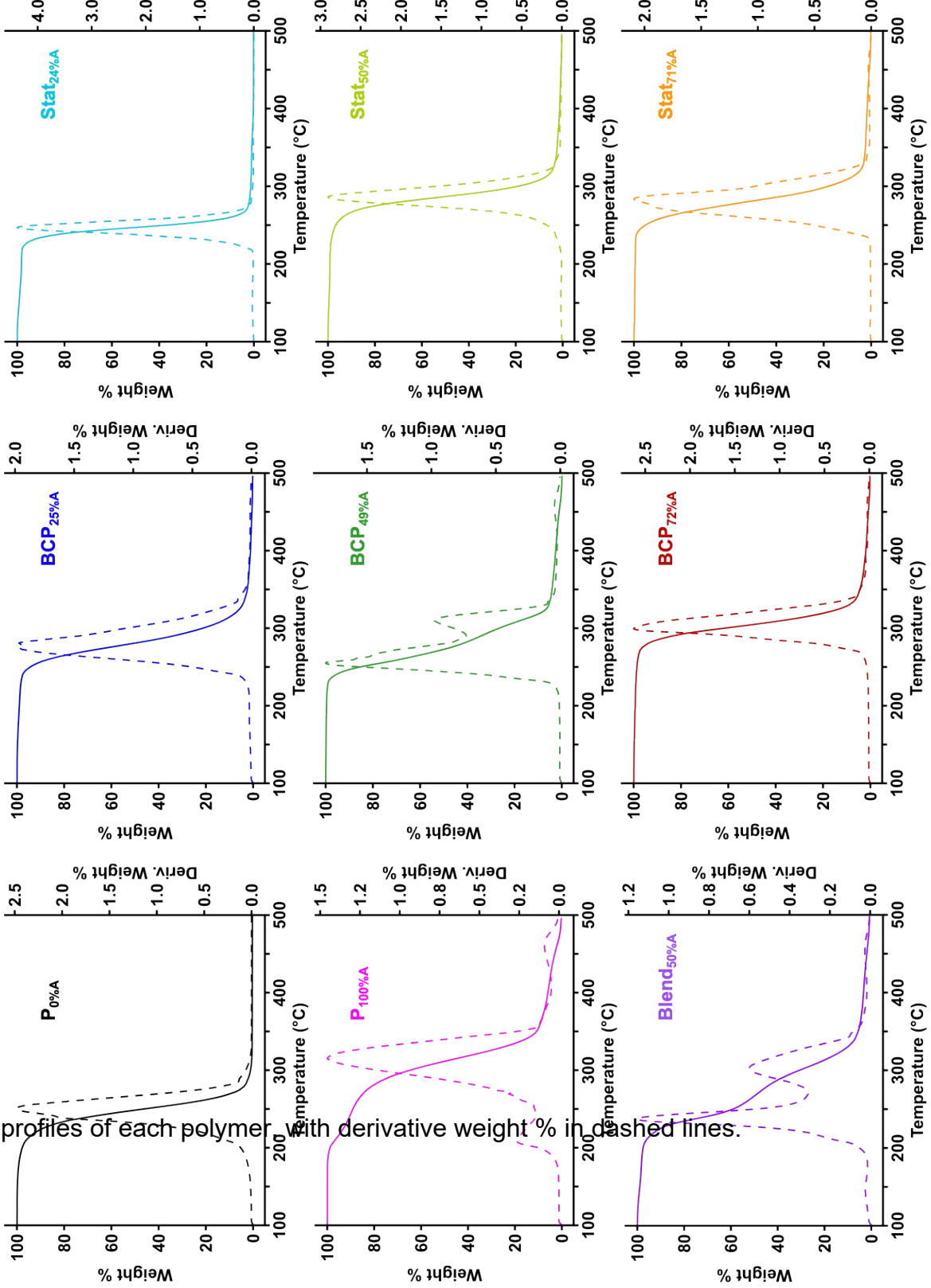


Figure S12. TGA profiles of each polymer with derivative weight % in dashed lines.

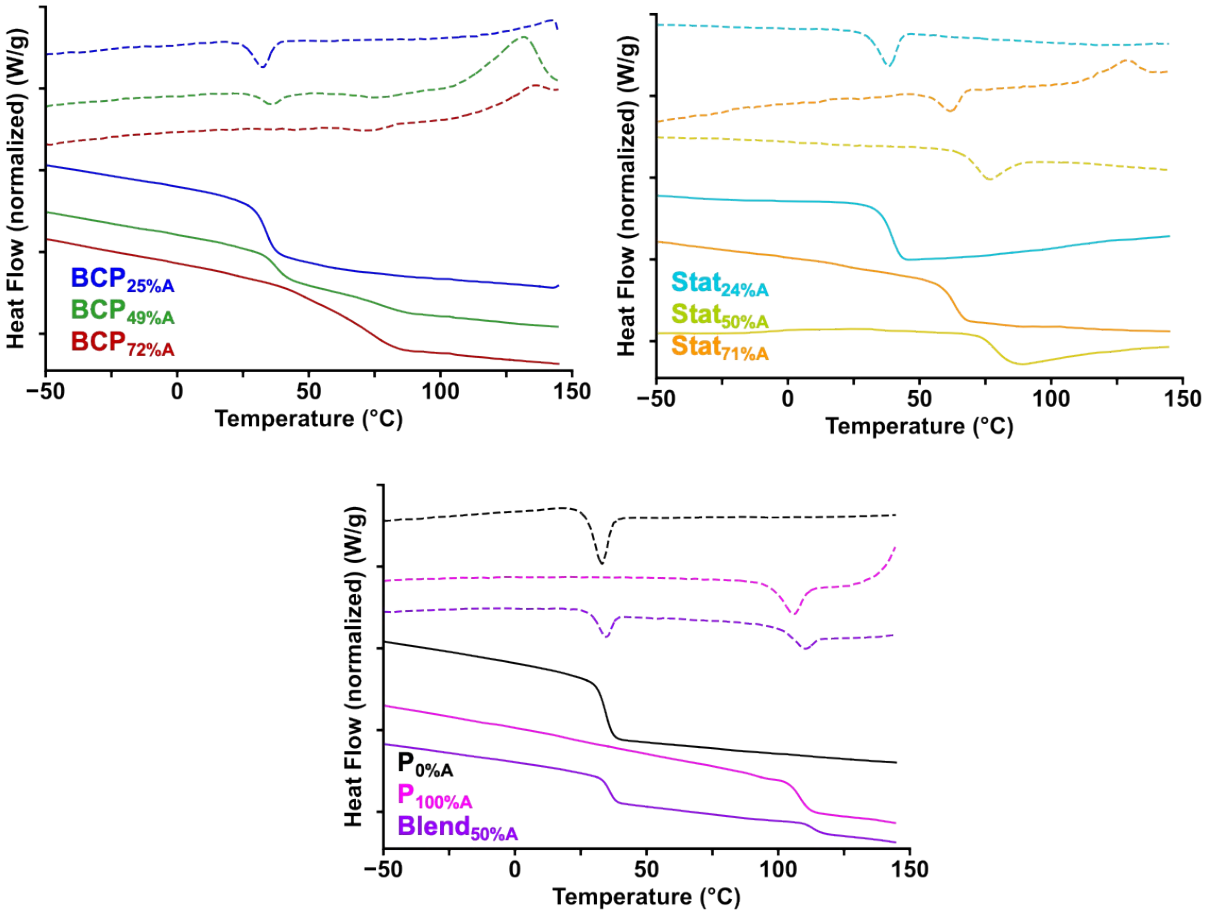


Figure S13. Modulated DSC for each polymer and the blend, separated into normalized nonreversing (dashed) and reversing (solid) heat flow. Y-axis tick marks are 0.02 W/g for all plots.

