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

Rapid macroscale shape morphing of 3D-printed polyrotaxane monoliths amplified from pH-controlled nanoscale ring motions

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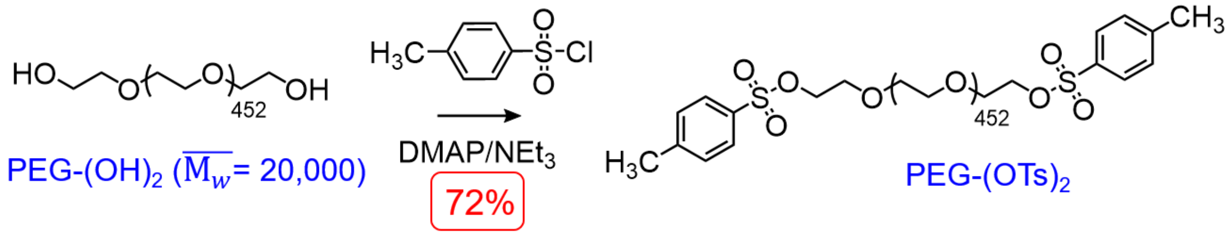
S1. General Information

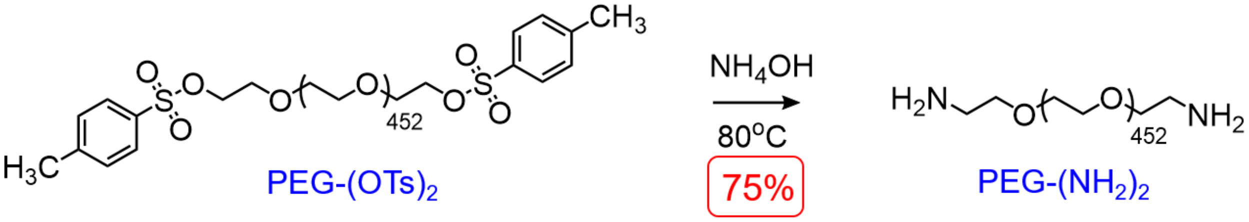
All reagents were purchased from commercial suppliers (Acros and Alfa) and used as received without further purifications. α-Cyclodextrin was generously gifted by Wacker Chemical Corp. Polyethyl glycol ($\overline{M_w}$= 20,000) was purchased from Sigma. Nuclear magnetic resonance (NMR) spectra were measured on Burker Ascend 600 or 500 NMR spectrometers. Optical microscope images were recorded using AmScope SM-1TSW2 stereomicroscope, other optical images were recorded using a regular camera.

S2. Synthetic Procedures



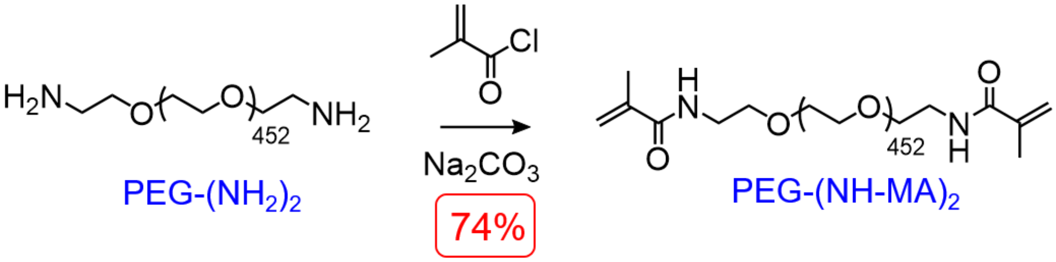
Scheme S1. Synthesis of telechelic polymer PEG-(OTs)$_2$.

PEG–(OTs)$_2$: PEG-(OH)$_2$ was dried using Dean-Stark apparatus to azeotropically remove the water residual using toluene. Then, in a 250 mL round bottom flask, anhydrous PEG-OH$_2$ (10.0 g, 0.5 mmol) was dissolved in anhydrous CH_2Cl_2 (200 mL) before 4-toluenesulfonyl chloride (0.95 g, 5.0 mmol), 4-Dimethylaminopyridine (DMAP, 0.006g, 0.05 mmol) and triethylamine (NEt_3, 0.84 mL, 6 mmol) were added. The reaction mixture was stirred at room temperature for 48 h. The mixture was washed with 1 M HCl aqueous solution (30 mL), saturated NaCl aqueous solution (30 mL), respectively. The organic phase was collected, dried over Na_2SO_4, and the solvent was removed under the reduced pressure. The crude product was re-dissolved in CH_2Cl_2 and precipitated in an excess of diethyl ether. The product was collected by filtration and dried at 40°C under the reduced pressure for 24 h, affording PEG-(OTs)$_2$ as a white powder (72 % yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.3 Hz, 4H), 7.32 (d, *J* = 8.1 Hz, 4H), 4.15 – 4.12 (m, 4H), 3.62 (s, 2098H), 2.43 (s, 6H).



Scheme S2. Synthesis of telechelic polymer PEG-(NH$_2$)$_2$.

PEG-(NH$_2$)$_2$: In a 250 mL pressure flask, PEG-(OTs)$_2$ (5 g, 0.25 mmol) was dissolved in NH_3•H_2O (25 % wt, 50 mL) and the reaction mixture was stirred at 90 °C for 72 h. The excess NH_3•H_2O was removed under the reduced pressure. The residue was dissolved in CH_2Cl_2 (500 mL) and washed using saturated NaCl aqueous solution (50 mL × 2). The organic phase was collected and the solvent was removed under the reduced pressure to afford the crude product, which was subsequently re-dissolved in CH_2Cl_2 and precipitated in an excess of diethyl ether. The product was collected by filtration and dried at 40°C under the reduced pressure for 24 h, affording PEG-$(NH_2)_2$ as a white powder in 75 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.64 (bs, 1818H).



Scheme S3. Synthesis of telechelic polymer PEG-(NH-MA)$_2$.

PEG-(NH-MA)$_2$: In a 100 mL round bottom flask, PEG-$(NH_2)_2$ (2.5 g, 0.125 mmol) and Na_2CO_3 (0.53g, 5.0 mmol) were dissolved in H_2O (25 mL), and the reaction was cooled to 0 °C in an ice bath. Metahacryloyl chloride (0.49 mL, 5.0 mmol) was added to the reaction dropwise over 30 min and the reaction mixture was stirred for another 24 h at room temperature. After the reaction completed, the pH of the solution was carefully adjusted to 7 using dilute HCl aqueous solution. The crude product was extracted using CH_2Cl_2 (250 mL) and the organic phase was washed with saturated NaCl aqueous solution (25 mL × 2). The organic phase was dried over Na_2SO_4 and the solvent was removed under the reduced pressure. The crude product was re-dissolved in CH_2Cl_2 and precipitated in an excess of diethyl ether to afford the final product PEG-(NH-MA)$_2$ as a white powder in 74 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.38 (s, 1H), 5.71 (d, *J* = 1.3 Hz, 2H), 5.32 (d, *J* = 1.5 Hz, 2H), 3.64 (s, 2506H), 1.97 (t, *J* = 1.3 Hz, 6H).

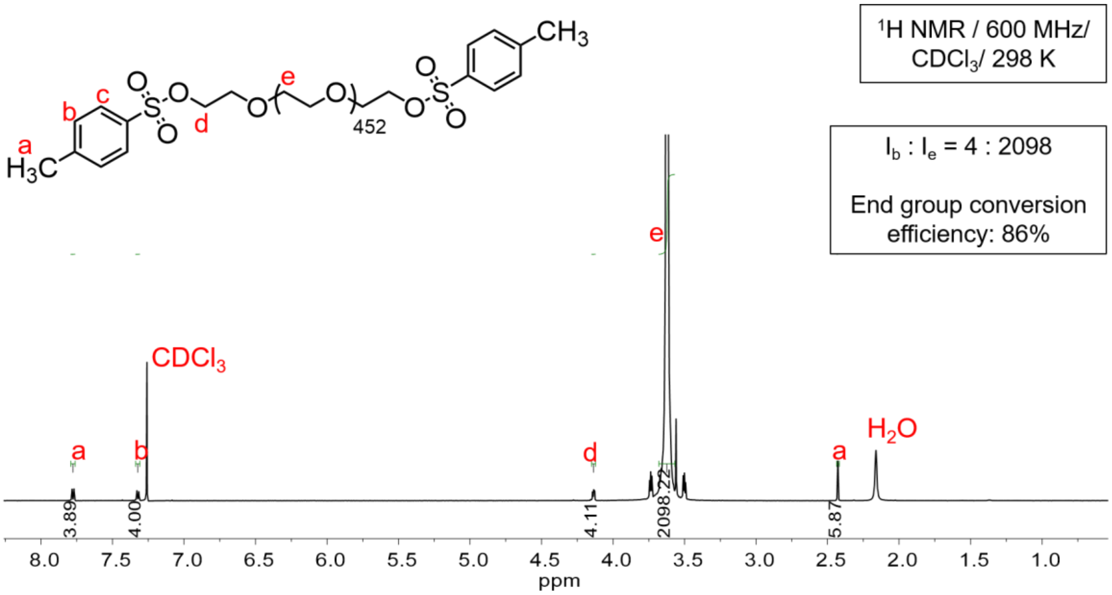


Figure S1. ^{1}H NMR spectrum (600 MHz) of PEG-$(OTs)_2$ in $CDCl_3$ at 298 K.

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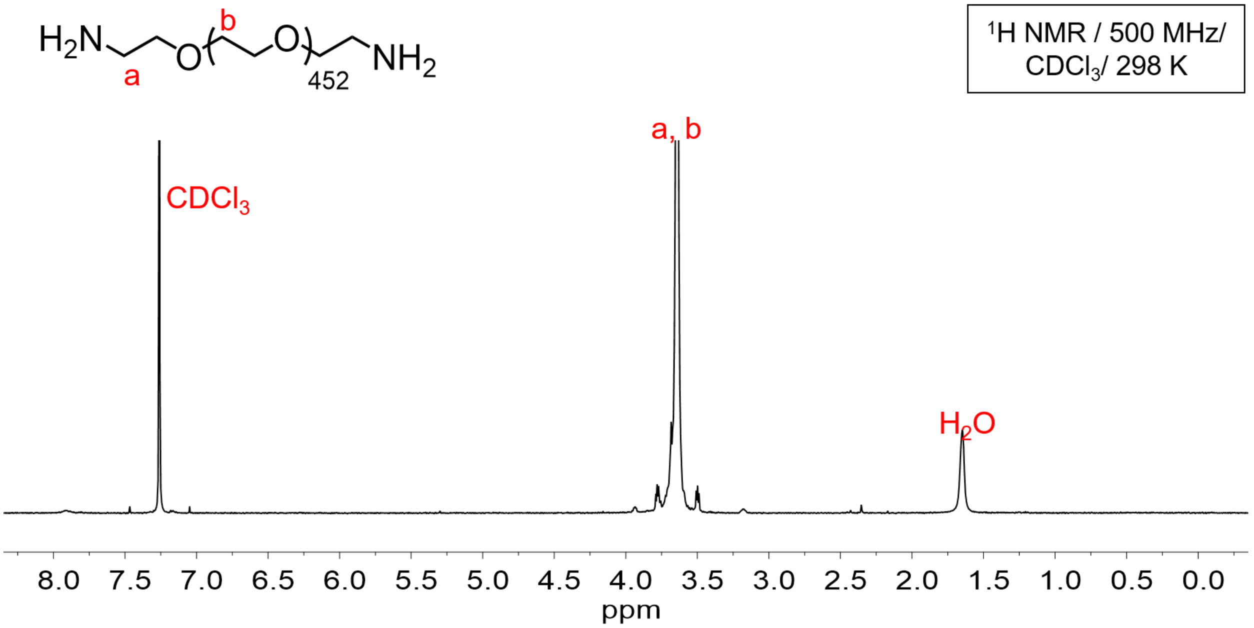


Figure S2. ^{1}H NMR spectrum (500 MHz) of PEG-$(NH_2)_2$ in $CDCl_3$ at 298 K.

