

Supporting Information for

**3D-Printed Ketoenamine Crosslinked Polyrotaxane Hydrogels
and Their Mechanochromic Responsiveness**

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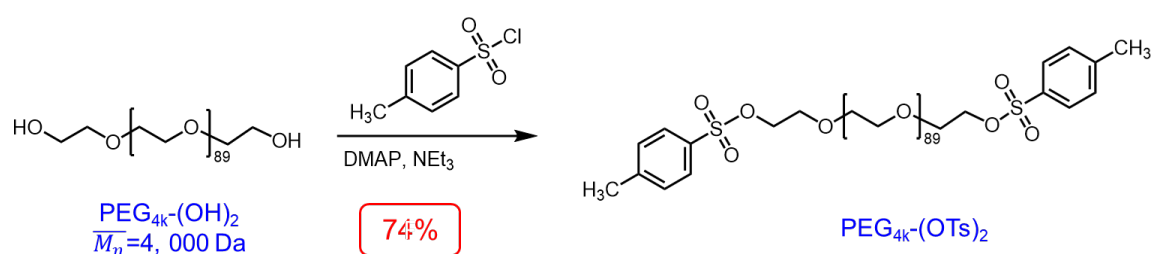
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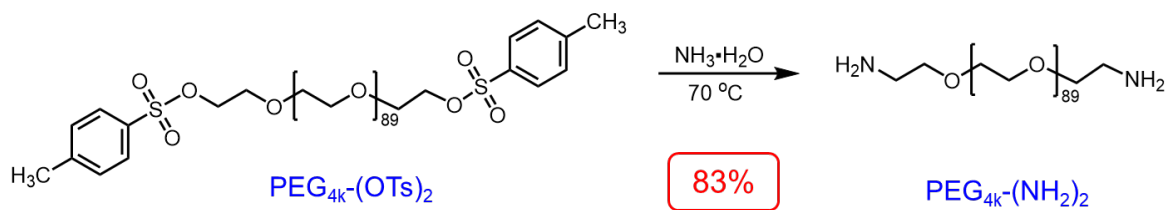
S1. General information

Chemicals were commercially available and used directly without any further purification unless otherwise noted. α -Cyclodextrin (α -CD) was generously provided by Wacker Chemical Corporation. 1,3,5-triformylphloroglucinol (TP)^{S1}, 2,5,8,11-tetraoxatridecan-13-amine (MeO-TEG-NH₂)², TEG-(NH₂)₂^{S2} and PEG_{4k}-(NH₂)₂^{S3} were synthesized according to previously reported methods. Nuclear magnetic resonance (NMR) spectra were obtained on Bruker Avance III™ HD 500/600 MHz spectrometers, with the working frequencies of 500/600 MHz for ¹H and 125/150 MHz for ¹³C nuclei. Unless otherwise specified, chemical shifts in ppm relative to solvent residual signals were referenced as follows: (¹H) CDCl₃, 7.26 ppm; (¹H) D₂O, 4.79 ppm; (¹H) DMSO-*d*₆, 2.50 ppm. Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku MiniFlex X-ray diffractometer with a 600 W (40 kV, 15 mA) CuK α ($\alpha = 1.54 \text{ \AA}$) radiation source. Fourier transform infrared (FT-IR) spectra were recorded on a Jasco 6200 spectrometer. Fluorescence spectra were recorded on Horriba QuantaMaster Fluorescence System, and UV-Vis spectra were recorded on a Shimadzu UV-1800 UV-Vis spectrometer. A consumer-grade camera recorded optical images.

S2. Synthetic methods



PEG_{4k}-(OTs)₂: α,ω -dihydroxyl-polyethylene glycol (PEG_{4k}-(OH)₂, $\overline{M}_n = 4,000$ Da) was refluxed in toluene by a Dean-Stark apparatus to remove the remaining water azeotropically. In a 250-mL round bottom flask, anhydrous PEG_{4k}-(OH)₂ (10 g, 2.5 mmol) was dissolved in CH₂Cl₂ (60 mL) in an ice bath before 4-dimethylaminopyridine (DMAP, 61 mg, 0.5 mmol) and triethylamine (NEt₃, 1.60 mL, 12.5 mmol) were added. The solution of 4-toluenesulfonyl chloride (TsCl, 4.77 g, 25 mmol) in CH₂Cl₂ (30 mL) was then added dropwise within 10 min. The solution was allowed to warm up to room temperature and stirred overnight. The reaction solution was washed with saturated NaCl aqueous solution three times, and the organic layer was collected and dried over Na₂SO₄ powder. White crude was obtained after the solvent was removed under reduced pressure. The crude product was then re-dissolved in CH₂Cl₂ and precipitated in an excess of diethyl ether. The product was collected by filtration and dried at 40 °C under vacuum for 24 h, affording PEG_{4k}-(OTs)₂ as a white powder (8.05 g, 74 % yield). ¹H NMR (500 MHz, CDCl₃, ppm) $\delta = 7.80$ (d, $J = 8.4$ Hz, 4H), 7.34 (d, $J = 8.2$ Hz, 4H), 4.18 – 4.12 (m, 4H), 3.64 (s, 364H), 2.45 (s, 6H).



PEG_{4k}-(NH₂)₂: PEG_{4k}-(OTs)₂ (7.50 g, 1.74 mmol) was dissolved in ammonium hydroxide solution (5 wt%, 70 mL) in a 250-mL round bottom flask. The mixture was then stirred at 70 °C for 24 h. After cooling the reaction, the solution was extracted by CH₂Cl₂ (50 mL × 3). The organic layer was collected and washed with saturated NaCl solution three times. The crude product was obtained after the solvent was removed under reduced pressure, which was subsequently re-dissolved in CH₂Cl₂ and precipitated in an excess of diethyl ether. The product was collected by filtration and dried at 40 °C under vacuum for 24 h, affording PEG_{4k}-(NH₂)₂ as a white powder (5.80 g, 83% yield). ¹H NMR (500 MHz, CDCl₃, ppm) δ = 3.52 – 3.79 (m, 364H).

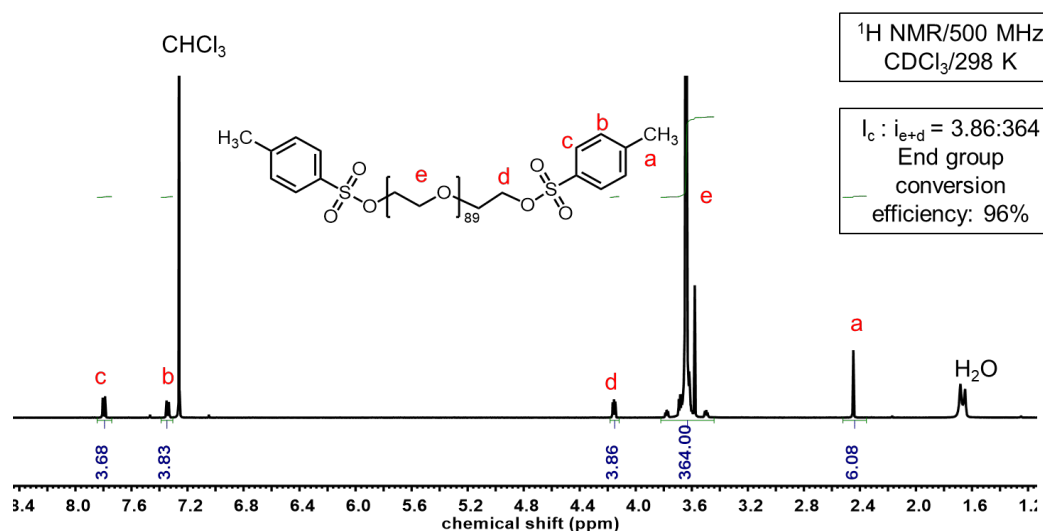


Figure S1. ¹H NMR spectrum of PEG_{4k}-(OTs)₂ (CDCl₃, 500 MHz, 298 K).