Equation S1. Linear combination of decomposition temperatures T_{d1} and T_{d2} (K) of homopolymers based on the weight fractions w_1 and w_2 of each component in the copolymer:

$$T_{d,mix} = w_1 T_{d1} + w_2 T_{d2} \quad \text{(S1)}$$

Equation S2. Fox equation[1] to describe composition dependence of thermal properties $T_{g,mix}$ (K) of copolymers, where w_1 and w_2 are the weight fractions of each component:

$$\frac{1}{T_{g,mix}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad \text{(S2)}$$

Table S2. Comparison of experimental and calculated thermodynamic properties using **Equations S1** and **S2.**

Polymer	w_A	w_B	T_d (K)	$T_{d,mix}$ (K)	T_g (K)	$T_{g,mix}$ (K)
$BCP_{25\%A}$	0.35	0.65	551	546	307	330
$BCP_{49\%A}$	0.61	0.39	528, 582	563	311, 354	349
$BCP_{72\%A}$	0.81	0.19	573	576	339	364
$Stat_{24\%A}$	0.34	0.66	520	545	312	329
$Stat_{50\%A}$	0.62	0.38	559	564	336	349
$Stat_{71\%A}$	0.80	0.20	556	575	352	364

2. Resin Formulation and 3D Printing

2.1. 3D Printing of bulk structures

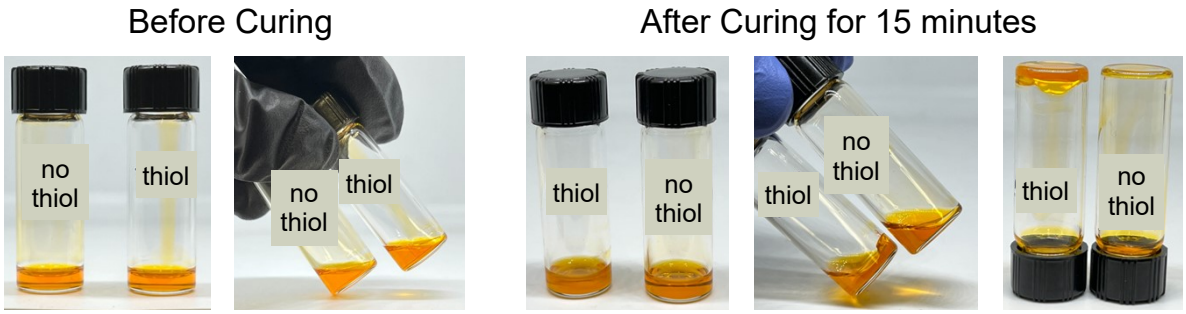


Figure S14. Curing control experiment. The same resin formulation was used for two samples, except no thiol was added to one. Both were exposed to the DLP printer light for 15 minutes.

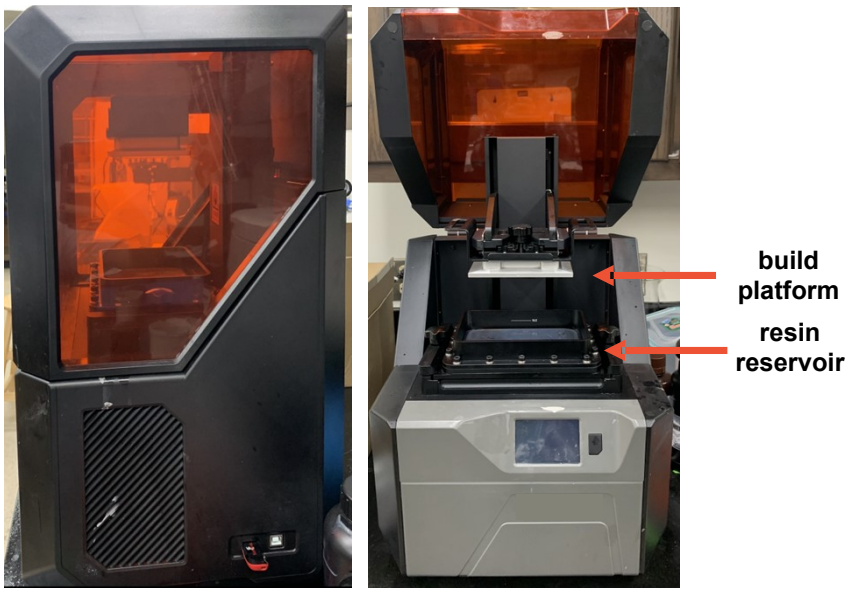


Figure S15. DLP 3D printer used in this work.

Equation S3. Calculation of resin stoichiometry of crosslinker relative to polymer:

$$\text{moles of alkene} = \frac{mol\%\ PVCHC \times M_n}{\left((mass_{PPC\ repeat\ unit} \times mol\%\ PPC) + (mass_{PVCHC\ repeat\ unit} \times mol\%\ PVCHC)\right)}$$

$$= \frac{mol\%\ PVCHC \times M_n}{\left(\left(102\frac{g}{mol} \times mol\%\ PPC\right) + \left(168\frac{g}{mol} \times mol\%\ PVCHC\right)\right)}$$

Table S3. Resin components

Resin components	Specific Name	Amount
Solvent	Propylene Carbonate Ethyl Acetate	3:1 v/v
Polymer	Polycarbonate (BCP, Stat, Blend)	450 mg/mL
Crosslinking Agent	1,6-hexanedithiol	relative to mol% PVCHC
Photoinitiator	BAPO	0.5 wt%
Radical Inhibitor	1,2,3-trihydroxybenzene	0.1 wt%
Dye	Sudan I	0.02 wt%