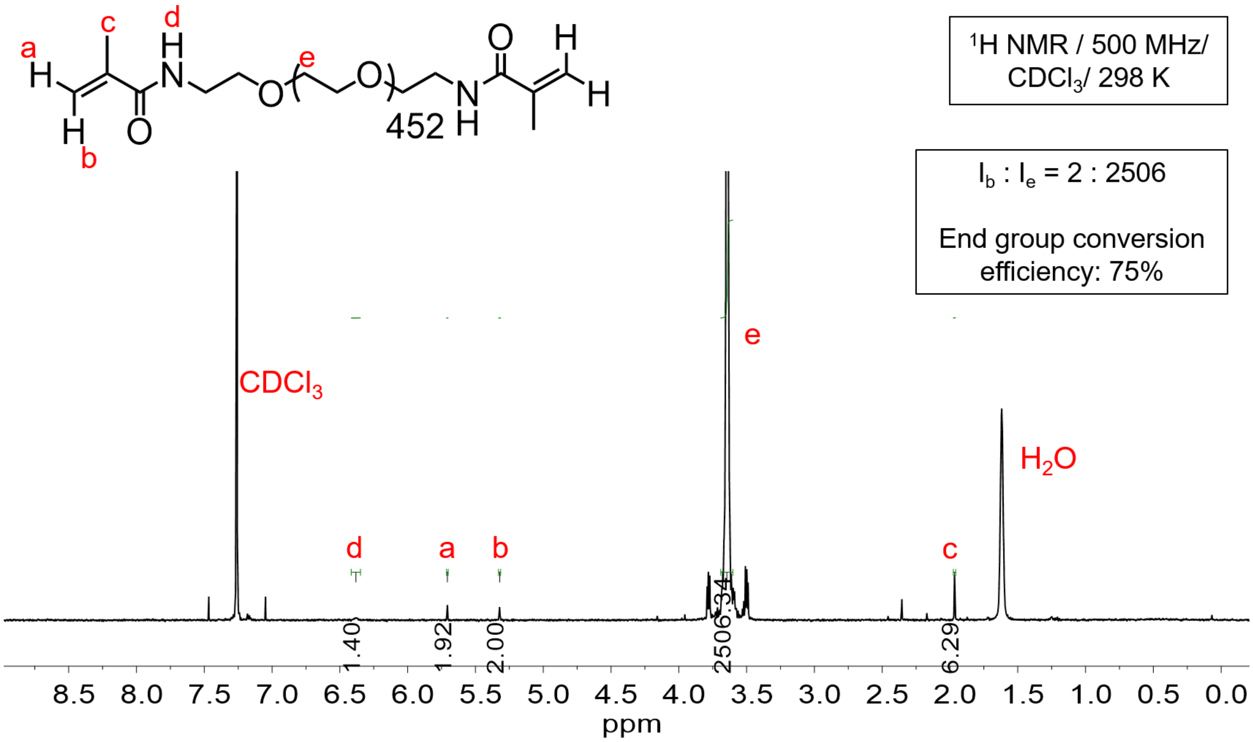
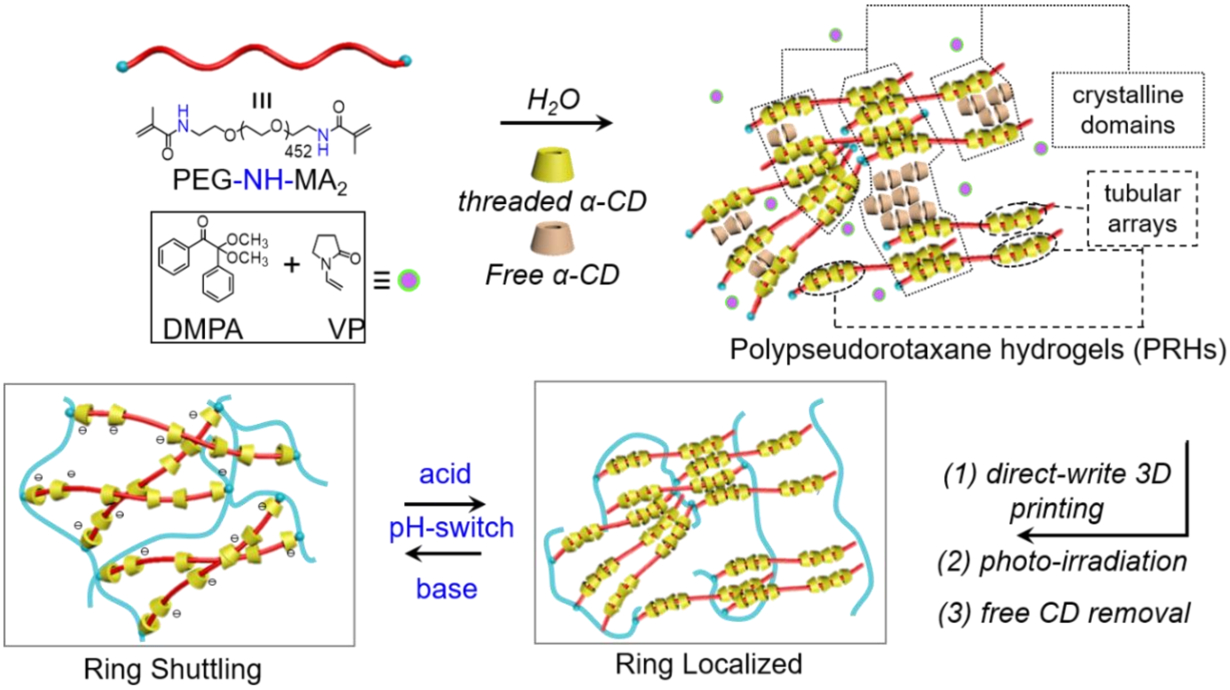


Figure S3. ^{1}H NMR spectrum (500MHz) of PEG-(NH-MA)$_2$ in $CDCl_3$ at 298 K.

Preparation of the Polypseudorotaxane Hydrogels (PRH$_{OH}$): In this study, PRH$_{OH}$ consisting of different molar ratios of PEG-(OH)$_2$ and α-CD were prepared as listed in Table S1. Typically, α-CD was dissolved in water at 60 ^{o}C before PEG-(OH)$_2$ was added. The reaction mixture was stirred for an additional 3 h at 60 ^{o}C to allow the formation of polypseudorotaxane. The reaction was then cooled down to room temperature and an opaque hydrogel was obtained. Finally, the hydrogel was consolidated at room temperature for 12 h before the rheological measurements and 3D printing experiments.



Scheme S4. Design and synthesis of 3D printable polypseudorotaxane hydrogels consisting of PEG-(NH-MA)$_2$ and α-CD. The ring motion is controlled by pH variation.

Synthesis of PM with varied PEG-(NH-MA)$_2$ to α-CD ratios: 10%, 14.5%, 20%, 30% w/v α-CD aqueous solution were prepared by dissloving diffent amounts of α-CD (1 g, 1.03 mmol; 1.45g, 1.49 mmol; 2 g, 2.06 mmol; 3 g, 3.08 mmol) in water (10 mL) at 60^{o}C respectively. Telechelic polymer PEG-(NH-MA)$_2$ (0.35 g, 0.0175 mmol) was added to the α-CD aqueous solutions and the reaction was stirred until PEG-(NH-MA)$_2$ was dissolved completely. The obtain solutions were stirred for 3 h for 60^{o}C before a 2,2-dimethoxy-2-phenylacetopheone (DMPA, 10.5 mg, 41 mmol) in *N*-vinylpyrrolidone (VP, 105 µL) solution was added. The reaction was stirred for an addition 30 min, kept in the dark, cooled down to room temperature and consolidate for 12 h. Then the obtained PRHs was photo-crosslinked under a UV lamp (365 nm) for 4 h in open air (the irradiation time may vary depending on the size and shape of the object and the irradiation path), washed by an excess of DMSO and H_2O, and lyophilized to obtain a form of powder PM[3.5, 10], [3.5, 14.5], [3.5, 20], [3.5, 30] for elemental analysis, which reveals the averaged number of rings locked in the monoliths. Elemental analysis:

PM[3.5, 10]: $[C_{916}H_{1828}N_2O_{455}]\cdot[C_{36}H_{60}O_{30}]_{9.9}\cdot[C_6H_9NO]_{20}\cdot[H_2O]_{60.1}$, calc: C 50.54%, H 8.29 %, N 0.93 %, O 40.23%; found: C 50.69 %, H 8.44 %, N 1.04 %, O 40.38 %.

PM[3.5, 14.5]: $[C_{916}H_{1828}N_2O_{455}]\cdot[C_{36}H_{60}O_{30}]_{19.25}\cdot[C_6H_9NO]_{20.05}\cdot[H_2O]_{102.05}$, calc: C 48.36%, H 7.9 %, N 0.72 %, O 43.01%; found: C 48.36 %, H 7.9 %, N 0.89 %, O 42.45 %.

PM[3.5, 20]: $[C_{916}H_{1828}N_2O_{455}]\cdot[C_{36}H_{60}O_{30}]_{30}\cdot[C_6H_9NO]_{48.45}\cdot[H_2O]_{208.3}$, calc: C 46.97%, H 7.72 %, N 1.21 %, O 44.10%; found: C 46.44 %, H 8.06 %, N 0.68 %, O 43.57 %.

PM[3.5, 30]: $[C_{916}H_{1828}N_2O_{455}]\cdot[C_{36}H_{60}O_{30}]_{32.35}\cdot[C_6H_9NO]_{20}\cdot[H_2O]_{295.25}$, calc: C 44.67%, H 7.73 %, N 0.52 %, O 46.73%; found: C 44.33 %, H 7.39 %, N 0.45 %, O 46.73 %.

Table S1. Preparation of PRH$_{OH}$s with varied PEG-OH$_2$ to α-CD ratios.

PRH$_{OH}$s	PEG-OH$_2$ (w/v %)	α-CD (w/v %)	Molar ratio	
			EO/α-CD [a]	PEG/ α-CD
[1.8[b], 5[c]]	1.8%	5%	7.6:1	1:59.8
[1.8, 10]	1.8%	10%	3.9:1	1:116.5
[1.8, 14.5]	1.8%	14.5%	2.7:1	1:168.1
[1.8, 20]	1.8%	20%	2.0:1	1:227.2
[3.5, 10]	3.5%	10%	7.6:1	1:59.8
[3.5, 14.5]	3.5%	14.5%	14.5:1	1:85.6
[3.5, 20]	3.5%	20%	5.3:1	1:119.6
[3.5, 30]	3.5%	30%	3.8:1	1:181.8
[7.0, 10]	7.0%	10%	15.2:1	1:43.3
[7.0, 14.5]	7.0%	14.5%	10.5:1	1:56.8
[7.0, 20]	7.0%	20%	7.6:1	1:89.1
[7.0, 30]	7.0%	30%	5.1:1	1:52.3

[a] the molar number of the repeating unit ethylene oxide (EO) was calculated based on 454 units per PEG-OH$_2$, [b] w/v % of PEG-OH$_2$ in a PRH$_{OH}$, and [c] w/v % of α-CD in a PRH$_{OH}$.

Preparation of PRH$_{NH}$ for 3D printing and rheological measurements: A 20 % w/v α-CD aqueous solution was prepared by dissolving α-CD (2 g, 2.06 mmol) in water (10 mL) at 60 °C. Telechelic polymer PEG-(NH-MA)$_2$ (0.35 g, 0.0175 mmol) was added to the α-CD aqueous solution and the reaction was stirred until PEG-(NH-MA)$_2$ was dissolved completely. The obtained solution was stirred for 3 h at 60 °C before a DMPA (10.5 mg, 41 mmol) in VP (105 µL) solution was added. The reaction was stirred for an additional 30 min, kept in the dark, cooled down to room temperature and consolidated for 12 h before 3D printing and rheological measurements.

Photo-crosslinking of the 3D-printed PRH$_{\mathrm{NH}}$ monoliths: After direct-writing, the printed object was photo-crosslinked under a UV lamp (365 nm) for 4 h, affording the polyrotaxane monolith (PM). After crosslinking, the object was immersed in an excess of DMSO for 24 h to remove unreacted species. The monolith was re-hydrated in H_2O for 24 h.