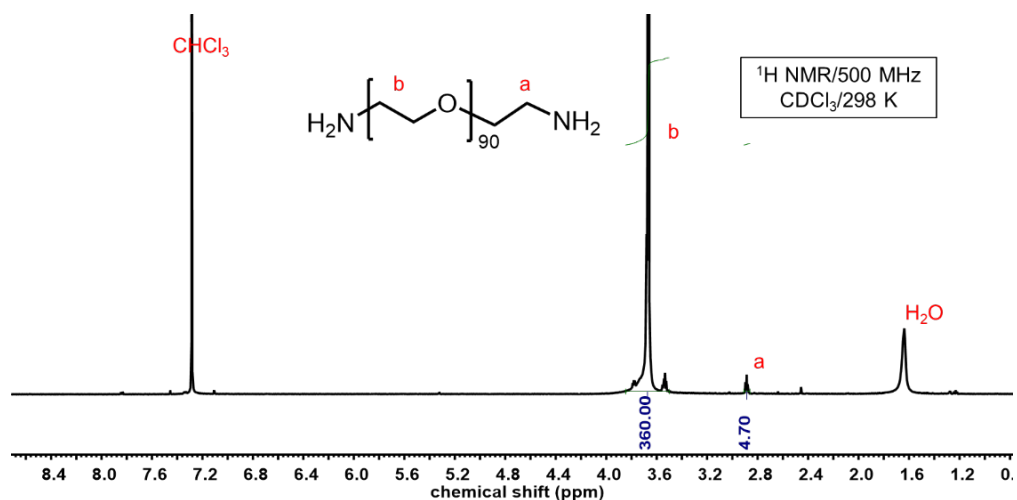


Figure S2. ¹H NMR spectrum of PEG_{4k}-(NH₂)₂ (CDCl₃, 500 MHz, 298 K).

S3. Dynamic behavior investigation of crosslinker

To investigate the semi-reversible behavior of **TP** reacting with PEG_{4k}-(NH₂)₂, temperature-varied time-dependent ¹H NMR experiments were performed on the reaction of PEG_{4k}-(NH₂)₂ (75.0 mM) and **TP** (50.0 mM) at 25 °C and 60 °C. D₂O solutions of PEG_{4k}-(NH₂)₂ (75.0 mM) and **TP** (50.0 mM) were added to NMR tubes right before the acquisition. Upon heating the solution at 60 °C, the ratio of the ketoenamine protons to the aldehyde protons increased from 0.4:1.0 at room temperature to 2.6:1.0 at 60 °C after 2 h and 2.4:1.0 after cooled down.

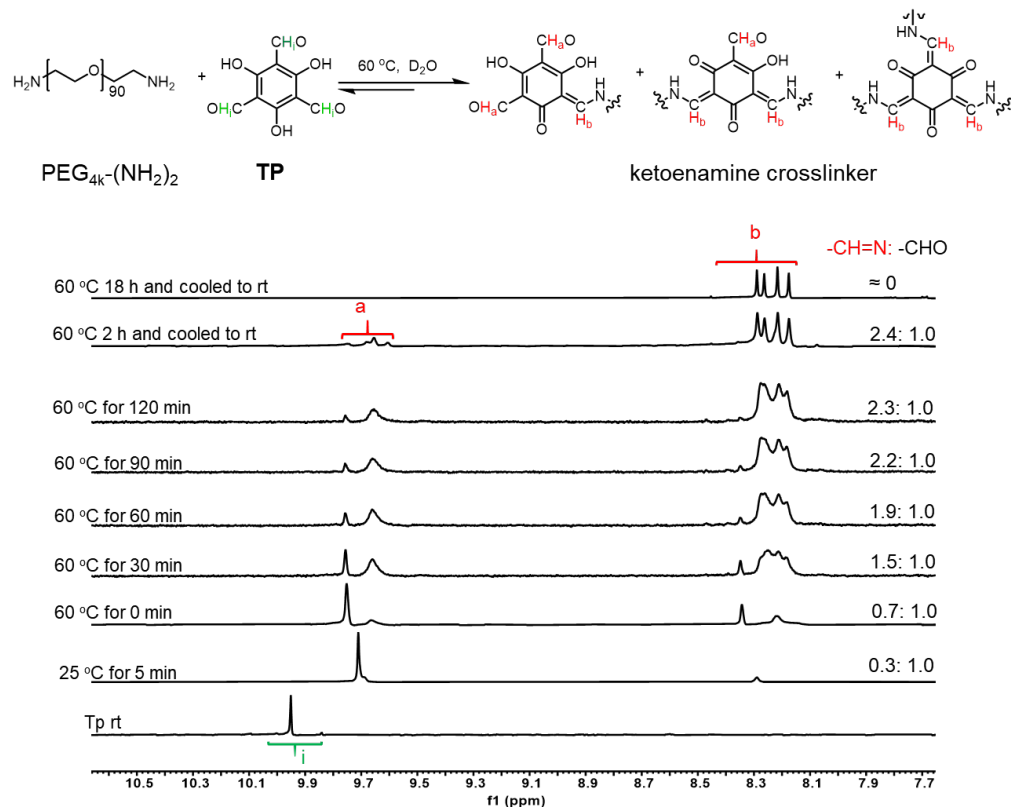


Figure S3. Time-dependent ¹H NMR spectra of PEG_{4k}-(NH₂)₂ (10.0 mM) and **TP** (6.7 mM) (500 MHz, 298 K or 333 K) in D₂O. The chemical shifts were referenced to the PEG backbone (3.72 ppm).

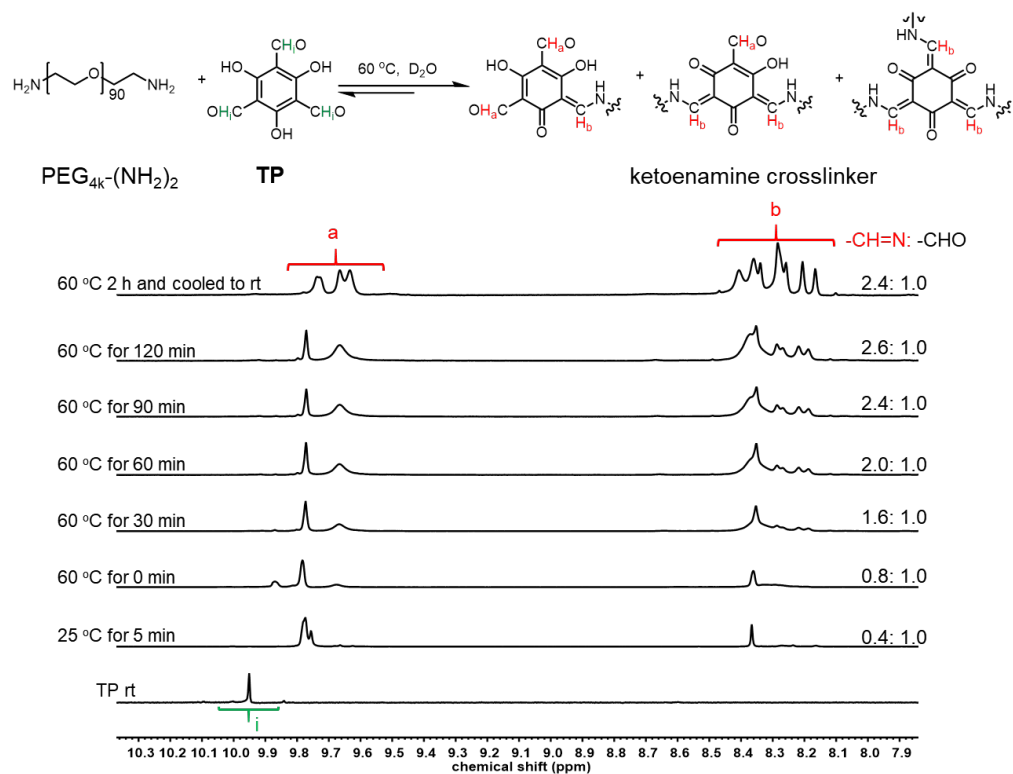


Figure S4. Time-dependent ¹H NMR spectra of PEG_{4k}-(NH₂)₂ (75.0 mM) and TP (50.0 mM) in D₂O (500 MHz, 298 K or 333 K). The chemical shifts were referenced to the PEG backbone (3.72 ppm).