Table S4. Printing parameters

Parameter	Value
Curing time	60 s
Layer height	100 µm
Light Wavelength	405 nm

Light intensity 200%

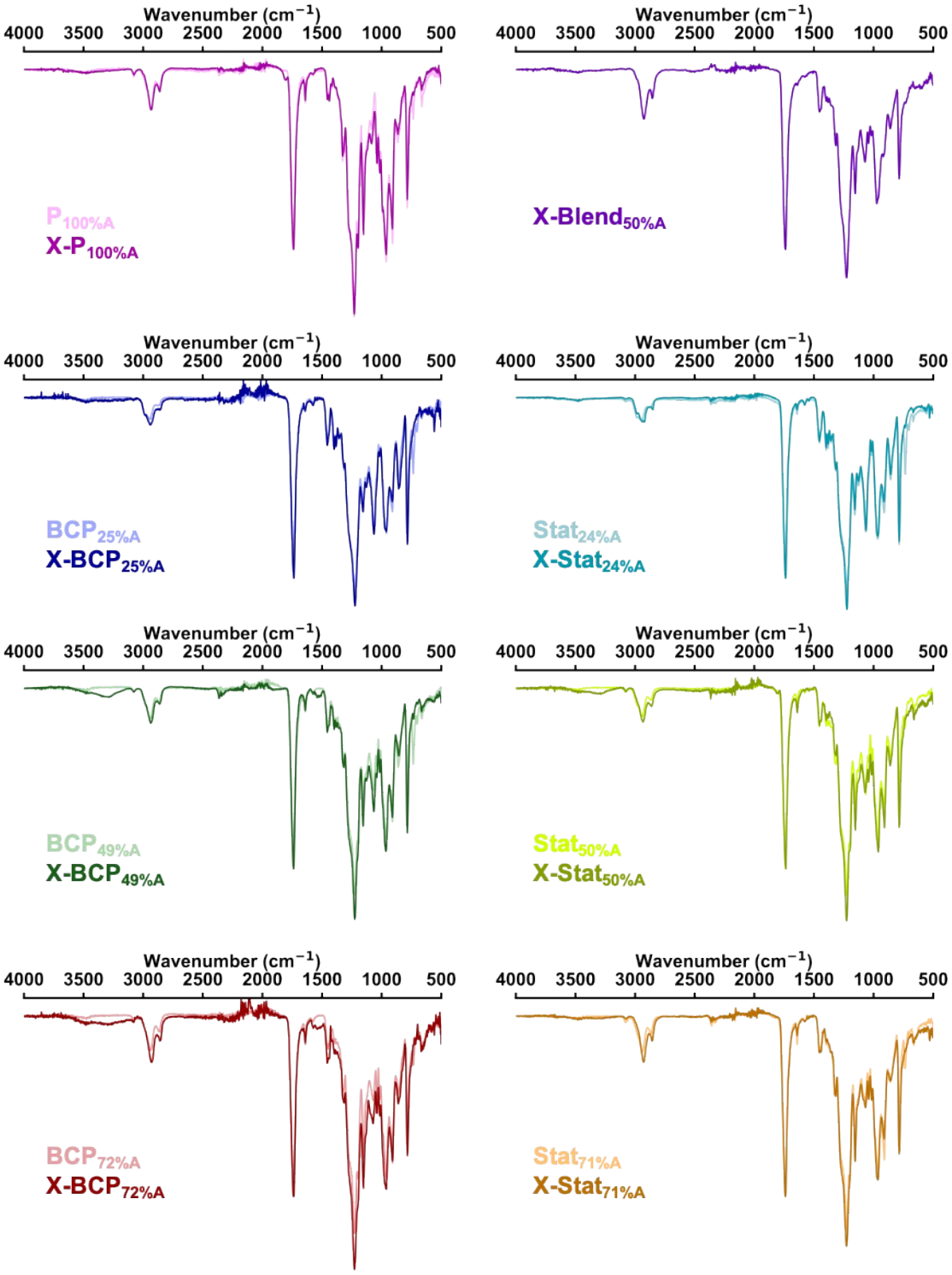


Figure S16. FTIR comparing pristine polymer (light trace) to printed polymer (dark trace).

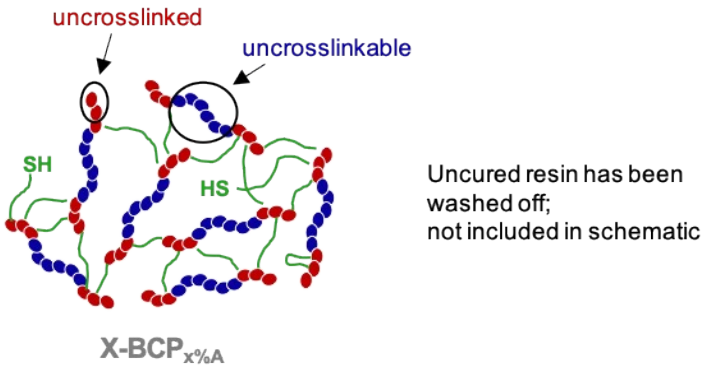


Figure S17. Schematic of uncrosslinked and uncrosslinkable polymer.

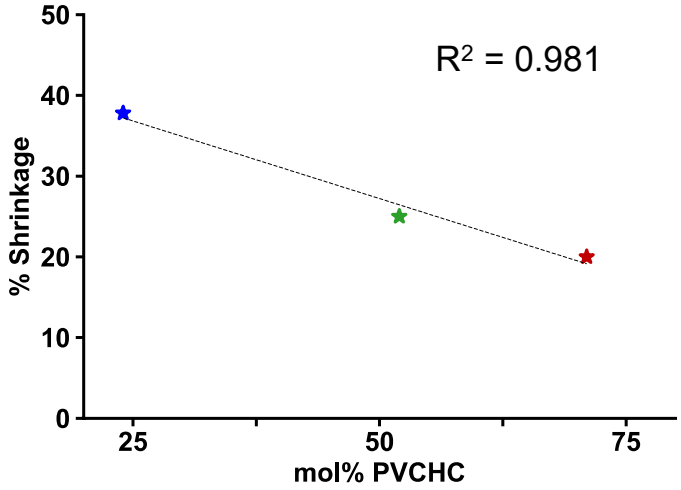


Figure S18. Plot of % shrinkage vs mol% PVCHC, as calculated by dividing the dry length by the original print dimensions (30 mm).

Table S5. Crosslinked polymer thermal properties and swelling ratio.

Polymer	T_g (ºC)	T_d (ºC)	[a]Mass Loss (%)	[b]Swelling Ratio (%)
X-P$_{100\%A}$	--	332, 369	43	140 ± 3
X-BCP$_{25\%A}$	-7.9	301, 360*	81	411 ± 18
X-BCP$_{49\%A}$	2.5	310, 365	53	157 ± 6
X-BCP$_{72\%A}$	--	323, 369	39	108 ± 11
X-Stat$_{24\%A}$	5.2	313, 360*	85	326 ± 10