Thermostability of PM: The thermostability of the extensive photo-crosslinked PM was investigated by ^{1}H NMR experiment. The lyophilized PM sample was soaked in basic D2O ([NaOD] = 1 M) at 80 ^{o}C overnight and cooled down to room temperature before measurement.

Synthesis of polyrotaxane monoliths (PM$_{\mathrm{NMR}}$) with low crosslinking degrees: In order to confirm the formation of polyrotaxane structure, PM$_{\mathrm{NMR}}$ with a low crosslinking degree that is soluble in DMSO-d_6 for NMR analysis was prepared by reducing the photo-irradiation time. After direct-writing, the lattice cube was photo-irradiated for 20 min. The obtained lattice cubes were washed extensively with a large excess of water. After washing, the printed cube lost their 3D structure with significant weight loss recorded. Then the product was dissolved in DMSO and dialyzed (cut off M_w = 8000 Da) in DMSO and H_2O respectively to remove the unreacted species and lyophilized as the powder form. The PM$_{\mathrm{NMR}}$ was analyzed by ^{1}H, ^{1}H-^{1}H COSY, and ^{1}H-^{1}H NOESY NMR spectra. The ^{1}H NMR spectrum analysis suggests ~ 8 rings per PEG are interlocked mechanically in the crosslinking polymer network.

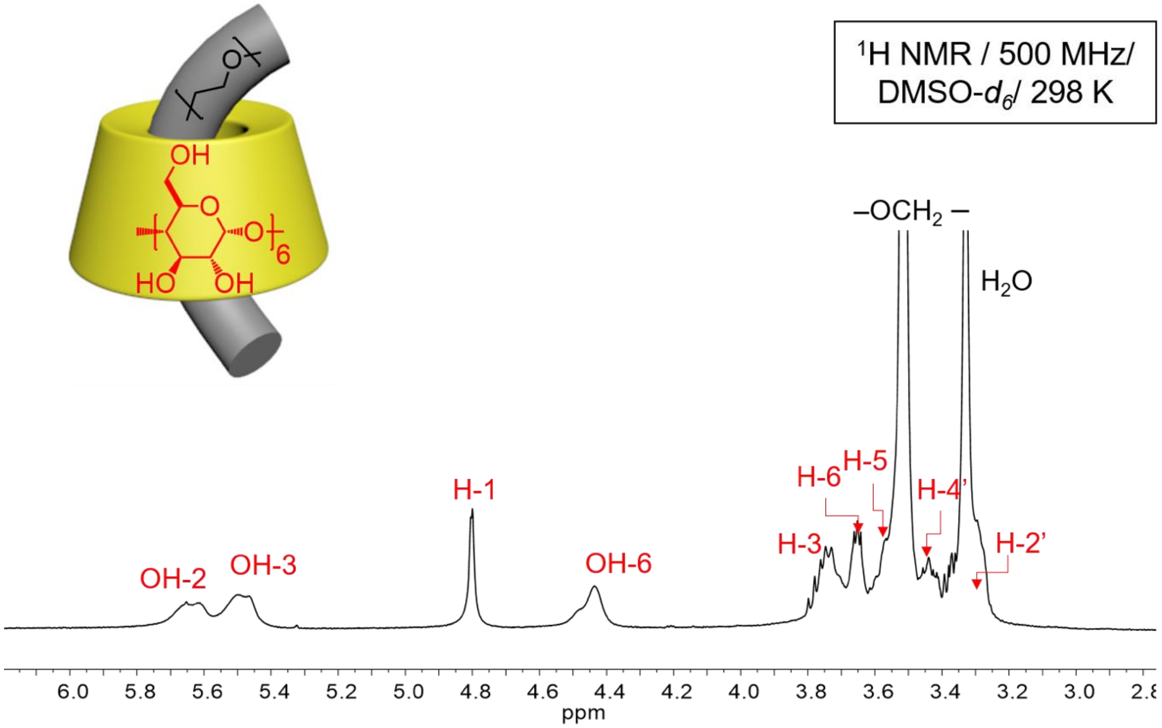


Figure S4. ^{1}H NMR spectrum of PM$_{\mathrm{NMR}}$ in DMSO-d_6 at 298 K.

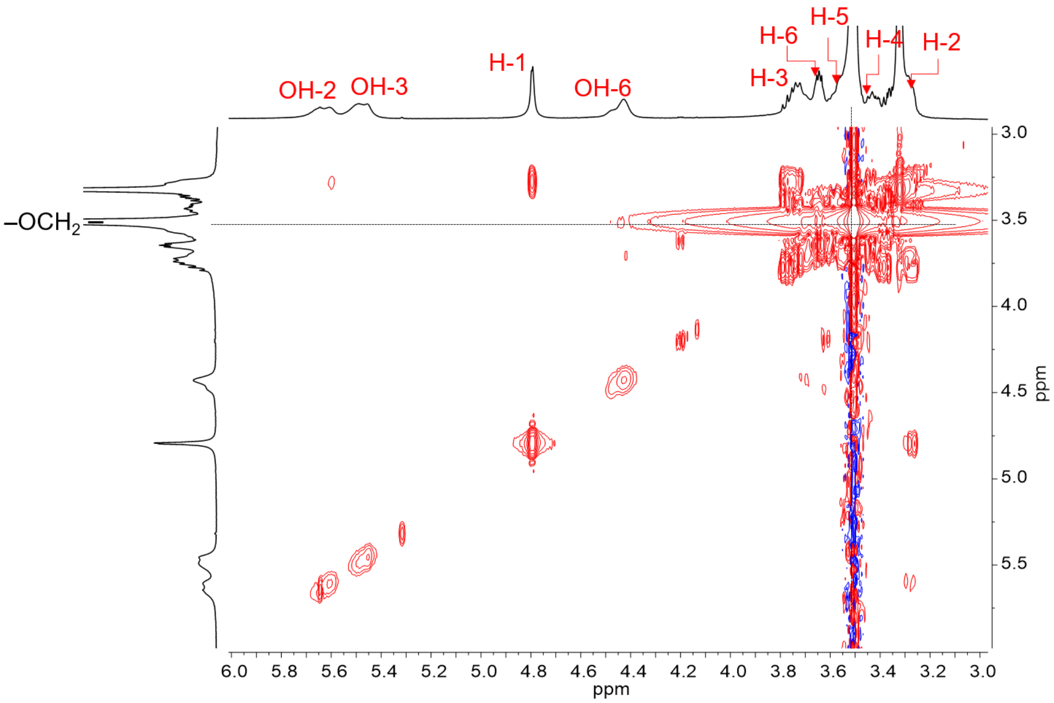


Figure S5. ^{1}H-^{1}H COSY spectrum of PM$_{NMR}$ in DMSO-d_6 at 298 K.

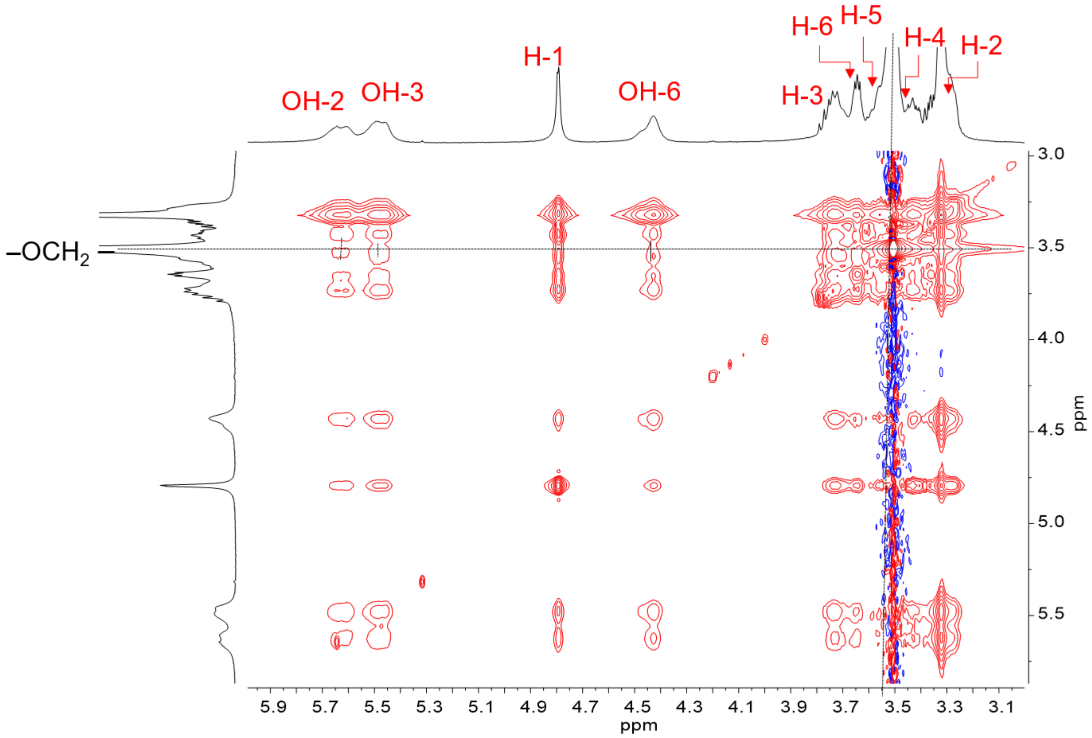


Figure S6. ^{1}H-^{1}H NOESY spectrum of PM$_{NMR}$ in DMSO-d_6 at 298 K, mixing time = 300 ms.

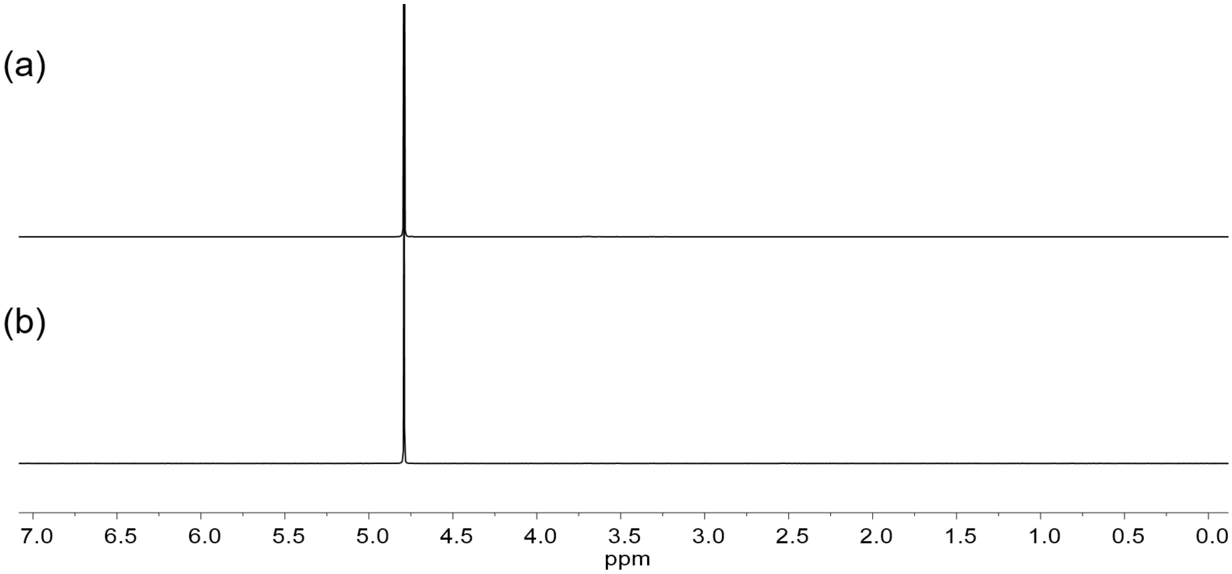
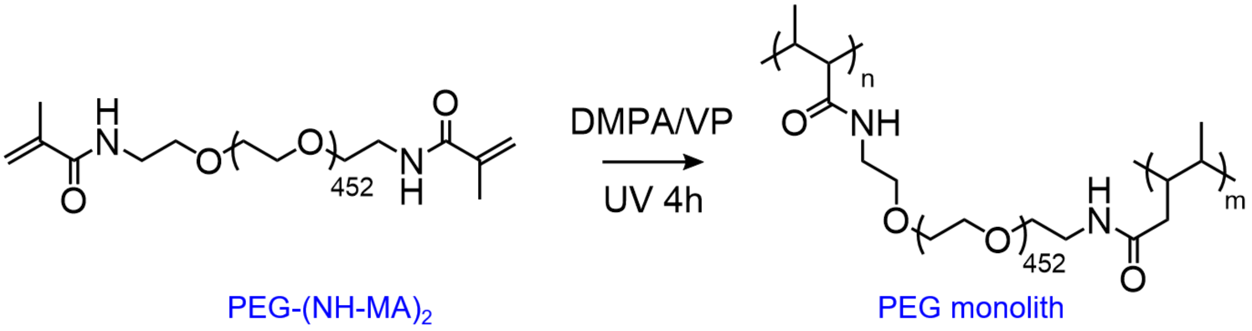