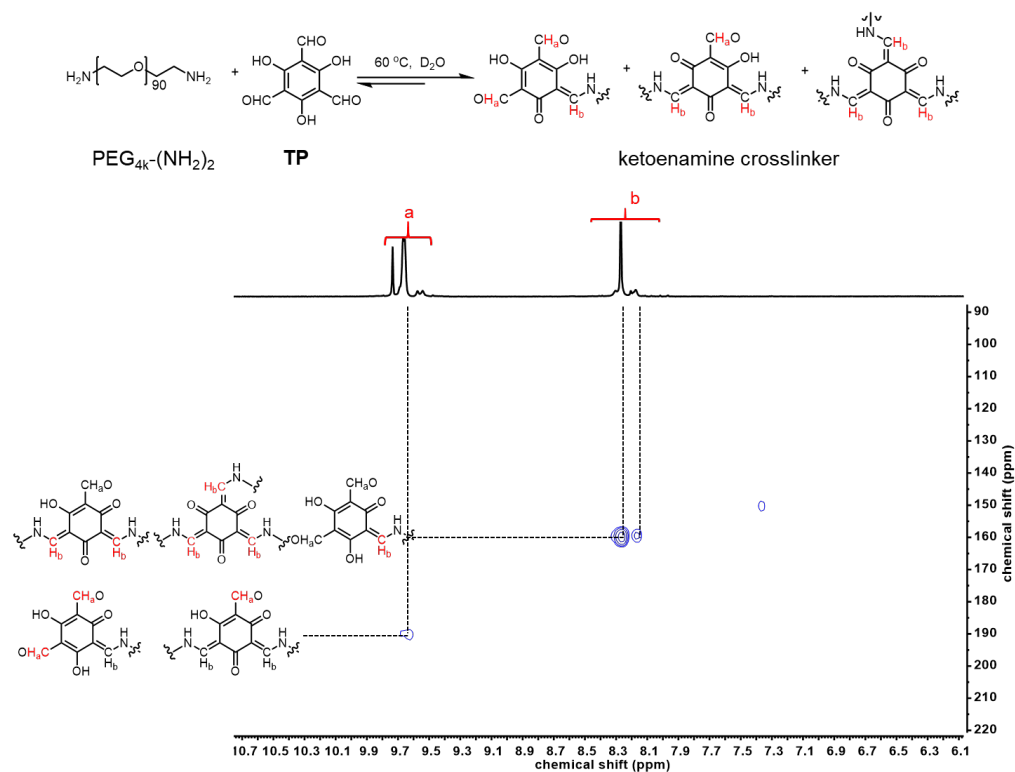


Figure S5. A partial ¹H-¹³C HSQC spectrum of the reaction of PEG_{4k}-(NH₂)₂ (50.0 mM) and TP (33.3 mM) in D₂O after mixing for 7 h at room temperature (600 MHz, 298 K).

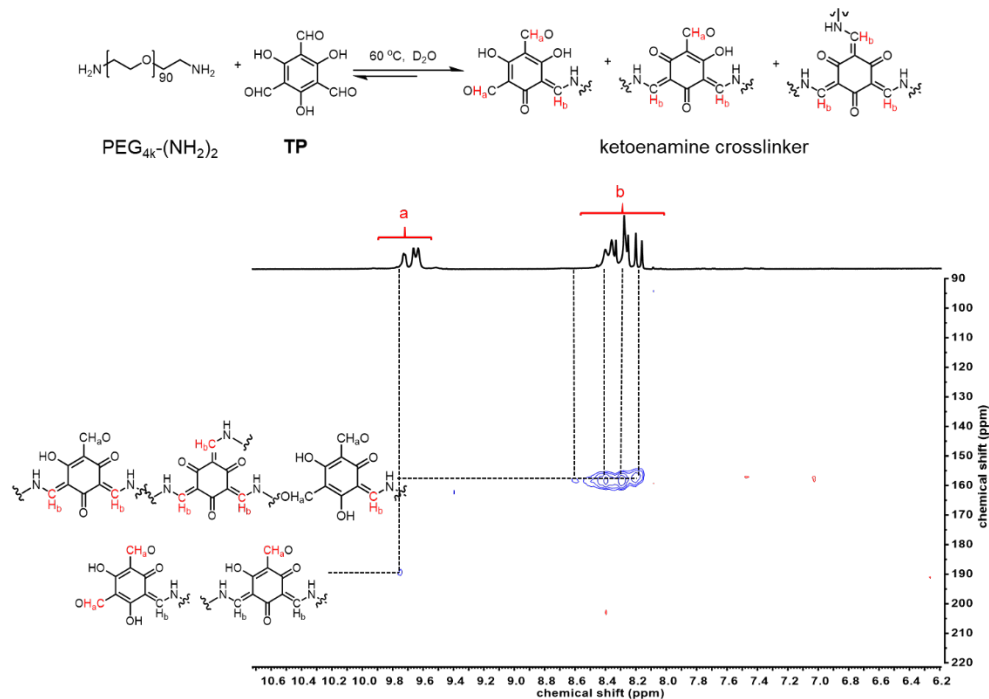


Figure S6. A partial ¹H-¹³C HSQC spectrum of the solution with PEG_{4k}-(NH₂)₂ (50.0 mM) and TP (33.3 mM) in D₂O after being heated at 60 °C for 2 h and cooled down to room temperature (600 MHz, 298 K).

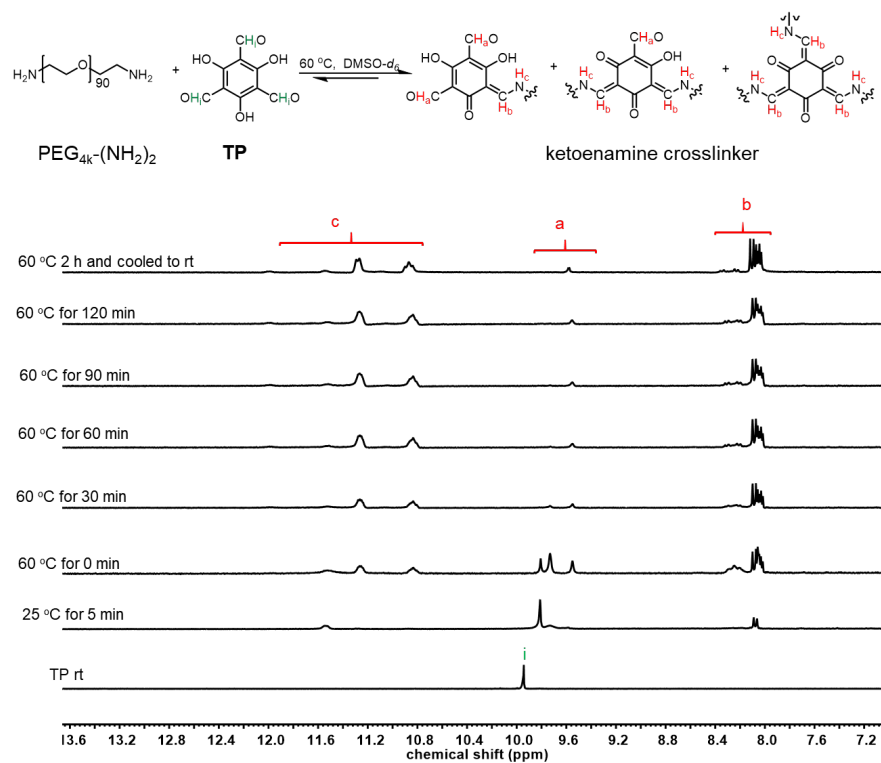


Figure S7. Time-dependent ^1H NMR spectra of $\text{PEG}_{4k}-(\text{NH}_2)_2$ (10.0 mM) and TP (6.7 mM) in $\text{DMSO}-d_6$ (500 MHz, 298 K or 333 K).

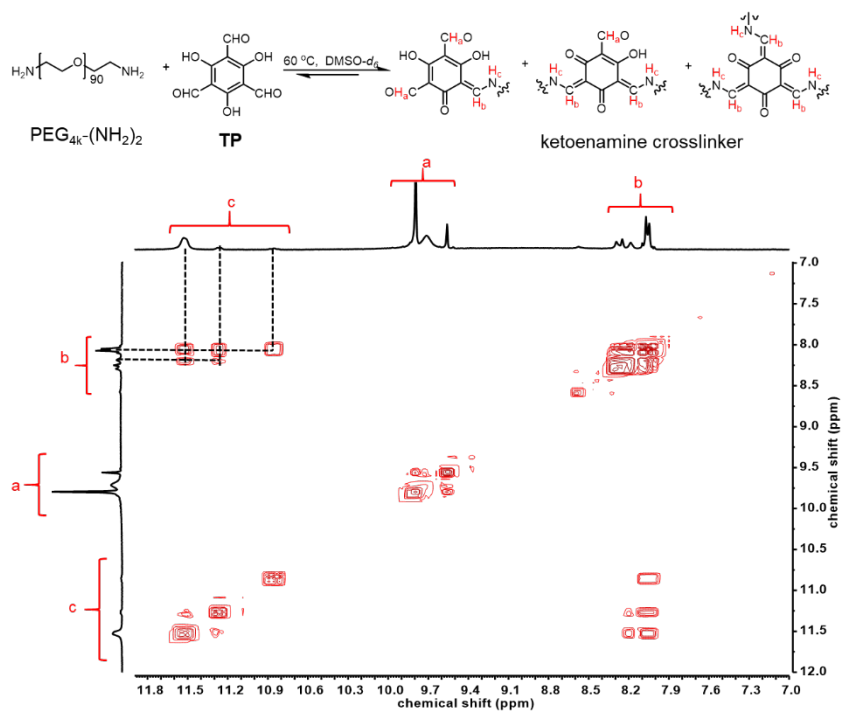


Figure S8. A partial $^1\text{H}-^1\text{H}$ COSY spectrum of the solution of $\text{PEG}_{4k}-(\text{NH}_2)_2$ (50.0 mM) and TP (33.3 mM) in $\text{DMSO}-d_6$ at room temperature before heating (500 MHz, 298 K).