X-Stat$_{50\%A}$	9.0	324, 384	49	80 ± 7
X-Stat$_{71\%A}$	--	334, 384	51	97 ± 6

[a] Total % mass loss in each step. [b] n=3

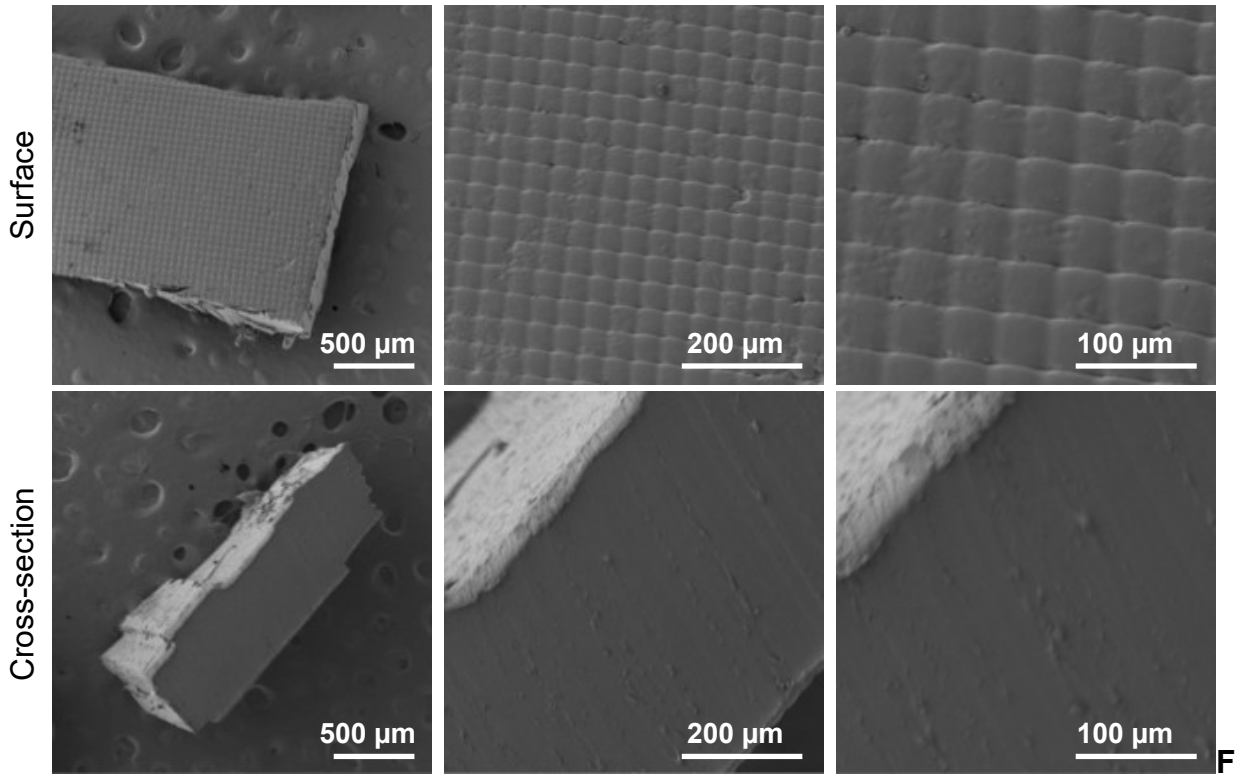


Figure S19. SEM images of surface and cross-section of X-BCP$_{25\%A}$.

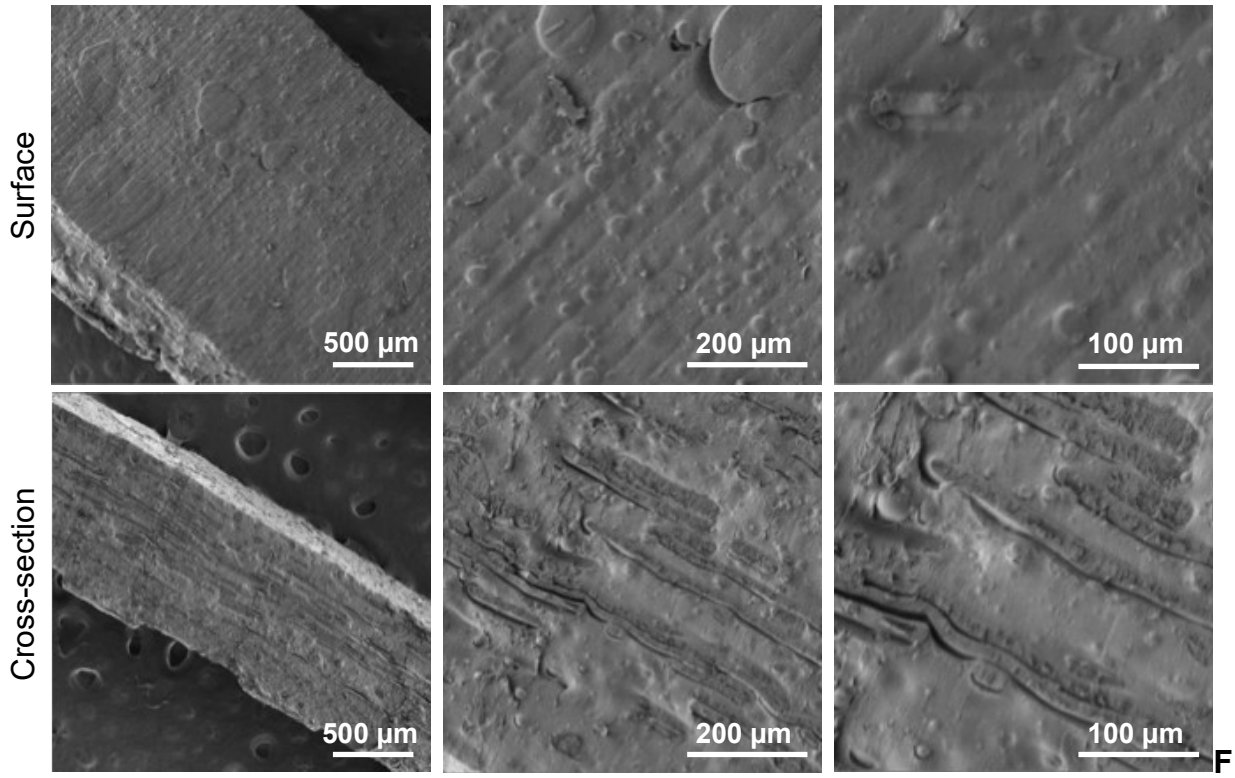


Figure S20. SEM images of surface and cross-section of X-BCP$_{49\%A}$.

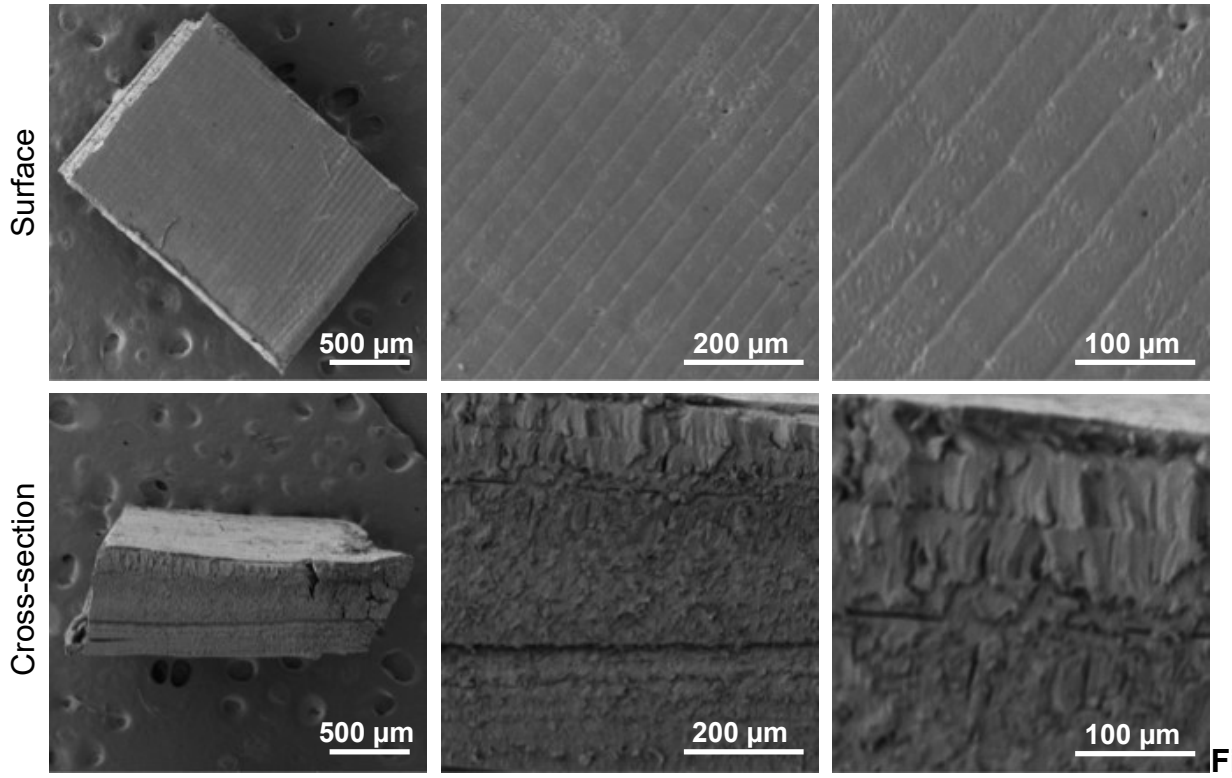
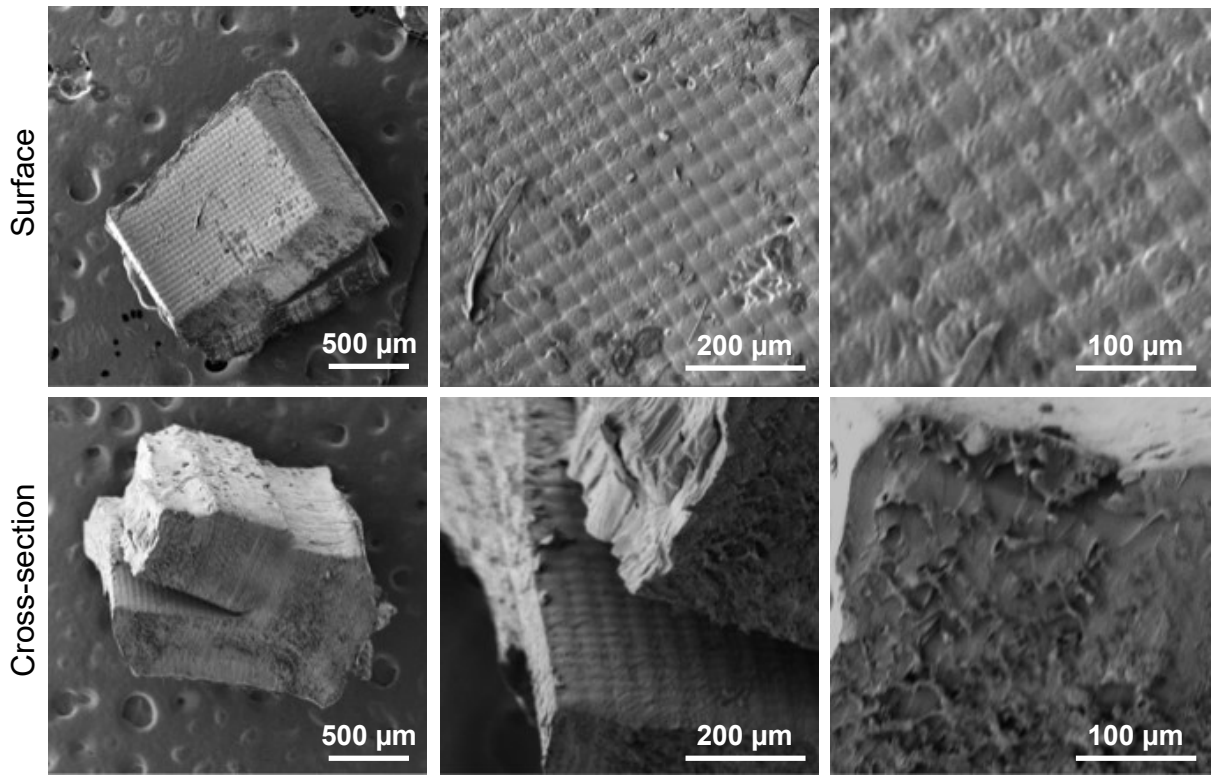