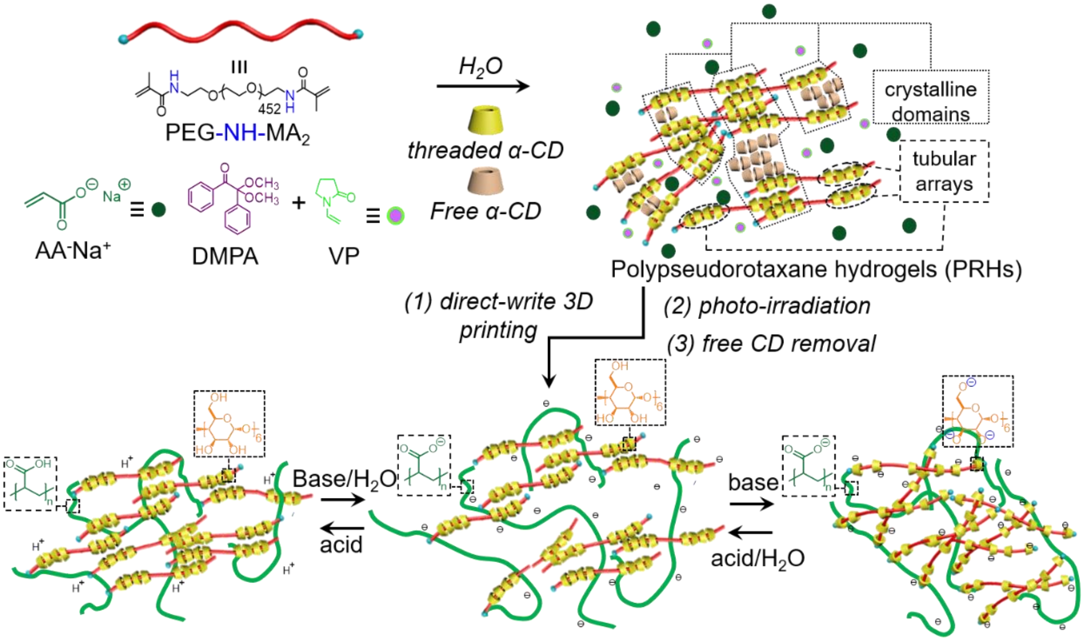
Figure S7. ^{1}H NMR spectrum of insoluble PM in basic D_2O ([NaOD] = 1 M) at 273 K (a) before and (b) after heating overnight at 80°C.



Scheme S5. Synthesis for PEG monolith (PEGM).

Synthesis of PEG monolith: Telechelic polymer PEG-(NH-MA)$_2$ (0.35 g, 0.0175 mmol) was dissolved in water (10 mL), DMPA's (10.5 mg, 41 mmol) VP (105 µL) solution was added. The obtained solution was irradiated under a UV lamp (365 nm) for 4 h, affording a transparent hydrogel PEG monolith. After crosslinking, the obtained PEG monolith was washed by with an excess of DMSO and H_2O respectively to remove the unreacted species.

Elemental analysis: $[C_{916}H_{1828}N_2O_{455}]\cdot[C_6H_9NO]_{18}\cdot[H_2O]_{88.05}$, calc: C 51.81%, H 9.2 %, N 1.18 %, O 37.87 %; found: C 52.06 %, H 8.92 %, N 1.44 %, O 38.09 %.



Scheme S5. Design and synthesis of 3D printable PRH$_{SA}$.

Preparation of the PRH$_{SA}$: α-CD (2 g, 2.06 mmol) was dissolved in 10 mL water at 60°C then PEG-(NH-MA)$_2$ (0.35 g, 0.0175 mmol) was added into the solution. The mixture was stirred for an additional 3 h at 60 °C to allow the formation of polypseudorotaxane before sodium acrylate (0.5 g, 5.32 mmol, 304 *equiv.* to PEG-(NH-MA)$_2$, 0.67 *equiv.* to EO repeating unit, and 2.58 *equiv.* to α-CD) and a DMPA's (10.5 mg, 41 mmol) VP (105 μL) solution were added. The reaction was stirred for an additional 30 min and then was kept in the dark, cooled down to room temperature and consolidated for 12 h before direct-writing.

Photo-crosslinking of the 3D-printed PRH$_{SA}$ monoliths: After direct-writing, the printed PRH$_{SA}$ monolith was photo-crosslinked under a UV lamp (365 nm) for 4 h, affording the polyrotaxane-*co*-polyacrylate monolith (PM-PA). After crosslinking, the object was immersed in an excess of DMSO and for 24 h to remove unreacted species. The monolith was re-hydrated in H_2O for 24 h.

Elemental analysis was performed to reveal the averaged number of rings locked in the PM-PA: $[C_{916}H_{1828}N_2O_{455}]\cdot[C_{36}H_{60}O_{30}]_{27.4}\cdot[C_3H_3O_2Na]_{282.9}\cdot[C_6H_9NO]_{48.2}\cdot[H_2O]_{575.5}$, calc: C 41.04 %, H 6.69 %, N 0.69 %, O 44.17 %, found: C 40.64 %, H 7.29 %, N 0.79 %, O 43.77%.

Synthesis of PM-PA$_{NMR}$ with low crosslinking degrees: In order to confirm the PM-PA chemical structure, PM-PA$_{NMR}$ with low crosslinking degrees were prepared by reducing the photo-irradiation time. After direct-writing, the lattice cube was photo-irradiated for 20 min. The obtained lattice cubes were washed extensively with a large excess of water. After washing, the printed cube lost their 3D structure with significant weight loss recorded. Then the product was dissolved in DMSO and dialyzed (cut off M_w = 8000 Da) in DMSO and H_2O respectively to remove the unreacted species. The pH of the solution was adjusted to pH = 2 by diluted HCl solution. The PM-PA$_{\mathrm{NMR}}$ obtained after lyophilization was analyzed by ^{1}H NMR spectrum. The ^{1}H NMR spectrum analysis suggests ~ 5 rings per PEG are interlocked mechanically in the crosslinking polymer network.

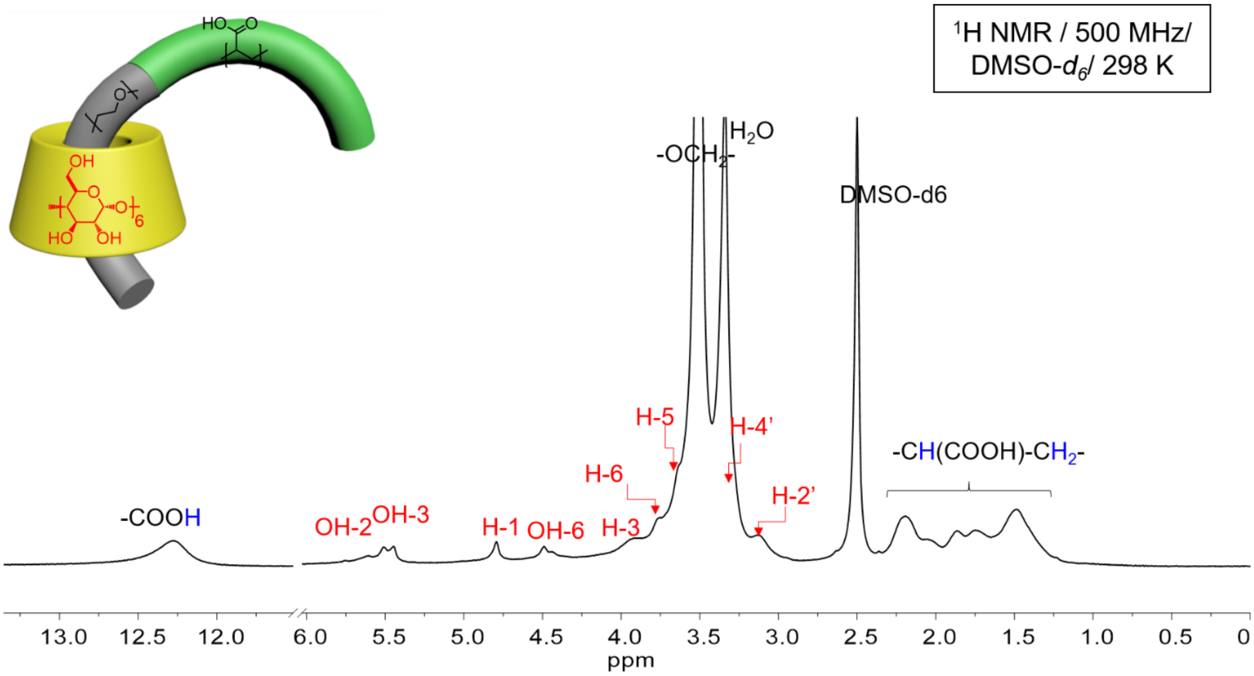
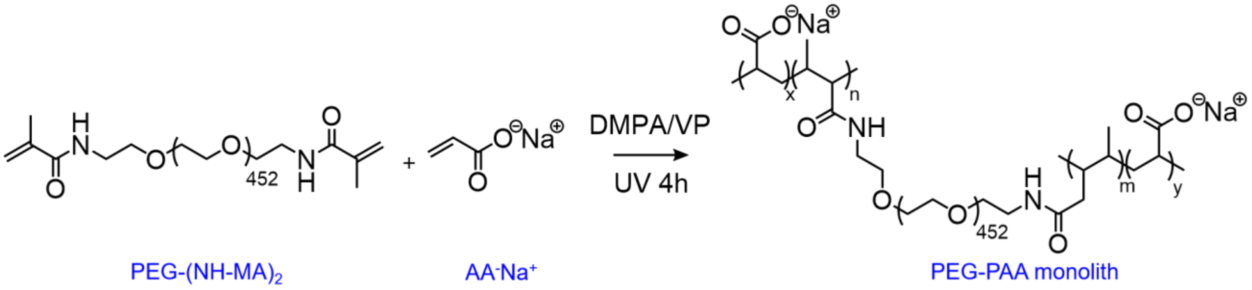


Figure S8. ^{1}H NMR spectrum of acidic PM-PA$_{\mathrm{NMR}}$ in DMSO-d_6 at 298 K.



Scheme S7. Synthesis of PEG-PAA monolith (PEGPAAM).

Synthesis of PEG-PA monolith: Telechelic polymer PEG-(NH-MA)$_2$ (0.35g, 0.0175 mmol) and sodium acrylate (0.5g, 5.32 mmol) were dissolved in water (10 mL) and then DMPA (10.5 mg, 41 mmol) VP (105 µL) solution was added. The obtained solution was irradiated under a UV lamp (365 nm) for 4 h, affording a transparent hydrogel PEG-PA monolith. After crosslinking, the obtained PEG-PA monolith was washed by with an excess H_2O respectively to remove the unreacted species. Elemental analysis: $[C_{916}H_{1828}N_2O_{455}]\cdot[C_3H_3O_2Na]_{89.15}\cdot[C_6H_9NO]_{53}\cdot[H_2O]_{240.2}$, calc: C 46.53 %, H 7.94 %, N 1.99 %, O 38.26 %; found: C 46.37 %, H 8.00 %, N 2.16 %, O 38.19 %.