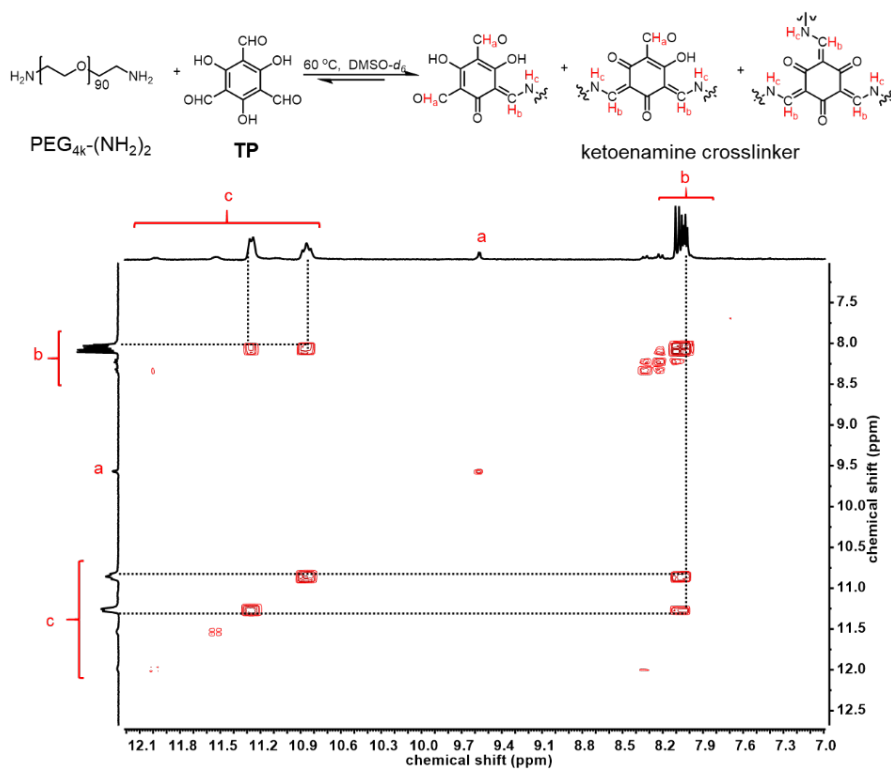


Figure S9. A partial ^1H - ^1H COSY spectrum of the solution of $\text{PEG}_{4k}-(\text{NH}_2)_2$ (10.0 mM) and TP (6.7 mM) in $\text{DMSO-}d_6$ after being heated at 60 °C for 2 h and cooled down to room temperature (500 MHz, 298 K).

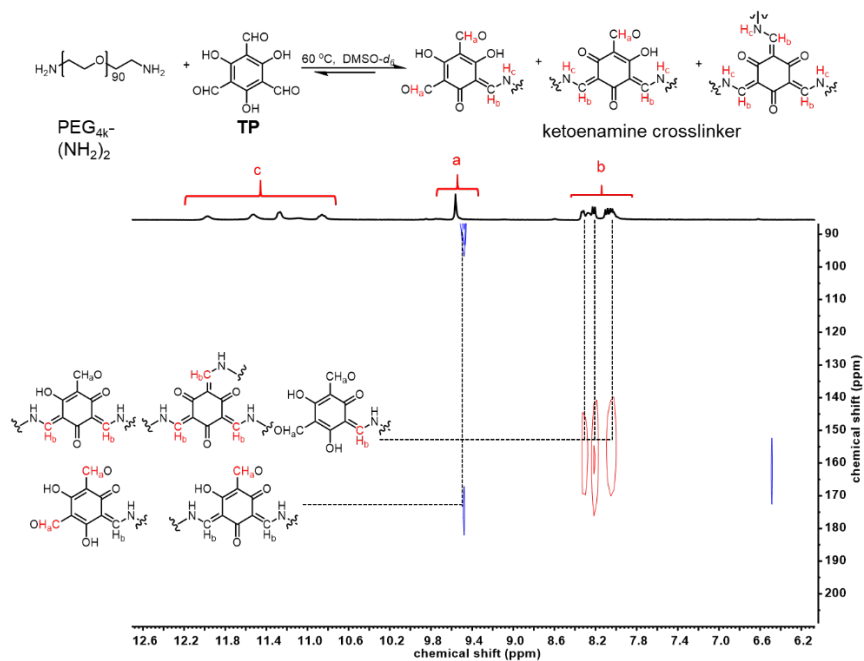


Figure S10. A partial ^1H - ^{13}C HSQC spectrum of the solution of $\text{PEG}_{4k}-(\text{NH}_2)_2$ (50.0 mM) and TP (33.3 mM) in $\text{DMSO-}d_6$ at room temperature before being heated (600 MHz, 298 K).

Investigation of TP reacting with TEG-(NH₂)₂: TEG-(NH₂)₂ (9.62 mg, 0.050 mmol) and TP (7.0 mg, 0.033 mol) were dissolved in 500 μ L D₂O in an NMR tube. The mixture was heated at 60 °C for 18 h and yellow precipitates gradually formed from the solution. After the D₂O was removed completely under vacuum, DMSO-*d*₆ was added to dissolve the product for ¹H NMR studies. ¹H NMR (500 MHz, DMSO-*d*₆) δ = 12.13 – 10.70 (m, 1H), 8.82 – 7.30 (m, 2H), 4.28 – 3.40 (m, 15H).

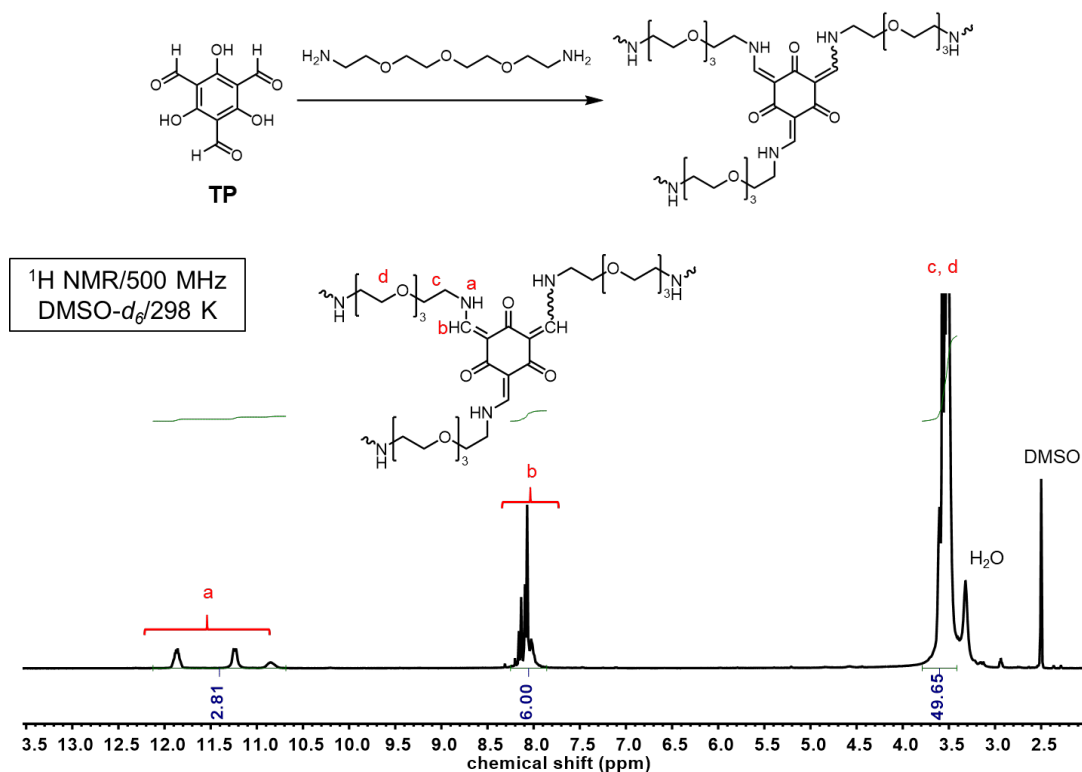
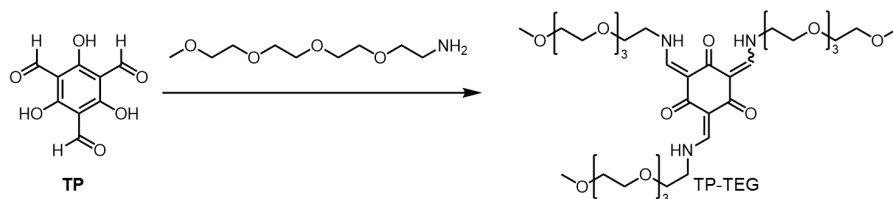


Figure S11. ¹H NMR spectrum of the reaction of TP and TEG-(NH₂)₂ mixed in DMSO-*d*₆ after 18 h (500 MHz, 298 K).