Figure S21. SEM images of surface and cross-section of X-BCP$_{72\%A}$.



igure S22. SEM images of surface and cross-section of X-Stat$_{50\%A}$.

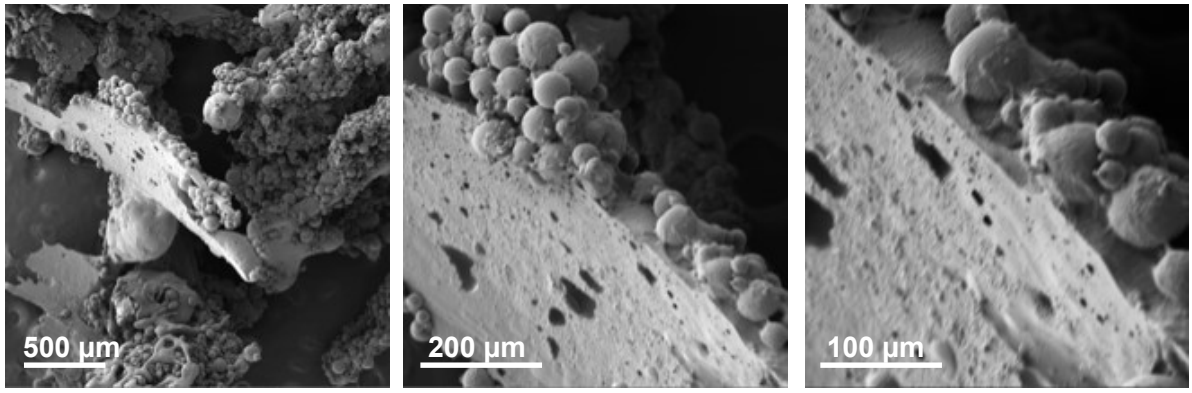


Figure S23. SEM images of surface and cross-section of X-Blend$_{50\%A}$.

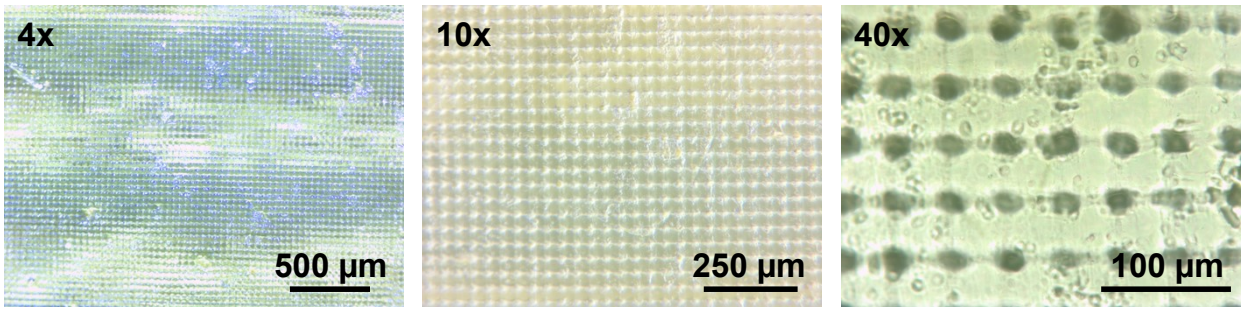


Figure S24. Optical microscopy images of the surface of X-$BCP_{49\%H}$ showing ~50 µm resolution.

2.2. Thermal and mechanical properties of printed structures

Table S6. Comparison of thermal properties of pristine polymers and their corresponding prints.