Powder X-ray diffraction (PXRD) experiments: PXRD experiments were performed on a Rigaku MiniFlex diffractometer. The voltage was set to 40 kV, and the current was 40 mA. The detector collected data over the range $2\theta = 5\text{-}35^{o}$. Solid-state samples of PM and PM-PA were prepared by washing the hydrogels with an excess of DMSO and water to remove the unreacted species and lyophilized as the powder form.

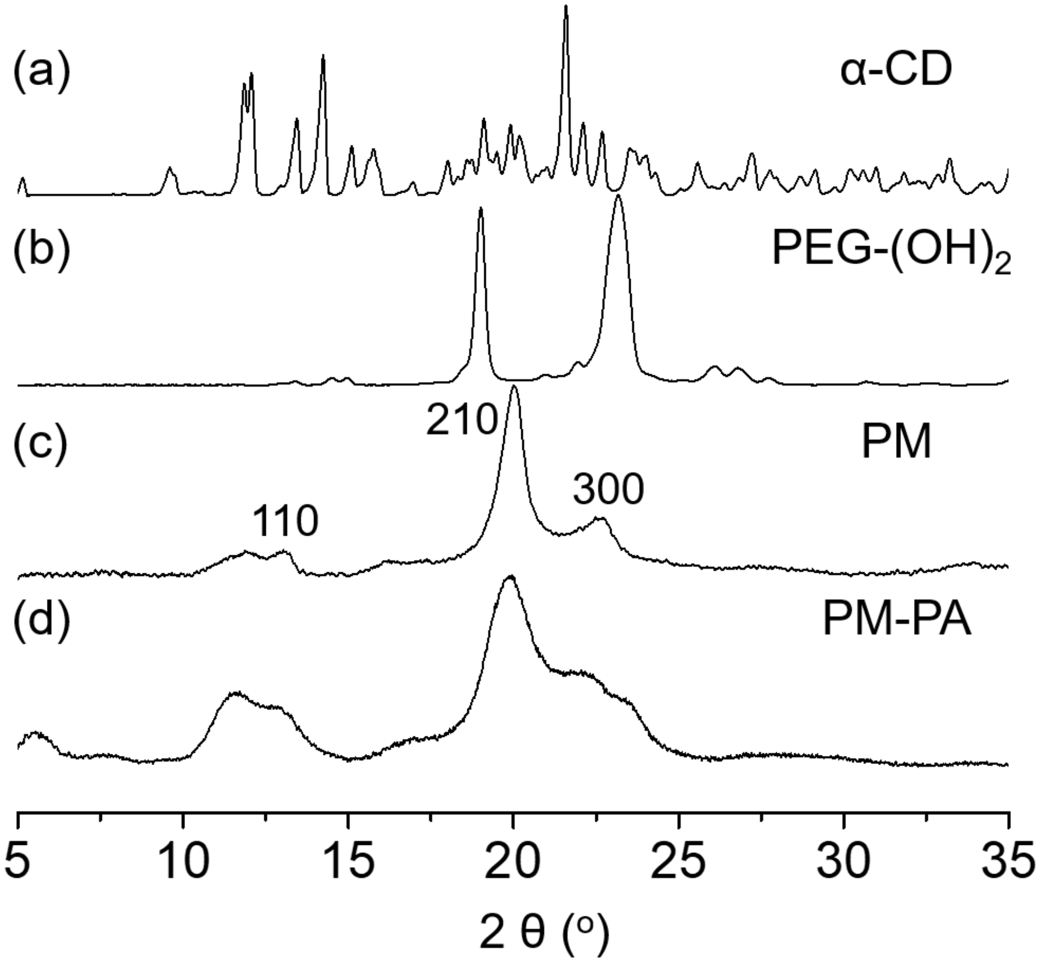


Figure S9. Powder X-ray diffraction profiles of (a) α-CD; (b) PEG-(OH)$_2$ of $\overline{M_w}$= 20,000; (c) lyophilized PM sample; (d) lyophilized PM-PA sample, respectively.

Preparation of PM and PM-PA disks: The PRH_{NH} and PRH_{SA} hydrogels were molded as thin disks (diameter = 13 mm, height = 2 mm). The samples were photo-crosslinked under UV irradiation for 4 h, washed with 1M NaOH solution to remove unreacted species, affording round-shaped PM and PM-PA hydrogels, respectively.

S3. Rheological Studies

Rheological measurements: To evaluate the 3D printability of PRH_{OH}, PRH_{NH} and PRH_{SA} inks, the storage (G') and loss moduli (G"), viscosity (ƞ), shear-thinning and self-healing behaviours of the PRH_{OH}s were investigated. Three types of rheological measurements were performed at room temperature on a stress-controlled rheometer (TA instruments, DHR-2) with a 20-mm diameter parallel plate geometry and a measuring gap of 1 mm.

Oscillation strain sweep: The G' and G" of the prepared inks were recorded with the oscillation strains increased from 0.1% to 100% and an angular frequency of 10 rad/s. *Shear rate flow sweep:* ƞ were recorded over a range of shear rate increased from 0 to 100 s^{-1}. *Dynamic step strain amplitude test:* G' and G" were recorded with a strain of 0.1% and 100% alternatively at a frequency of 10 rad/s. The period of each step is 15 s and no equilibrium time is set in between.

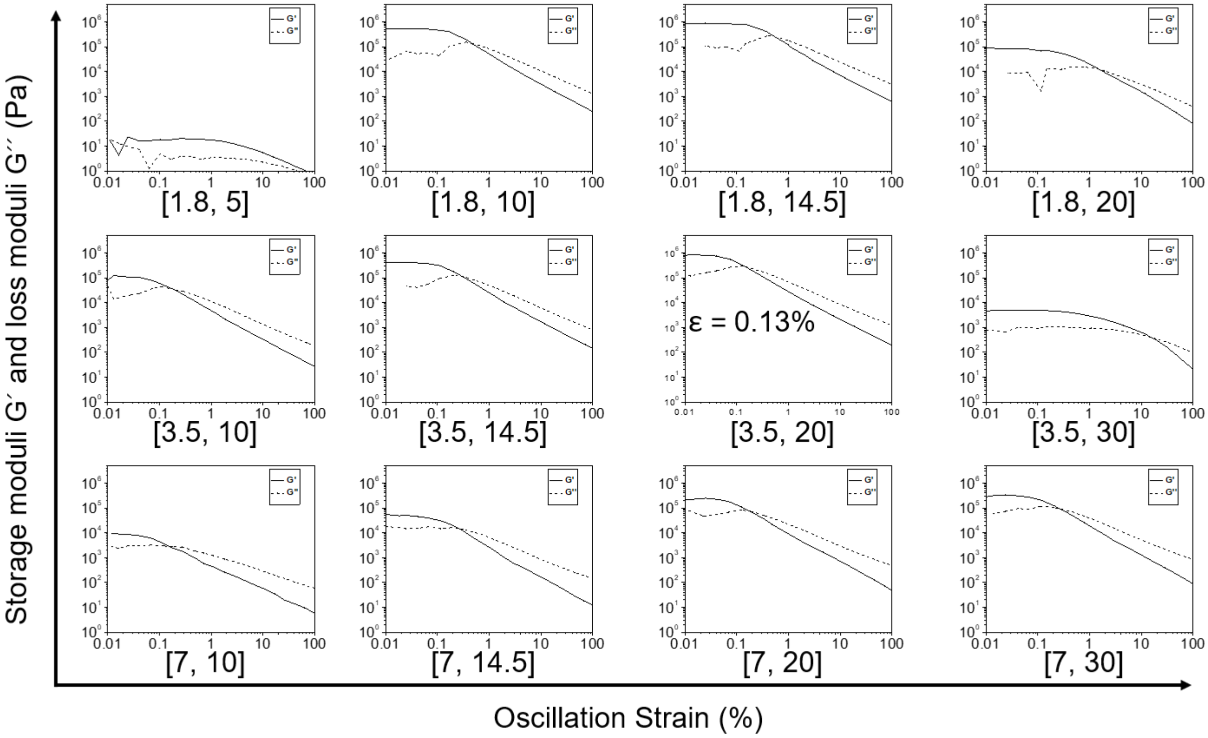


Figure S9. Oscillation strain sweep profiles of PRH_{OH}s listed in Table S1.

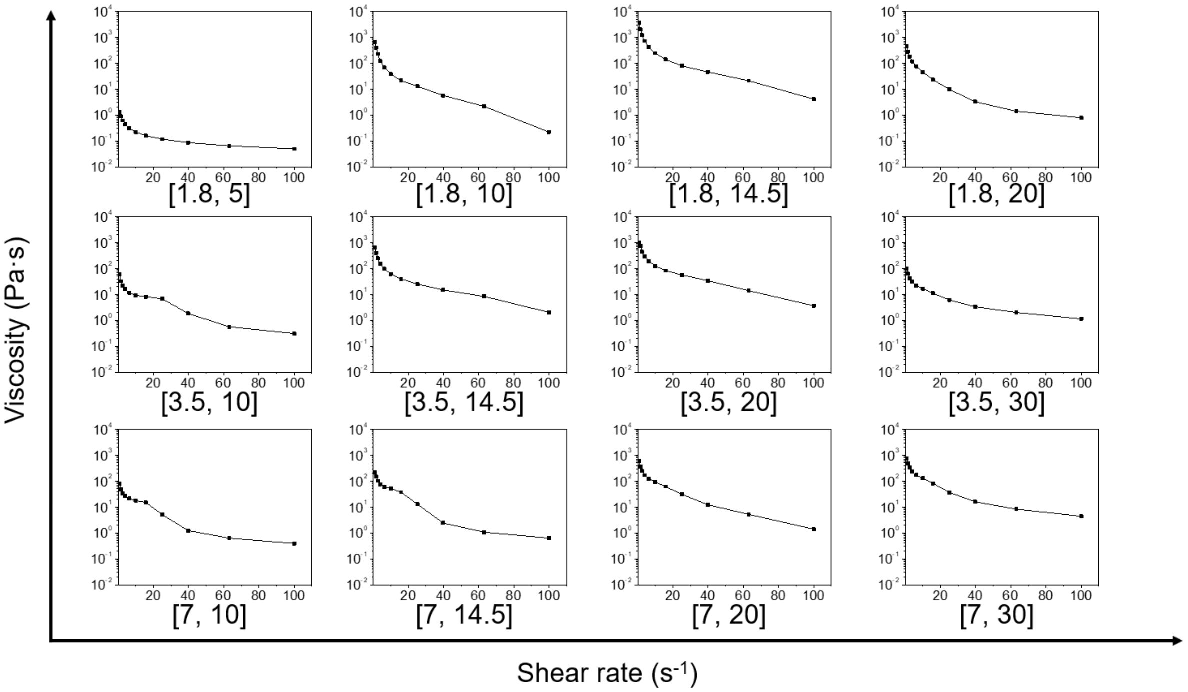


Figure S11. Steady shear rate sweep profiles of PRH$_{OH}$s listed in Table S1.