TP-TEG: In a 50-mL round bottom flask, TP (52.5 mg, 0.25 mmol) and MeO-TEG-NH₂ (300 mg, 1.34 mmol) were dissolved in 15 mL ethanol and refluxed overnight. When cooled down, the solvent was removed under reduced pressure as orange oil. The crude was dissolved in CH₂Cl₂ and washed with water three times. The organic layer was dried over Na₂SO₄. Removing the solvent afforded TP-TEG as an oil. Yield: 89%. ¹H NMR (600 MHz, DMSO-*d*₆) δ = 11.25 (dd, *J* = 13.6, 7.0 Hz, 1H), 8.16 – 7.98 (m, 1H), 3.69 – 3.45 (m, 15H), 3.41 (p, *J* = 2.8 Hz, 2H), 3.24 (s, 3H).

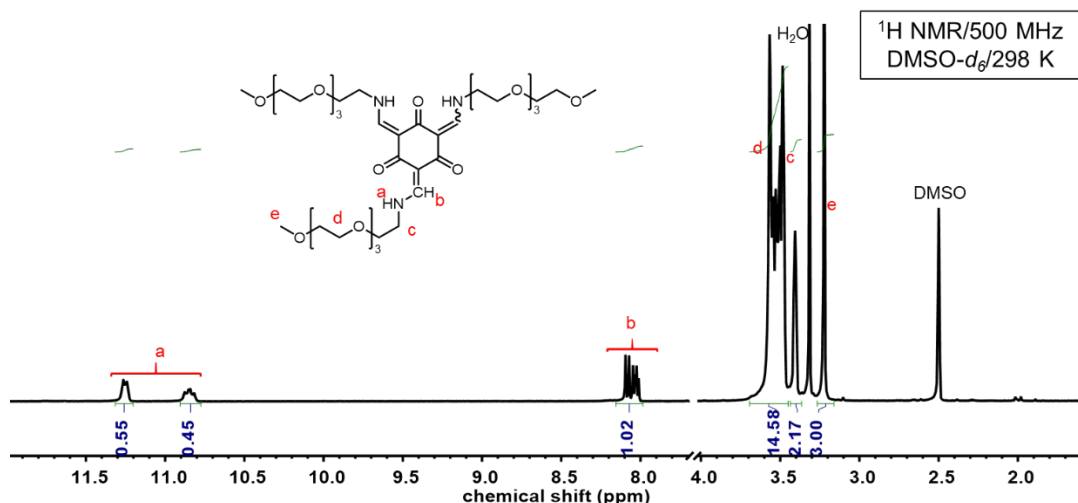


Figure S12. ^1H NMR spectrum of the TP-TEG (DMSO- d_6 , 500 MHz, 298 K).

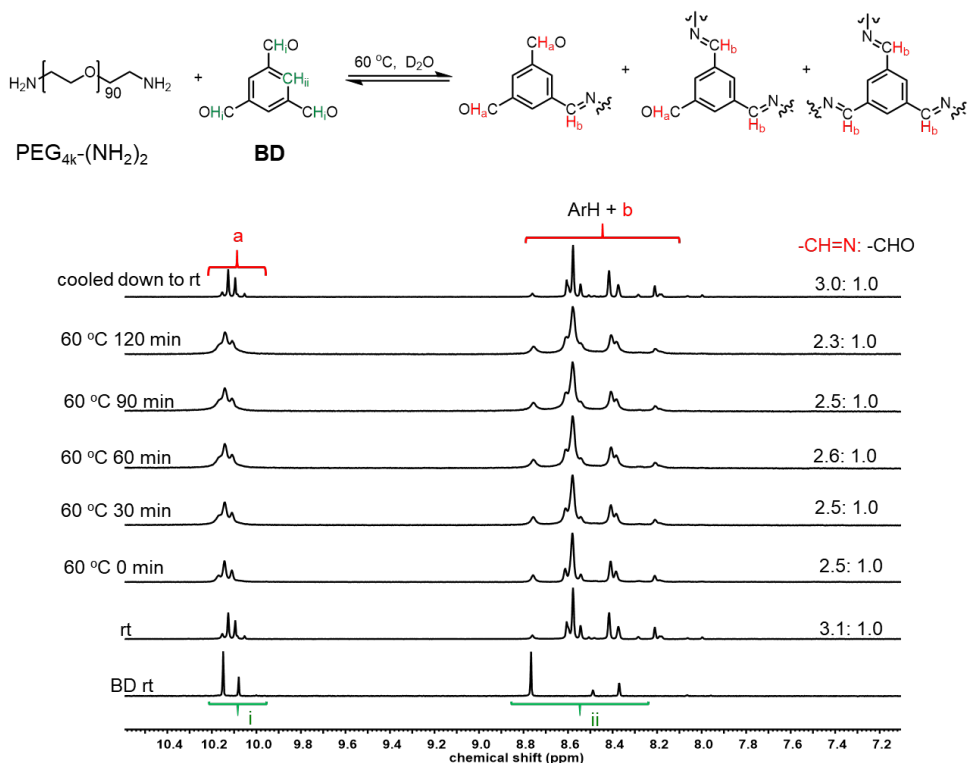


Figure S13. Time-dependent ^1H NMR spectra of PEG $_{4k}$ -(NH $_2$) $_2$ (50.0 mM) and **BD** (33.3 mM) (500 MHz, 298 K or 333 K) in D $_2$ O. The chemical shifts were referenced to the PEG backbone (3.72 ppm).

To investigate the dynamic behavior of **BD** reacting with PEG $_{4k}$ -(NH $_2$) $_2$, temperature-varied time-dependent ^1H NMR experiments were performed on the reaction of PEG $_{4k}$ -(NH $_2$) $_2$ (50.0 mM) and **BD** (33.3.0 mM) at 60 °C. D $_2$ O solutions of PEG $_{4k}$ -(NH $_2$) $_2$ (50.0 mM) and **BD** (33.3 mM) were added to NMR tubes right before the acquisition. After heating the solution at 60 °C, the ratio of imine protons to aldehyde protons decreased from 3.1:1.0 at room temperature, and to 2.3:1.0 at 60

°C after 2 h, and 3.0:1.0 after cooling down, suggesting the high reversibility of the reaction between PEG_{4k}-(NH₂)₂ and **BD**.