	T_g (ºC)		T_d (ºC)		Enthalpy Recovery (J/g)	
Polymer	**Pristine**	**Print**	**Pristine**	**Print**	**Pristine**	**Print**
$P_{0\%A}$	34	N/A	250	N/A	2.26	N/A
[a]$P_{100\%A}$	108	--	315	332, 369	1.92	--
$Blend_{50\%A}$	36, 113	28.1	237, 303	336, 364	1.03, 0.85	0.19, --
$BCP_{25\%A}$	34	-7.9	278	301, 360*	1.33	1.29
$BCP_{49\%A}$	38, 81	2.5	255, 309	310, 365	0.63	0.58
$BCP_{72\%A}$	66	--	300	323, 369	--	--
$Stat_{24\%A}$	39	5.2	247	313, 365*	1.92	1.73
$Stat_{50\%A}$	63	9.0	286	324, 384	1.37	1.46
$Stat_{71\%A}$	79	--	283	334, 384	2.06	--

[a] “Print” is $P_{100\%A}$ that is cured as a bulk liquid, not printed

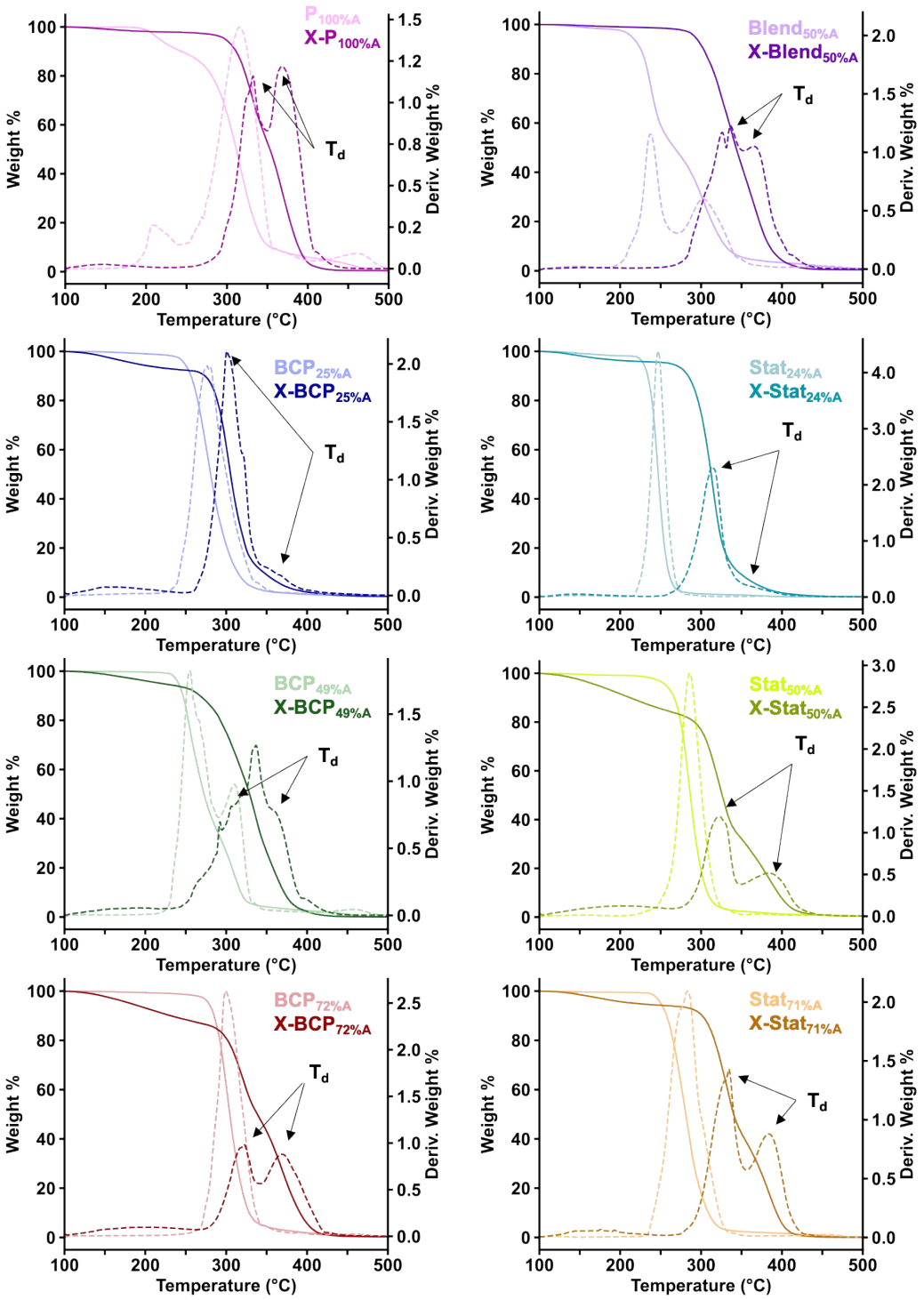


Figure S25. TGA weight loss profiles comparing pristine polymer (lighter color trace) to printed polymer (darker color trace), with first derivative of weight loss (dashed lines of corresponding colors). X-BCP$_{49\%A}$ indicates T_d's as the peaks of the deconvoluted derivative trace. X-Blend$_{50\%A}$ reports T_d as a single peak in the middle of the decomposition step.

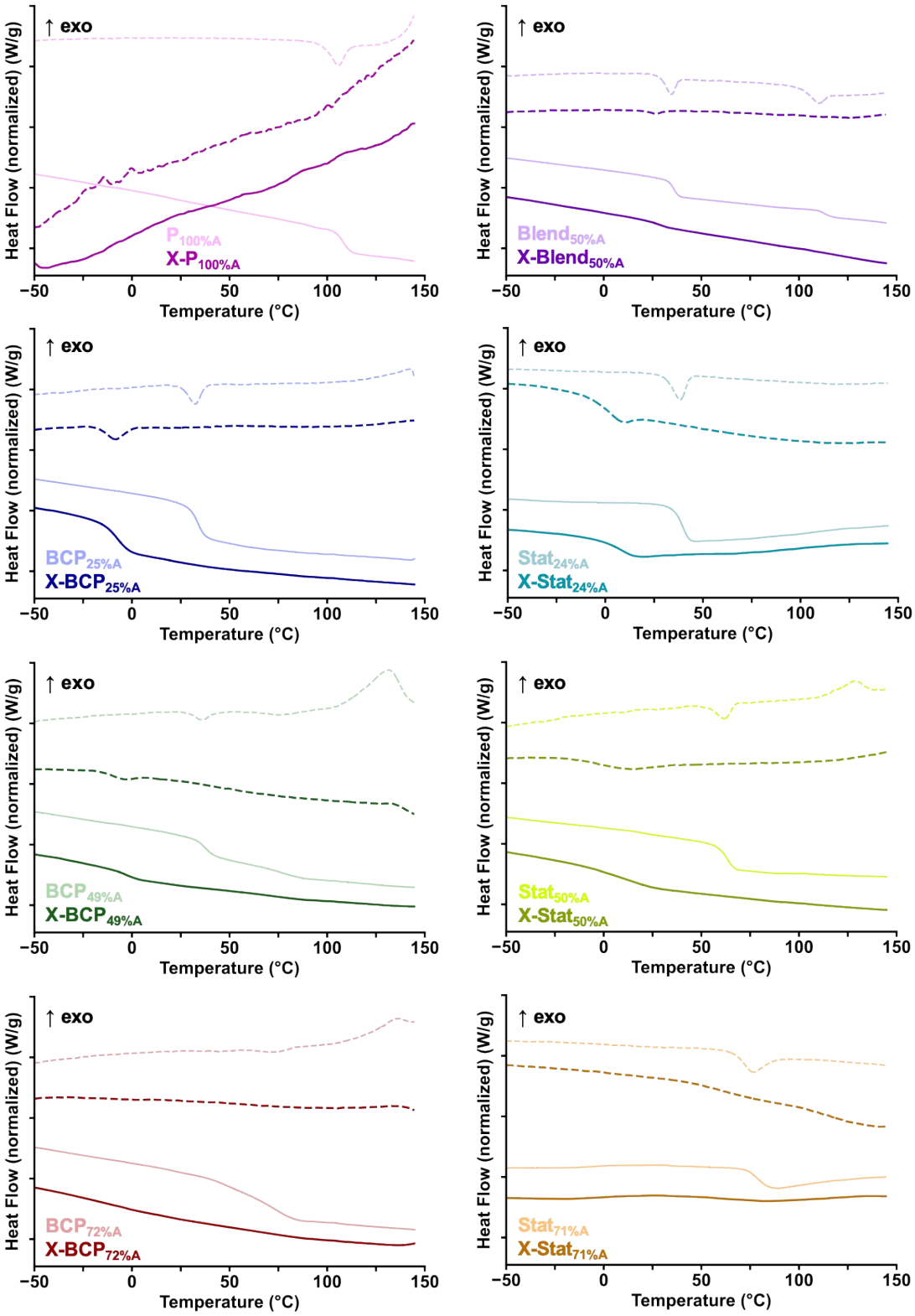


Figure S26. Modulated DSC comparing pristine polymer (light trace) to printed polymer (dark trace), separated into normalized non-reversing (dashed) and reversing (solid) heat flow. Y-axis tick marks are 0.02 W/g for all plots.