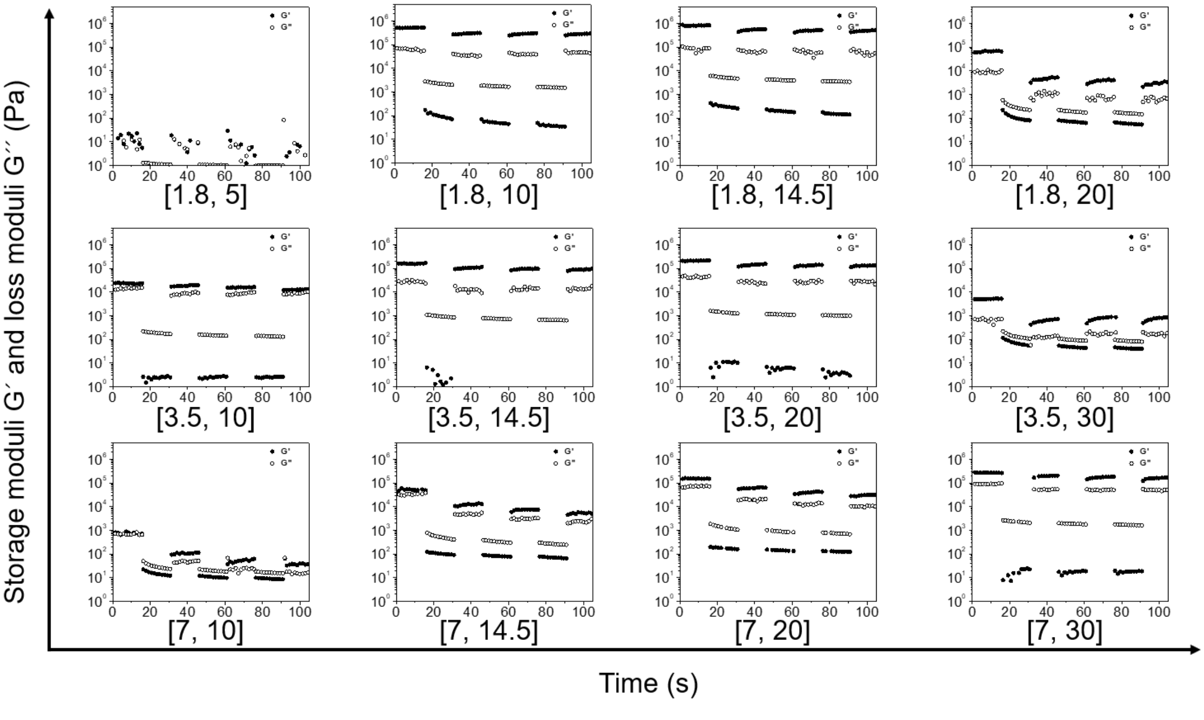


Figure S12. Dynamic step-strain amplitude test profiles of PRH$_{OH}$s listed in Table S1.

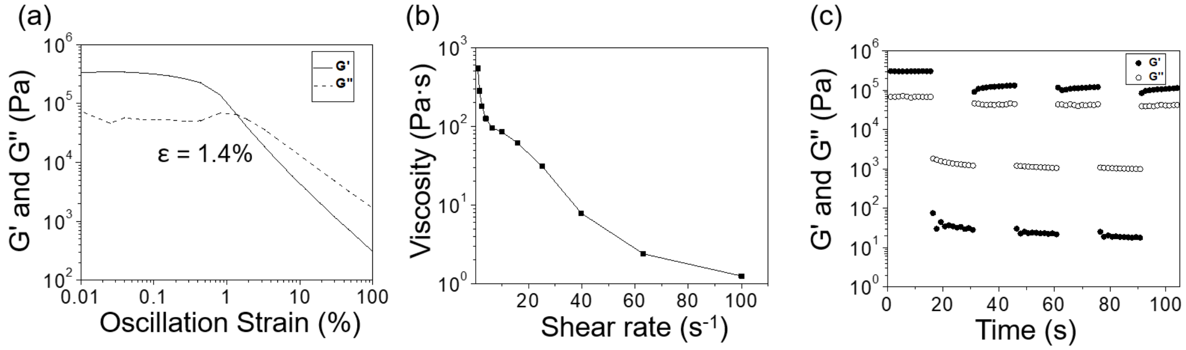


Figure S13. Rheological measurements of $PRH_{NH}[3.5,20]$. (a) A strain sweep, (b) a shear rate sweep and (c) a dynamic step strain sweep under alternative strains of 0.1% and 100%.

Rheological studies of PM, PEG, PM-PA and PEG-PAA monoliths at different pH: The storage and loss moduli of PM and PEG monoliths were measured by angular frequency sweep experiments in their hydrogel forms at different pH at 25 °C. The angular frequency applied to the sample was increased from 1 rad/s and 100 rad/s (frequency increased from 0.16 Hz to 15.92 Hz). The oscillation strain was set at 0.1 %. At a pH, the storage and loss moduli were determined by averaging their storage and loss moduli at different frequencies.

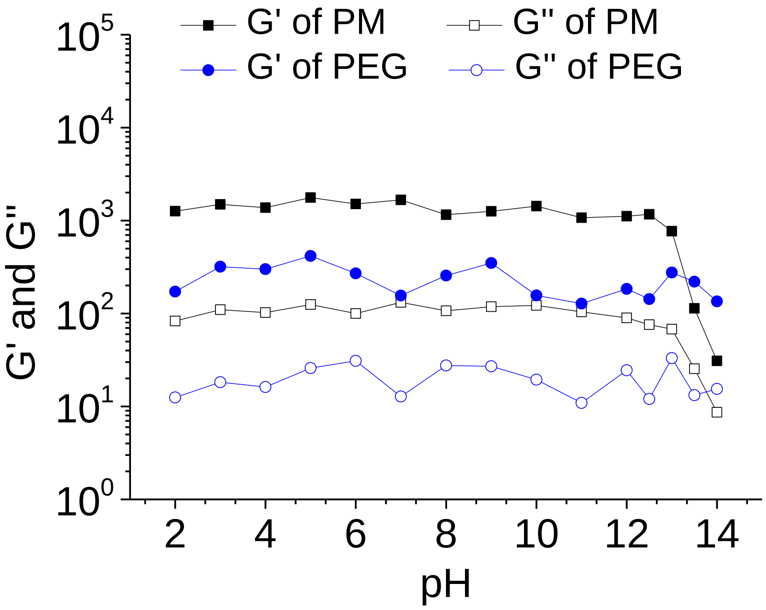


Figure S14. The storage and loss moduli of PM and PEG monoliths at different pH.

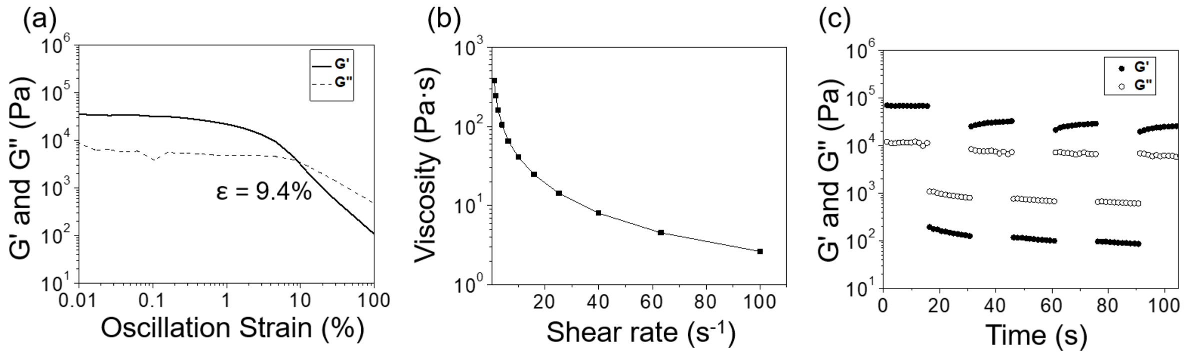


Figure S15. Rheological measurements of PRH_{SA}. (a) A strain sweep, (b) a shear rate sweep, and (c) a dynamic step strain sweep under alternative strains of 0.1% and 100%.

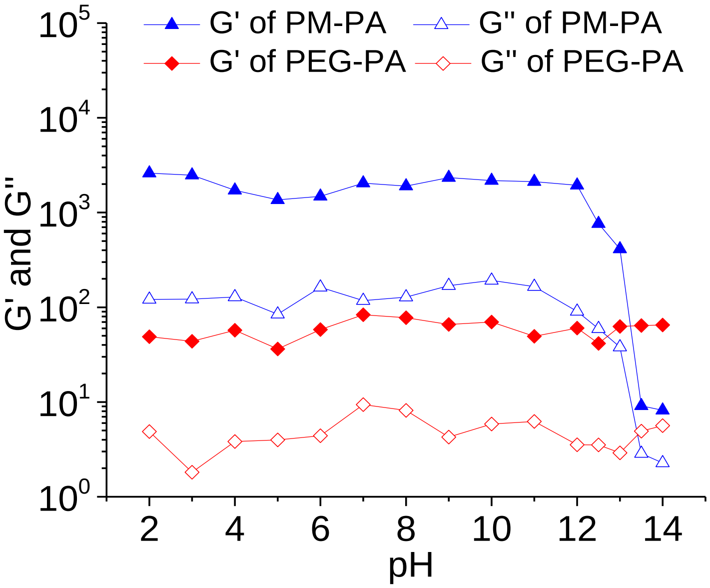


Figure S16. Storage and loss moduli profiles of PM-PA and PEG-PA at different pH.

S4. 3D Printing and Post-Printing Polymerization

General 3D printing methods: The 3D printing experiments were performed on an extrusion-based 3D printer (Tabletop, nScrypt) equipped with Nordson EFD precision smoothflower tapered tips. The hydrogel inks were loaded into Nordson EFD syringe barrels (3 mL) and installed onto the 3D printer. Printing paths files were generated by P-CAD software. Printing pressure was varied between 10 and 50 psi and the printing speed was varied between 5 and 40 mm/s, respectively. Woodpile lattice cubes and pyramids consisted of four repetitive layers were printed with good structural integrity on glass slides.

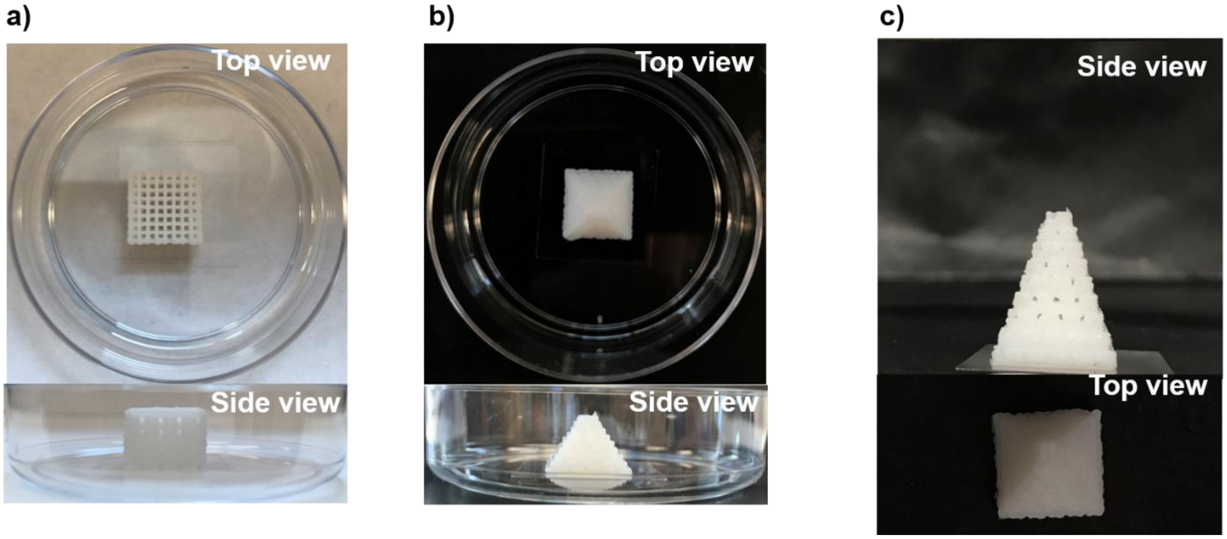


Figure S17. Images of as-printed PRH$_{NH}$[3.5, 20] with structures of (a) woodpile lattice cube; (b) low profile pyramid; and (c) high profile pyramid. Line width = 200 ~ 600 µm.