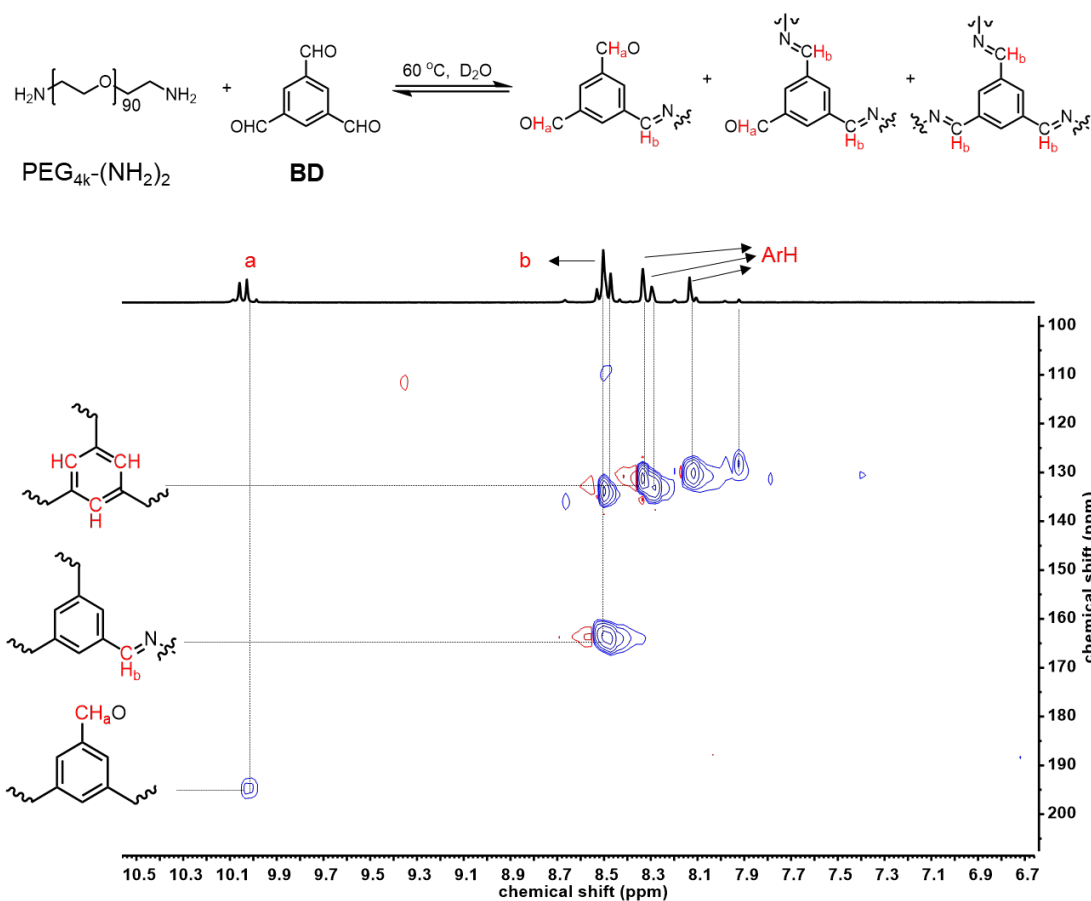


Figure S14. A partial ¹H-¹³C HSQC spectrum of PEG_{4k}-(NH₂)₂ (50.0 mM) and **BD** (33.3 mM) in D₂O after heating at 60 °C for 2 h and cooled down to room temperature (500 MHz, 298 K).

S4. Rheology Investigation

Hydrogel preparation methods: Poly(pseudo)rotaxane hydrogels (PpRHs) crosslinked with dynamic covalent crosslinkers were prepared at various concentrations of α -CDs and PEG_{4k}-(NH₂)₂ (Table S1).

A typical procedure to prepare PpRH_{TP}[3, 15] for DIW 3D-printing is described as follows: an aqueous solution of α -CD (15 wt%) was added to an aqueous solution of PEG_{4k}-(NH₂)₂ (3 wt%) in the presence of TP (5.20 mg) at room temperature. The mixture was stirred at 60 °C for 2 h. The reaction was then cooled to room temperature and an opaque hydrogel was obtained. The hydrogel was stabilized for 18 h before the rheological studies and 3D printing. Other PpRHs were prepared with the same method.

Preparation of crosslinked polyrotaxane hydrogel: The PpRHs were stored in a sealed container with a wet cloth. The container was then stored at 70 °C overnight (RH ~ 60%), followed by an additional 5 h annealing. After that, the lid of the container was left open at 70 °C to dehydrate the sample. The dehydrated hydrogel was washed with DMSO three times. The crosslinked hydrogels were obtained after a solvent exchange process in Na₂SO₄ (1 M) aqueous solution for 48 h.

Rheological measurements were performed on a stress-controlled rheometer (TA instruments, DHR-2) with a 20-mm diameter parallel plate geometry and a measuring gap of 1 mm at room temperature. All PpRHs were stabilized for at least 18 h at room temperature before the analysis unless otherwise specified. Strain sweep: oscillation strain sweep tests were performed to investigate the linear viscoelastic regions of the obtained PpRHs at 25 °C. The oscillation strain was increased from 0.01% to 100%. The angular frequency was set at 1 rad/s (0.16 Hz). Angular frequency sweep test: angular frequency sweep tests were performed to investigate the elastic (storage) and viscous (loss) moduli at 25 °C. The angular frequency was increased from 0.1 rad/s to 100 rad/s (frequency increased from 0.016 Hz to 15.92 Hz). The oscillation strain was set at 0.1 %. Dynamic step-strain amplitude test: dynamic step-strain amplitude tests were performed to investigate the self-healing properties of the PpRHs. The oscillation strain applied was 1% and 100% in each cycle at 1 rad/s angular frequency. The duration of strain at each step was 15 s. Steady rate sweep test: steady rate sweep tests were carried out to investigate the shear-thinning behaviors of the PpRHs at 25 °C. The shear rate was increased from 1 s⁻¹ to 100 s⁻¹.

Table S1. The summary of the preparation of TP crosslinked PpRH_{TP} hydrogels.

| PEG _{4k} -(NH ₂) ₂ | | α -CD | | TP | | Reaction time at 60 °C | Fed EG:CD |
|--|------|--------------|-----|-------|------|------------------------|-----------|
| wt% | mM | wt% | mM | wt% | mM | h | |
| 2.0 | 5.0 | 25.0 | 257 | 0.08 | 3.5 | 2 | 1.8:1 |
| | | 20.0 | 206 | | | | 2.2:1 |
| | | 15.0 | 154 | | | | 3.0:1 |
| 3 | 7.5 | 15.0 | 154 | 0 | 0 | 2 | 4.4:1 |
| 3 | 7.5 | 25.0 | 257 | 0.105 | 5.0 | 2 | 2.7:1 |
| | | 20.0 | 205 | | | 2 | 3.3:1 |
| | | 15.0 | 154 | | | 2 | 4.4:1 |
| | | 15.0 | 154 | | | 18 | 4.4:1 |
| | | 10.0 | 103 | | | 2 | 6.6:1 |
| | | 8.3 | 85 | | | 2 ^a | 8.0:1 |
| 4 | 10.0 | 25.0 | 257 | 0.14 | 6.7 | 2 | 3.5:1 |
| | | 20.0 | 206 | | | 2 | 4.4:1 |
| | | 20.0 | 206 | | | 18 | 4.4:1 |
| | | 15.0 | 154 | | | 2 | 6.0:1 |
| | | 11.0 | 113 | | | 2 | 8.0:1 |
| | | 10.0 | 103 | | | 2 | 8.8:1 |
| 6 | 15.0 | 30.0 | 308 | 0.21 | 10.0 | 2 | 4.4:1 |
| | | 30.0 | 308 | | | 18 | 4.4:1 |
| | | 25.0 | 257 | | | 2 | 5.3:1 |
| | | 20.0 | 206 | | | 2 | 8.8:1 |
| | | 16.6 | 171 | | | 2 | 8.0:1 |
| | | 15.0 | 113 | | | 2 | 12.1:1 |
| | | 10.0 | 103 | | | 2 | 13.3:1 |

^a It took 4 d for this sample to form a gel.