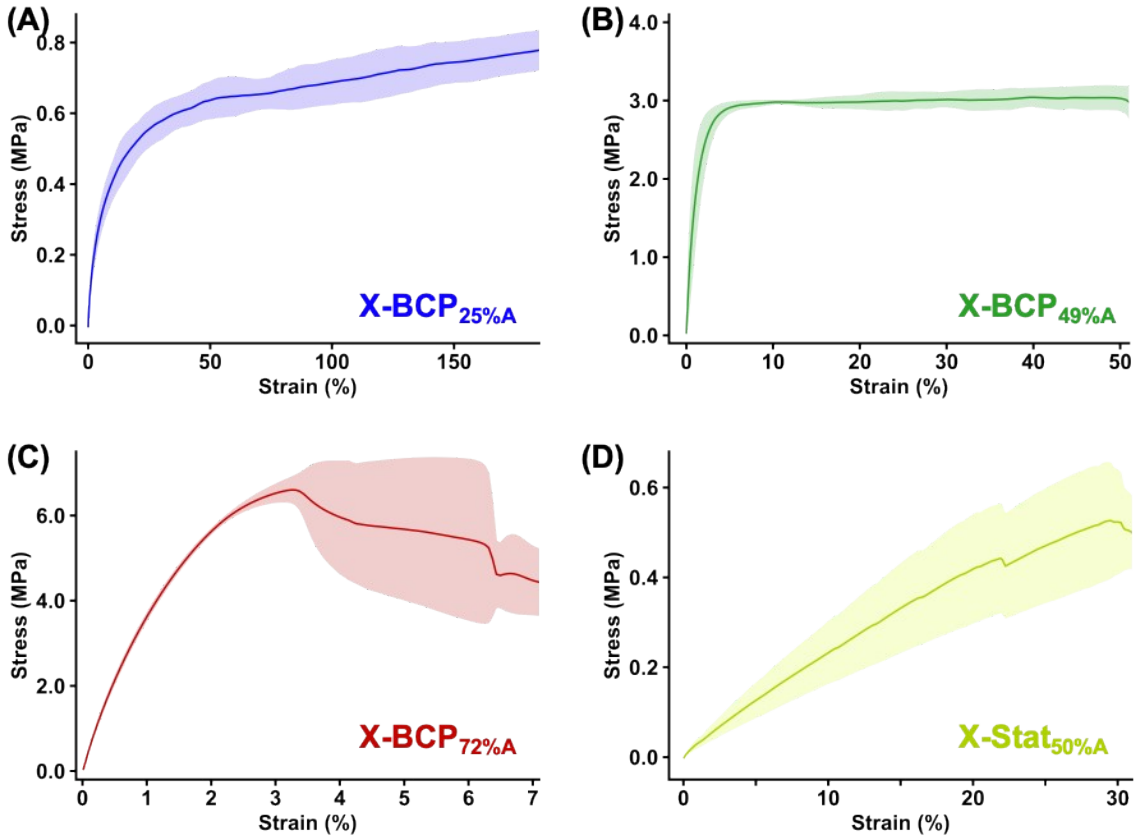


Figure S27. Full-scale plots of tensile test for **(A)** X-BCP$_{25\%A}$, **(B)** X-BCP$_{49\%A}$, **(C)** X-BCP$_{72\%A}$, and **(D)** X-Stat$_{50\%A}$. Shaded area shows deviation of three samples.

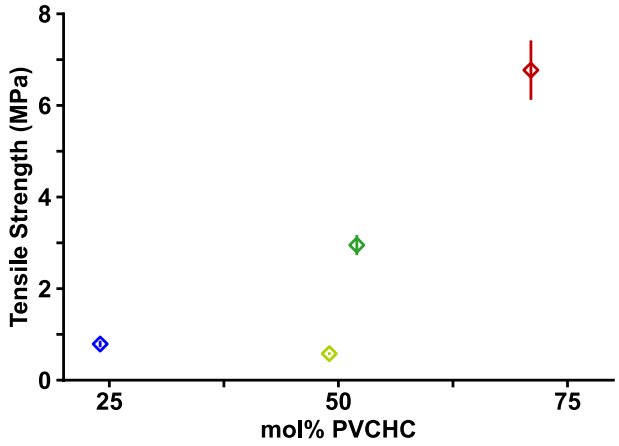


Figure S28. Tensile strength of printed resins based on mol% PVCHC.