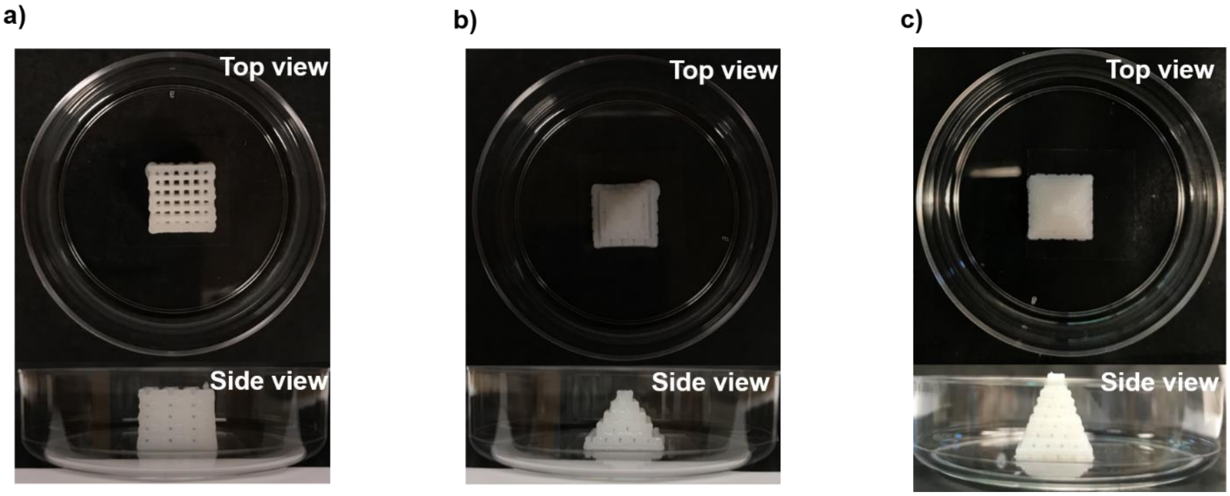


Figure S18. Images of as-printed PRH$_{SA}$ with a structure of a) woodpile lattice cube; b) low profile pyramid; and (c) high profile pyramid. Line width = 200 ~ 600 µm.

Dual-material 3D printing: PRH$_{NH}$ and PRH$_{SA}$ inks were loaded into two syringe barrels respectively and installed to different printing heads. The printed sample was photo-crosslinked under UV irradiation for 1 h and washed with 1M NaOH solution to remove unreacted species, affording a crosslinked hybrid.

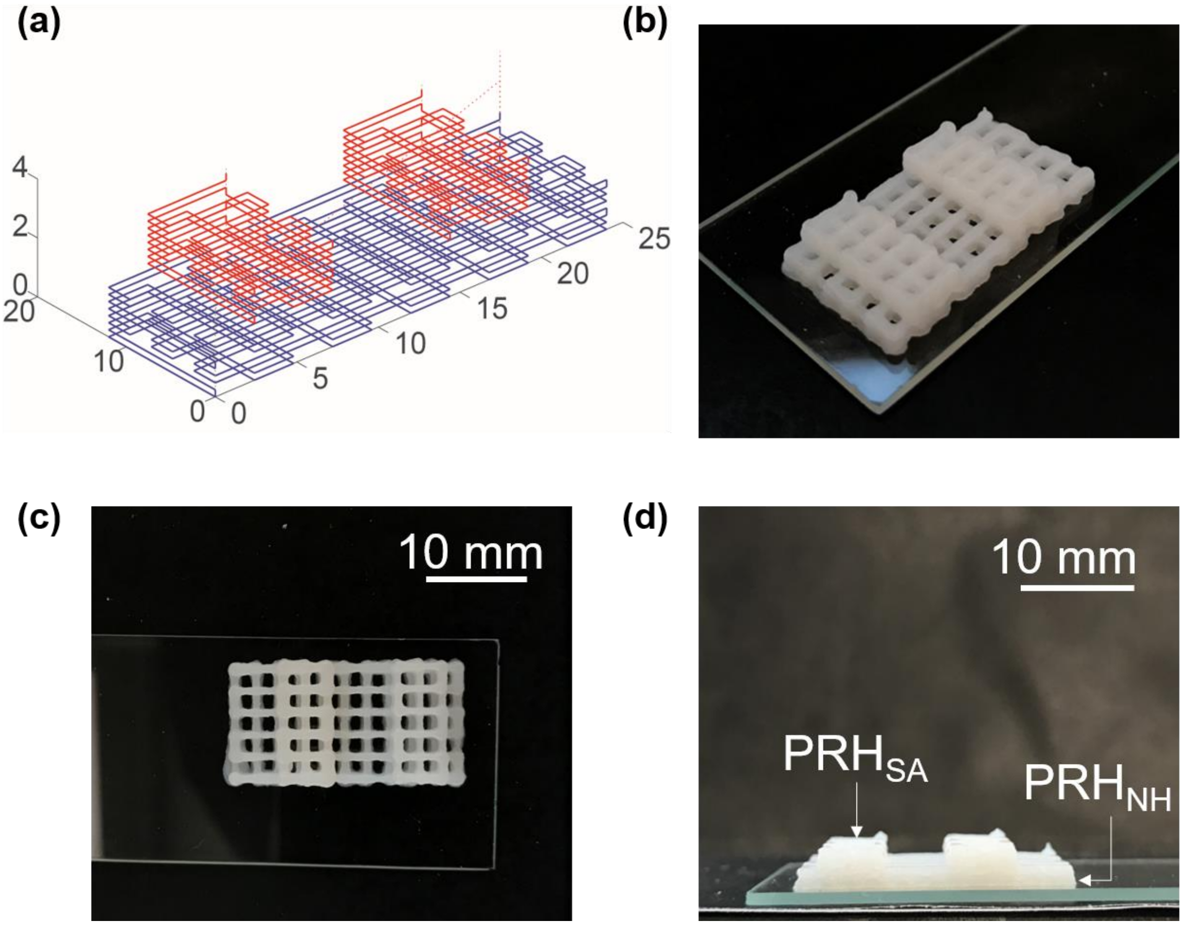


Figure S19. (a) Printing script of the hybrid structure using PRH$_{NH}$ and PRH$_{SA}$ modulated by Matlab® software (unit: mm). The red and blue sections were fabricated using PRH$_{SA}$ and PRH$_{NH}$, respectively. (b) Image of the as-printed hybrid. (c) Top and (d) side views of the as-printed object.

S5. Shape Morphing Experiments

PM shape morphing in NaOH (1 M) and neutral H_2O (pH = 7): A 3D-printed PM pyramid was soaked in 1M NaOH aqueous solution (pH = 14). The opaque PM hydrogel deformed from its as-designed 3D structure and transformed to a transparent hydrogel. The NaOH solution was removed and an excess of water was induced continuously to reduce pH to 7. The original pyramid 3D structure was rebuilt quickly. These shape morphing cycles have been repeated five times.

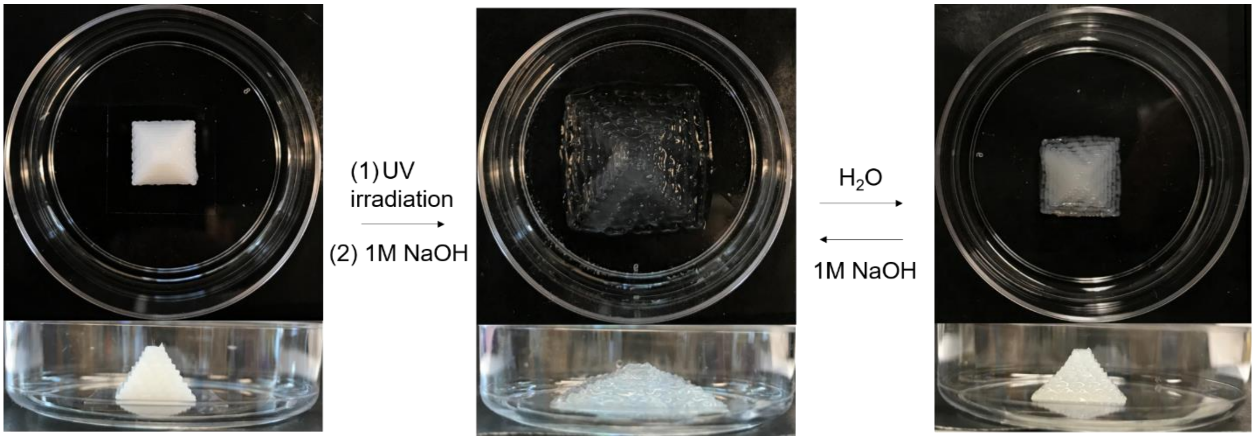


Figure S20. Shape morphing experiment of a 3D-printed PM pyramid (*left*) in 1M NaOH aqueous solution (pH = 14, *middle*) and H_2O (pH = 7, *right*).

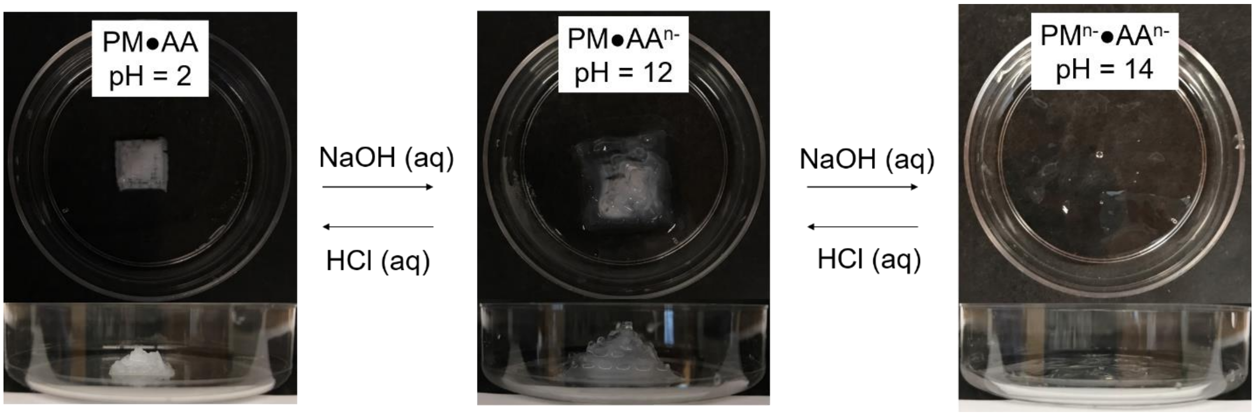


Figure S21. Shape morphing experiments of a 3D-printed PM-PA pyramid at different pH

Investigation of the swelling behaviours of PM and PM-PA thin disks.

PM swelling cycle (pH 14→9→7→2→7→9→14) in H_2O: PM thin disks were soaked in aqueous solutions of NaOH at pH = 14 for 24 h, and the pH of the solution was reduced subsequently by adding an excess of fresh H_2O and dilute HCl aqueous solution as shown in Figure S22. Then, the pH of the enviornment was increased backwards using fresh H_2O and NaOH aqueous solutions. *PM swelling cycle (pH 14→9→7→2→7→9→14) in the presence of 50 mM NaCl:* PM thin disks were soaked in aqueous solutions of NaOH at pH = 14 for 24 h, and the pH of the solution was reduced subsequently by adding an excess of fresh NaCl aqueous solution (pH = 7 or 2, [NaCl] = 50 mM) as shown in Figure S23. Then, the pH of the enviornment was increased backwards using fresh NaCl (pH = 7) and NaOH ([NaCl] = 50 mM) aqueous solutions. The pH was measured using a pH-meter and the samples were kept at certain pH until their size reach the constant value (2-24 h). The diameters of the samples were measured and the averaged diameters have been summarized in Figure S26. *PM-PA swelling cycle (pH 14→9→7→2→7→9→14) in H_2O* (Figure

S24) and *PM-PA swelling cycle (pH 14→9→7→2→7→9→14) in the precence of 50 mM NaCl* (Figure S25) were recorded following the same procedure as those of PM.

Shape morphing of hybrid hydrogel: The hybrid hydrogel sample were soaked in aqueous solutions of NaOH at pH = 14 for 24 h. The pH of the solution was reduced subsequently by adding an excess of fresh H_2O and dilute HCl aqueous solutions. In order to increase the contrast of the image, the hybrid sample was dyed using 0.005 w/v% rhodamine B.