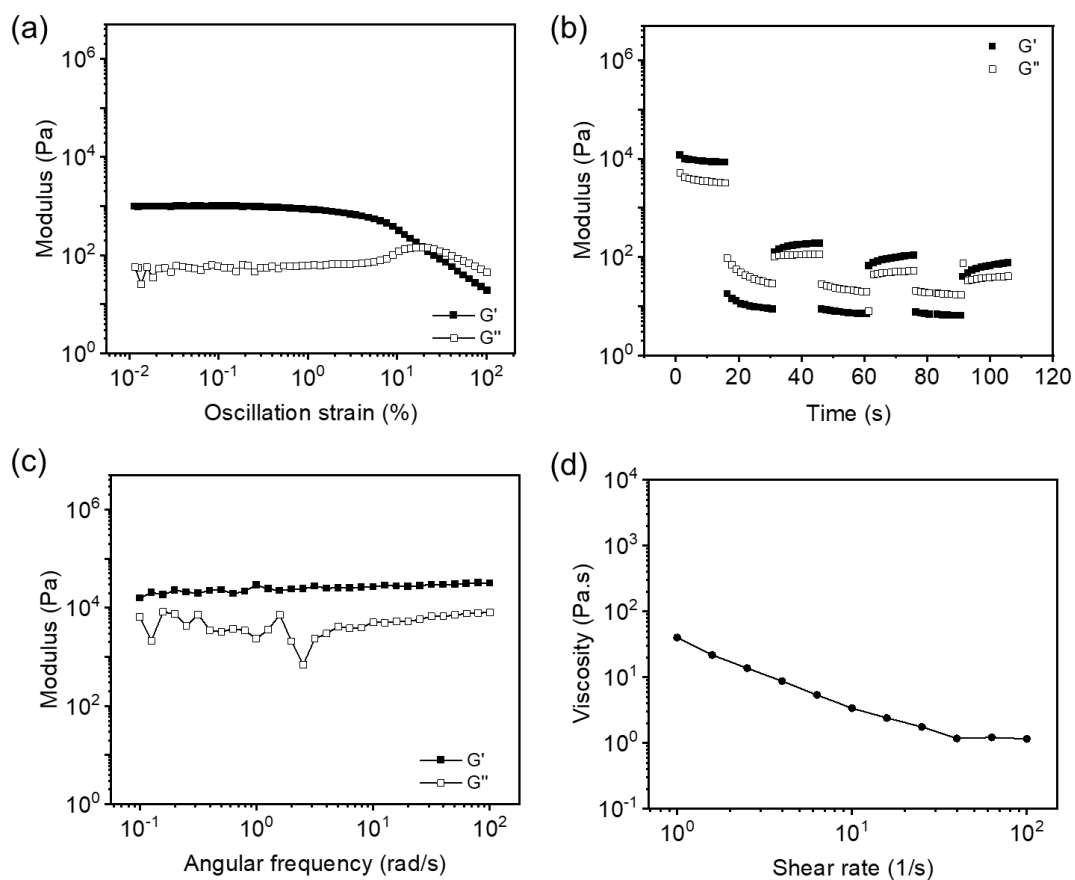


Figure S15. Rheological analysis of PpRH[3, 15] prepared with PEG_{4k}-(OH)₂ and α -CD at 25 °C. (a) Oscillation strain sweep of the hydrogel at the oscillation strain from 0.01% to 100%. (b) Dynamic step-strain amplitude sweep of the hydrogels. The applied oscillation strain was alternated between 1% and 100% every 15 s at 1 rad/s angular frequency. (c) Angular frequency sweep of the hydrogels at the angular frequency from 0.1 rad/s to 100 rad/s. (d) Steady rate sweep of the hydrogels at the shear rate from 1 s⁻¹ to 100 s⁻¹.

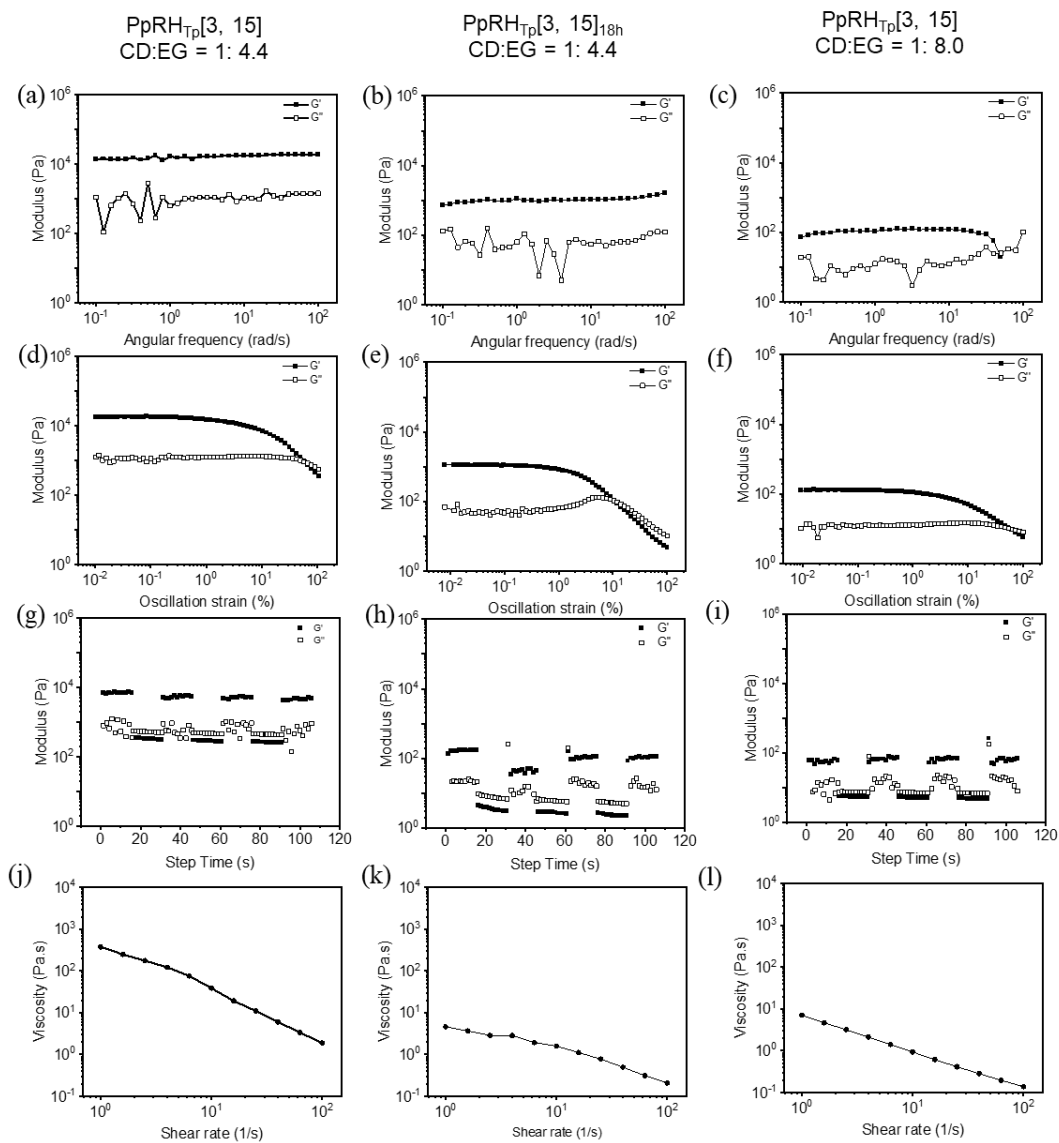


Figure S16. Rheological analysis of PpRH_{TP}[3, 15], PpRH_{TP}[3, 15]_{18 h} and PpRH_{TP}[3, 8.3] at 25 °C. (a-c) Oscillation strain sweeps of the hydrogels at the oscillation strain from 0.01% to 100%. (d-f) Angular frequency sweeps of the hydrogels at the angular frequency from 0.1 rad/s to 100 rad/s. (g-i) Dynamic step-strain amplitude sweeps of the hydrogels. The applied oscillation strain was alternated between 1% and 100% every 15 s at 1 rad/s angular frequency. (j-l) Steady rate sweeps of the hydrogels at the shear rate from 1 s⁻¹ to 100 s⁻¹.

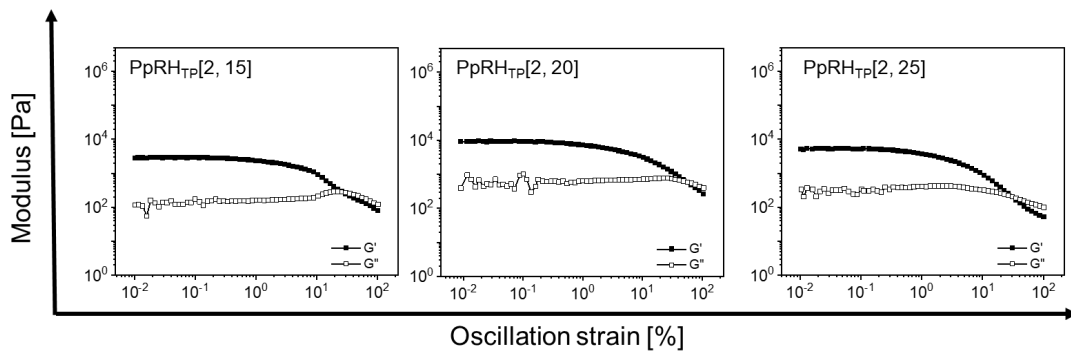


Figure S17. Oscillation strain sweep profiles of PpRH_{TP}[2, x] (x = 15, 20, 25).

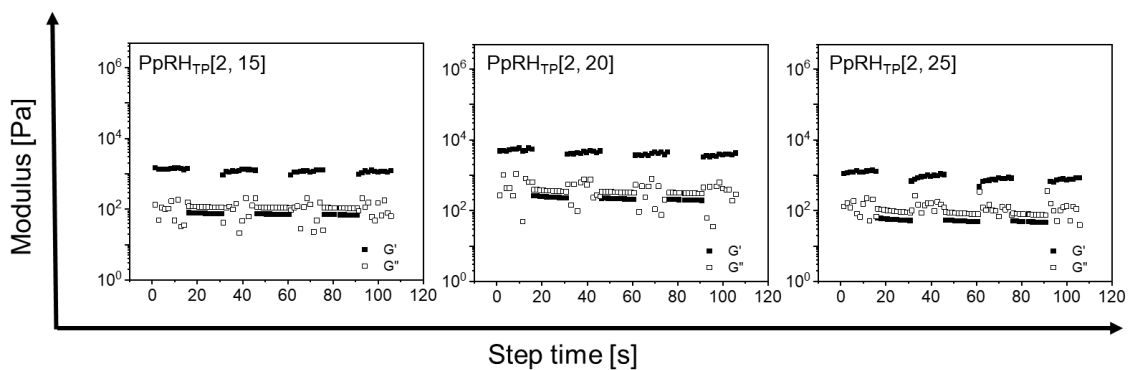


Figure S18. Dynamic step-strain amplitude test profiles of PpRH_{TP}[2, x] (x = 15, 20, 25).