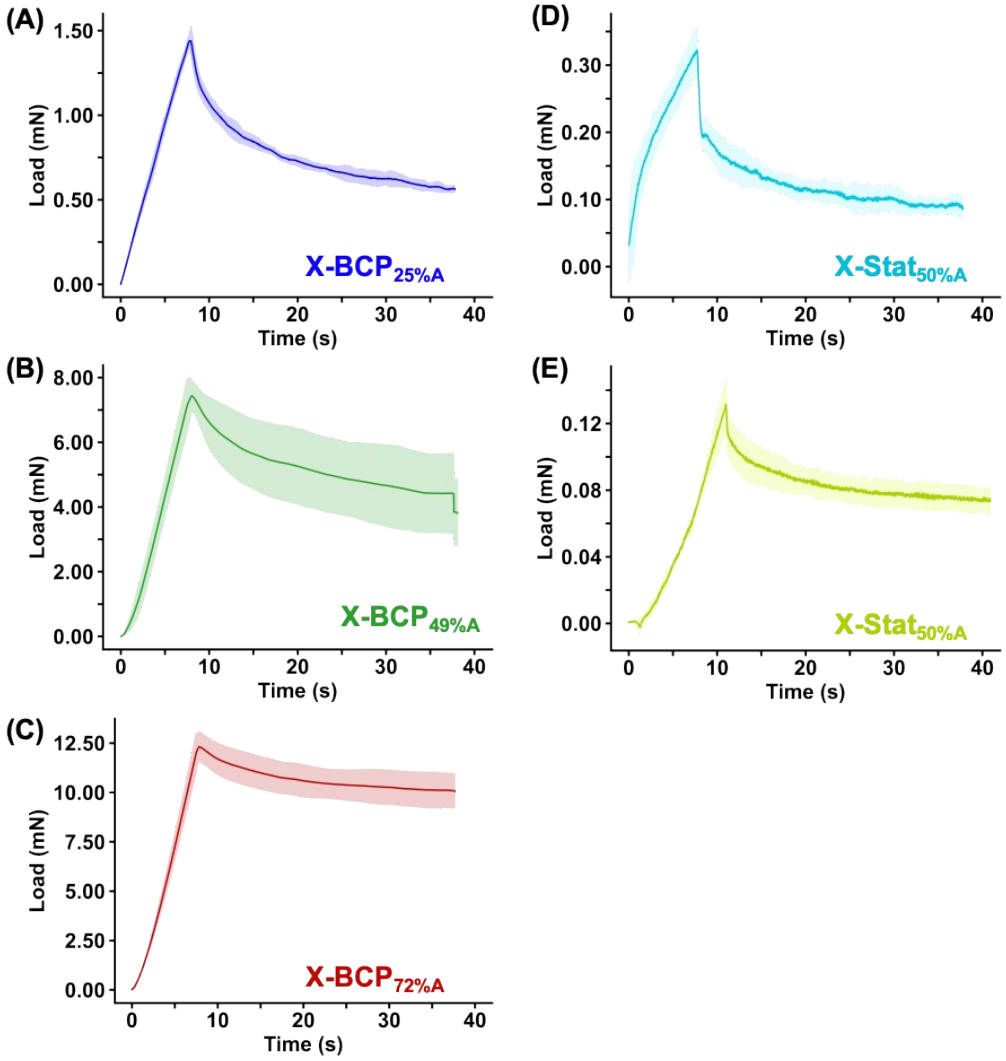


Figure S29. Full-scale plots of load vs time by nanoindentation for **(A)** X-BCP$_{25\%A}$, **(B)** X-BCP$_{49\%A}$, **(C)** X-BCP$_{72\%A}$, **(D)** X-Stat$_{24\%A}$, and **(E)** X-Stat$_{50\%A}$. Shaded area shows standard deviation of three sample.

Table S7. Complete nanoindentation results.

Polymer	Maximum Load (mN)	Final Load after Hold (mN)	Total Relaxation (mN)	Percent Relaxation (%)	Hardness (GPa)	[d]Young's Modulus (MPa)
X-BCP$_{25\%A}$	1.47 ± 0.05	0.61 ± 0.03	0.85 ± 0.06	58 ± 3	0.117 ± 0.004	6.6 ± 0.4
X-BCP$_{49\%A}$	7.17 ± 0.18	3.95 ± 0.70	3.22 ± 0.72	45 ± 8	1.0 ± 0.3	31 ± 2
X-BCP$_{72\%A}$	12.3 ± 0.8	10.4 ± 0.8	2.0 ± 1.1	16 ± 2	2.5 ± 0.3	51 ± 3
X-Stat$_{24\%A}$	0.329 ± 0.027	0.085 ± 0.014	0.244 ± 0.030	74 ± 11	0.018 ± 0.003	1.7 ± 0.2
X-Stat$_{50\%A}$	0.136 ± 0.013	0.079 ± 0.007	0.057 ± 0.015	42 ± 6	0.015 ± 0.001	0.58 ± 0.04

3. Hydrolysis of printed objects

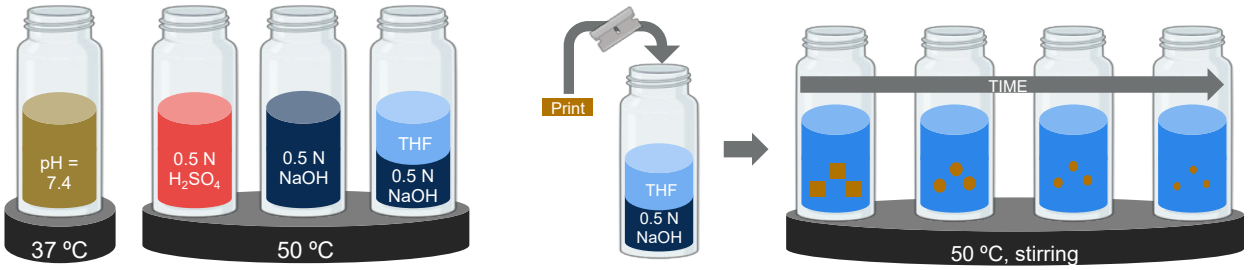


Figure S30. Cartoons demonstrating hydrolysis conditions employed in this study.

Table S8. Hydrolysis results in various conditions for X-BCP$_{49\%A}$

Condition	Temperature (ºC)	Time in Solution (days)	% Remaining (n=3)
pH = 7.4	37	60	97.2 ± 0.5
0.5 N H_2SO_4	50	7	92.6 ± 1.7
0.5 N NaOH	50	7	17.0 ± 6.2
0.5 N NaOH + THF (1/1 v/v)	50	7	0.0 ± 0.0

Table S9. Hydrolysis results for prints in 0.5 N NaOH + THF (1/1 v/v) at 50 ºC (n=3).

Sample	Time till Hydrolyzed (days)
X-BCP$_{25\%A}$	1
X-BCP$_{49\%A}$	2
X-BCP$_{72\%A}$	4
X-Stat$_{50\%A}$	3

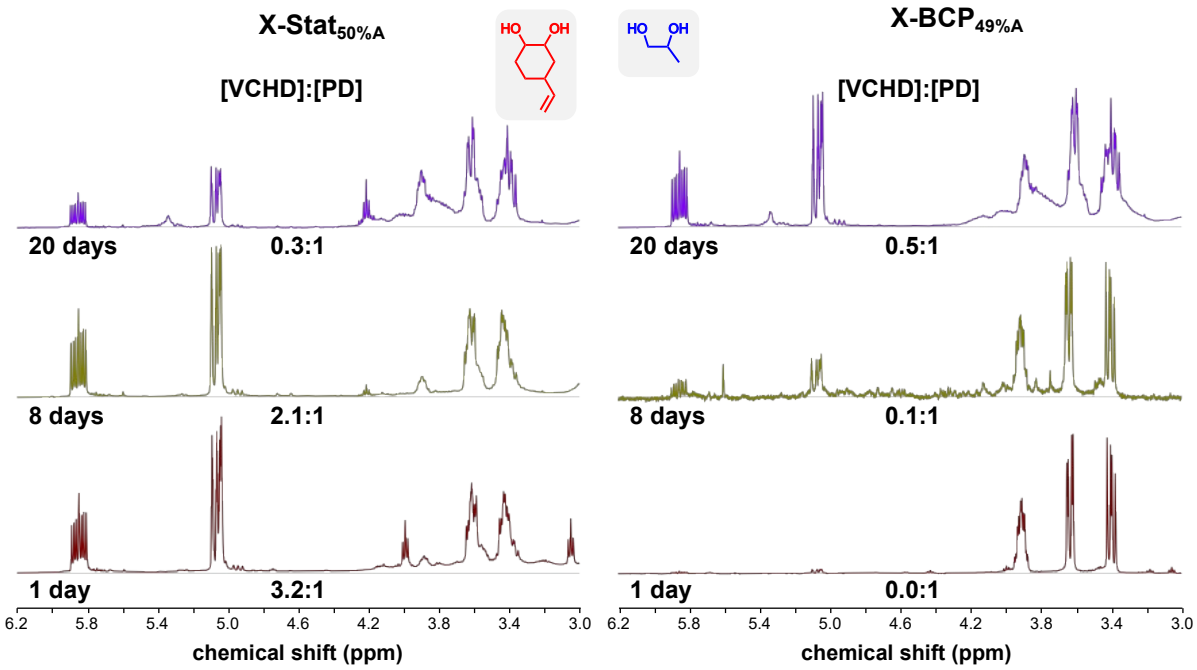


Figure S31. Hydrolysis ^{1}H NMR for X-Stat$_{50\%A}$ and X-BCP$_{49\%A}$ in 0.1 N NaOH + THF (1:1 v/v) at 50 ºC.

4. References:

(1) Fox, T. G. Influence of Diluent and of Copolymer Composition on the Glass Temperature of a Polymer System. *Bull. Am. Phys. Soc.* **1956**, *1*.