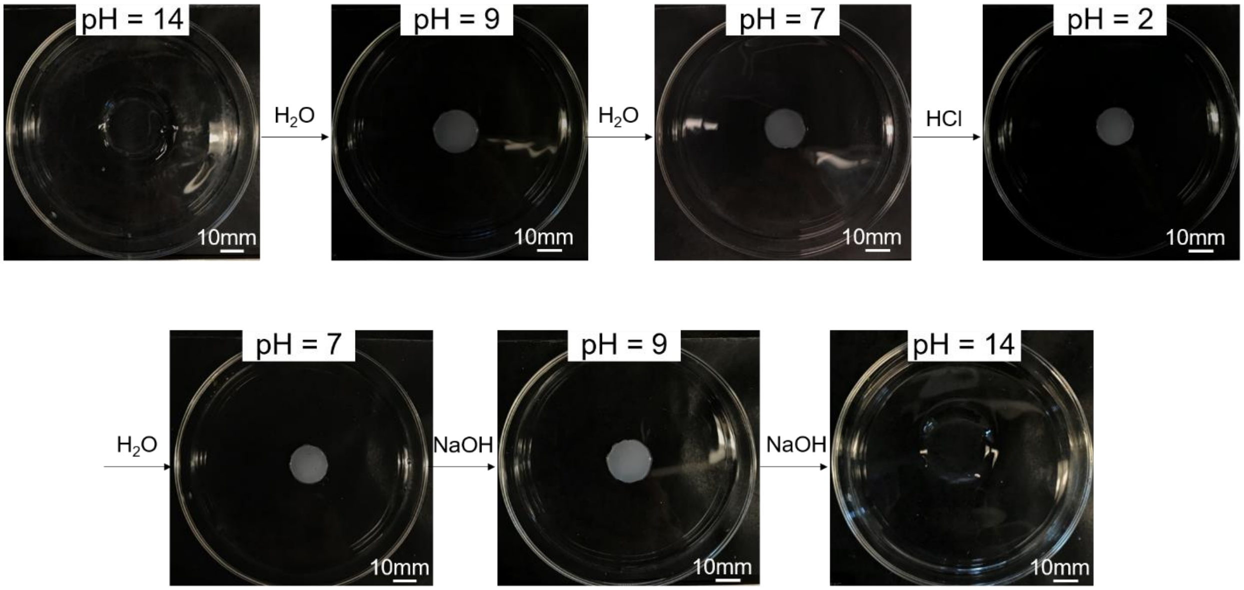


Figure S22. Images of PM hydrogel disks at different pH.

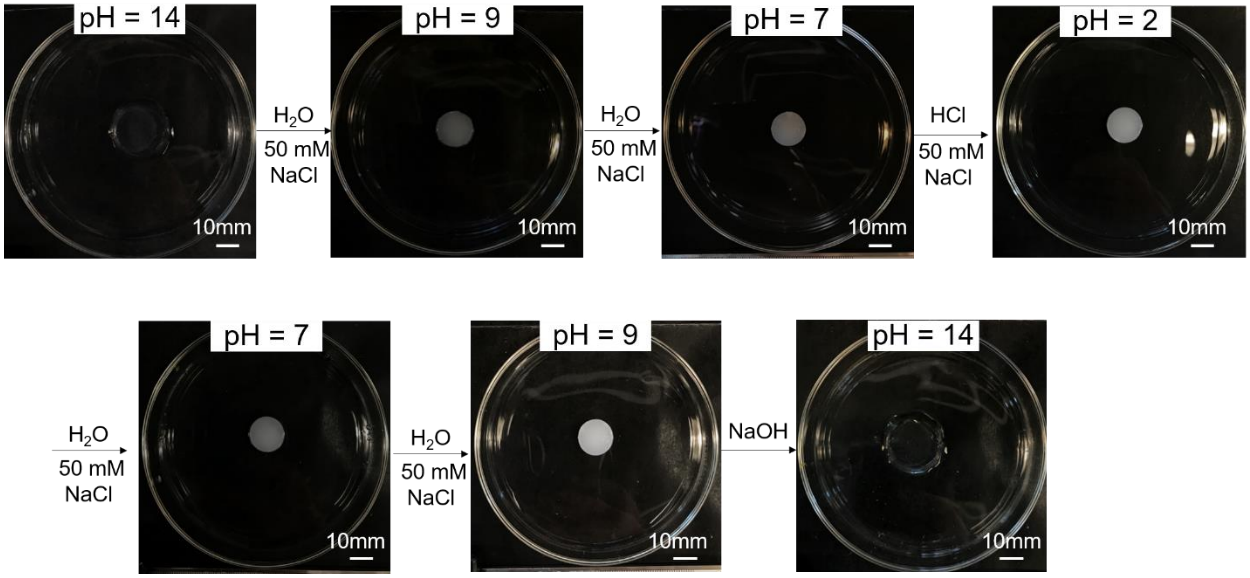


Figure S23. Images of PM hydrogel disks at different pH in the presence of 50 mM NaCl.

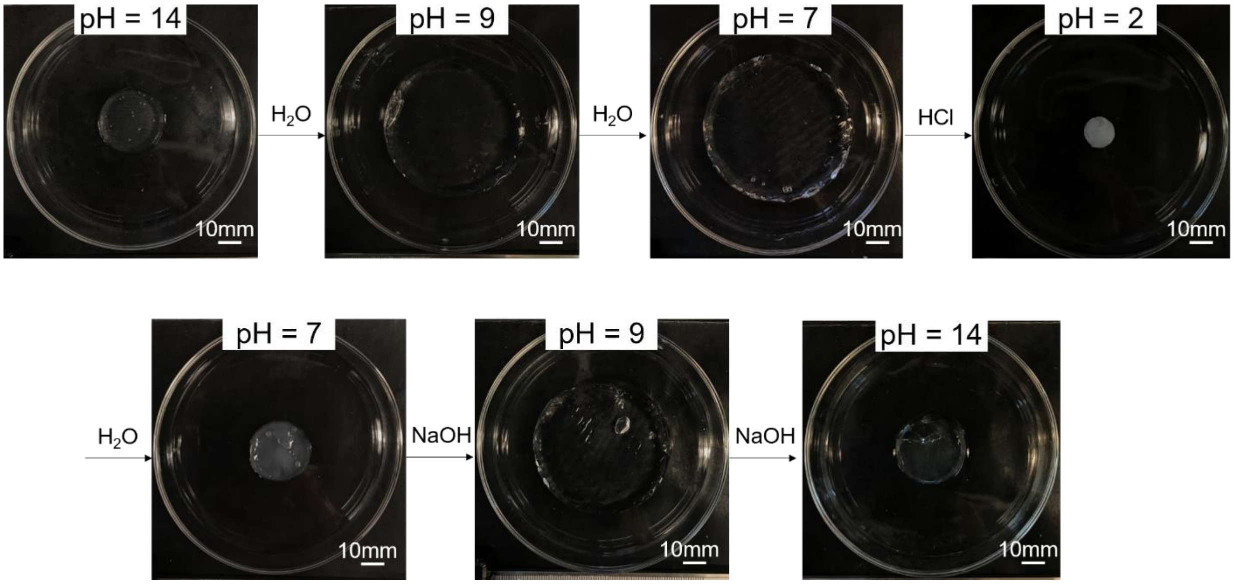


Figure S24. Images of PM-PA hydrogel disks at different pH.

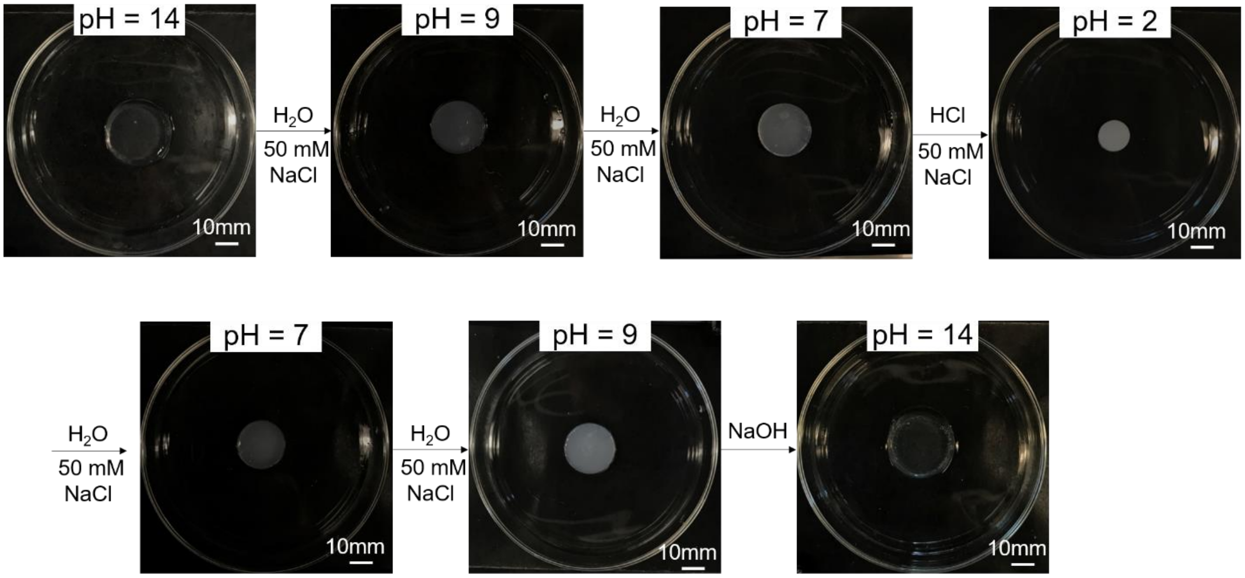


Figure S25. Images of PM-PA hydrogel disks at different pH in the presence of 50 mM NaCl.

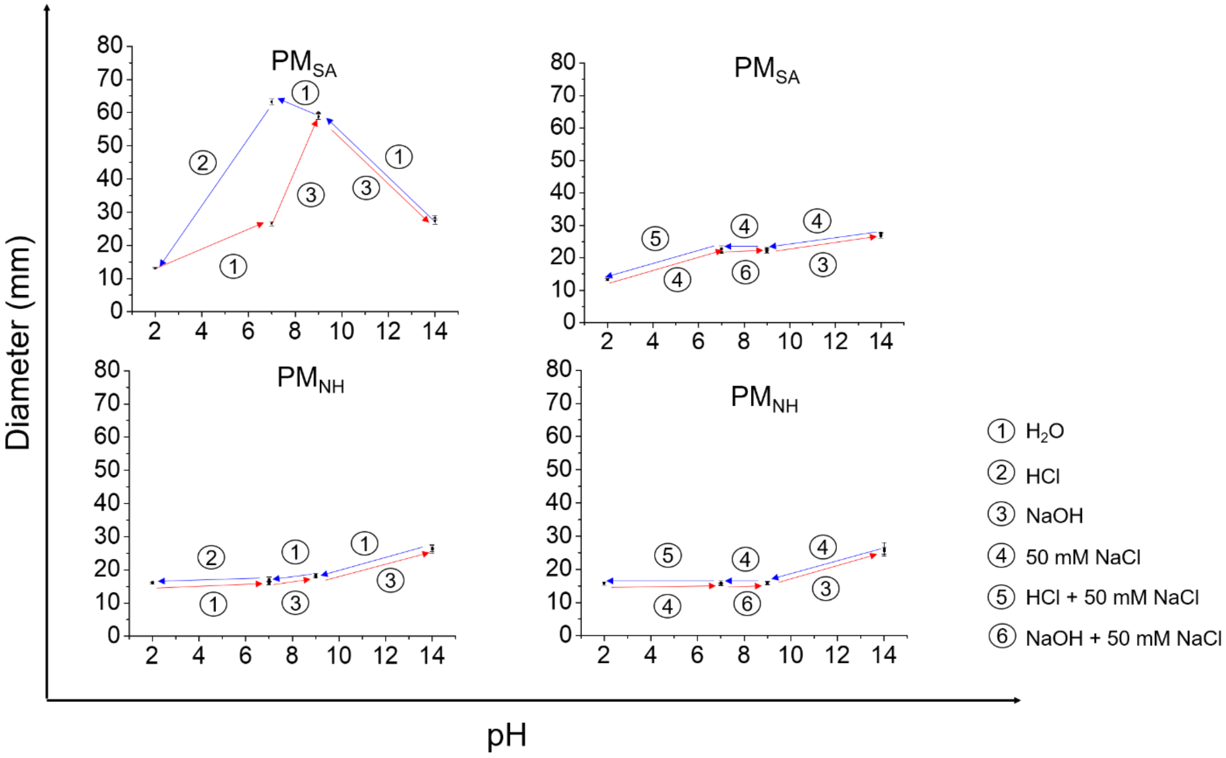


Figure S26. Averaged diameters of PM and PM-PA hydrogel disks at different pH.