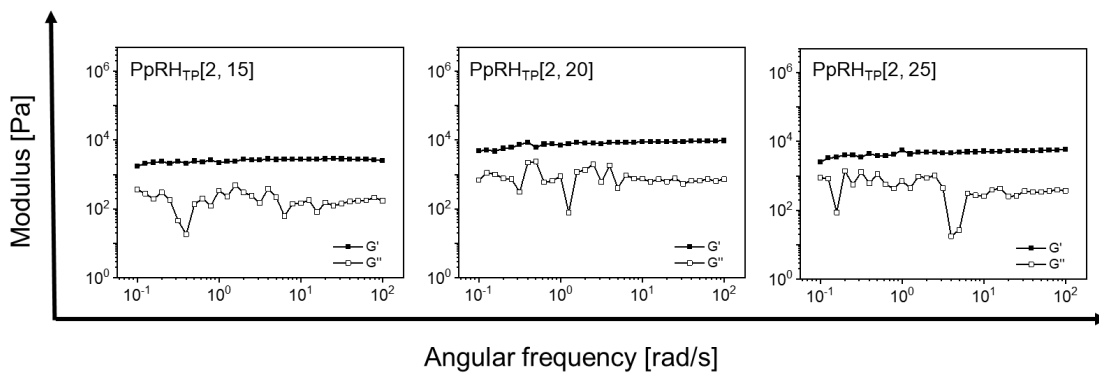


Figure S19. Angular frequency sweep profiles of PpRH_{TP}[2, x] (x = 15, 20, 25).

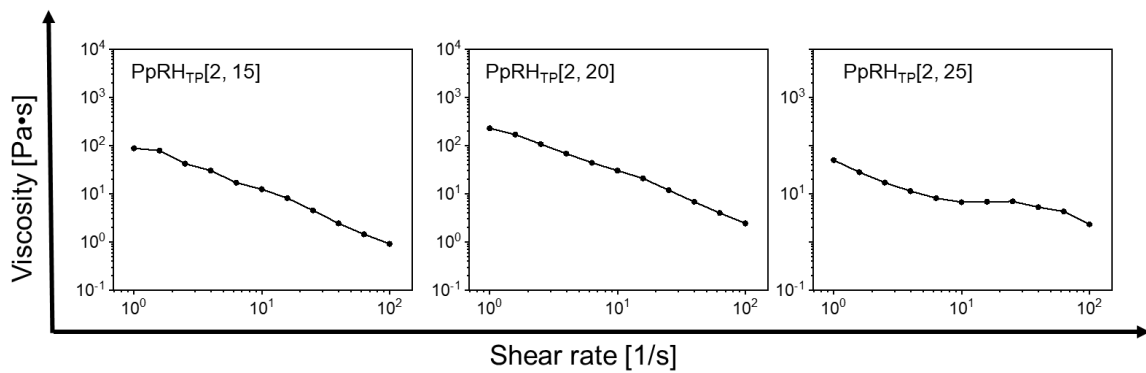


Figure S20. Steady shear rate sweep profiles of PpRH_{TP}[2, x] (x = 15, 20, 25).

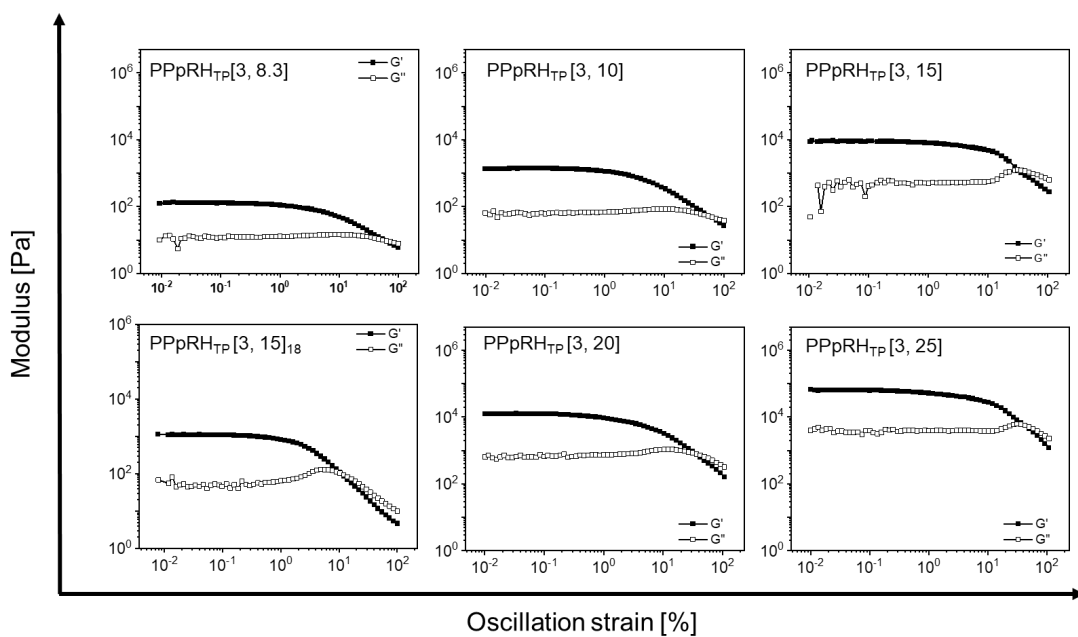


Figure S21. Oscillation strain sweep profiles of PpRH_{TP}[3, x] (x = 8.3, 10, 15, 20, 25). PpRH_{TP}[3, 15] was heated for 2 h and PpRH_{TP}[3, 15]₁₈ was heated for 18 h.

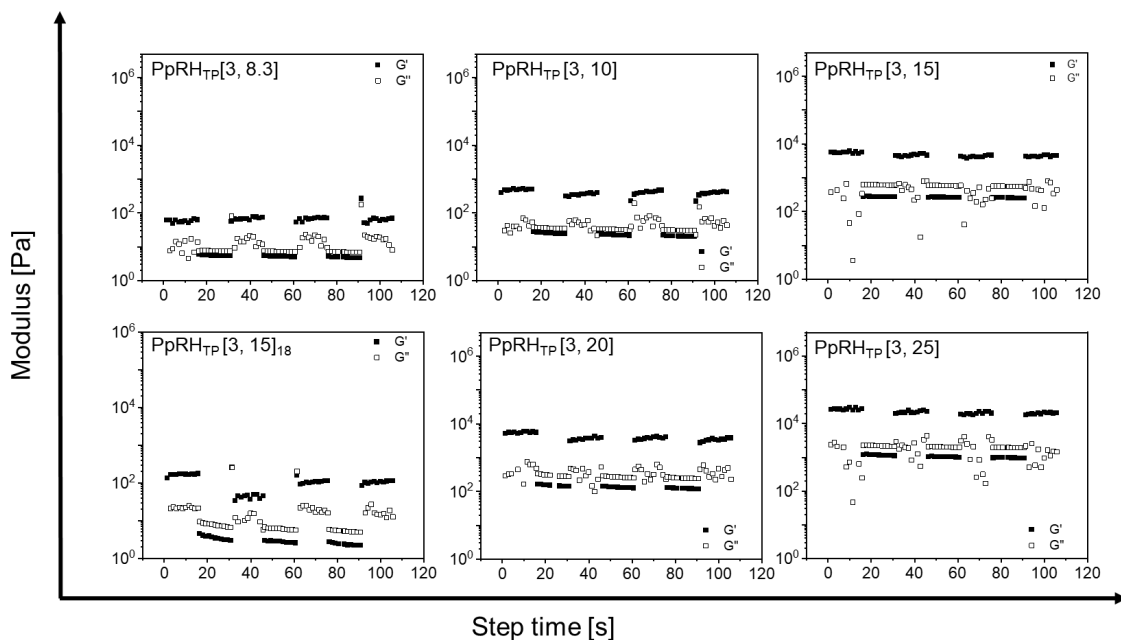


Figure S22. Dynamic step-strain amplitude test profiles of PpRH_{TP}[3, x] (x = 8.3, 10, 15, 20, 25). PpRH_{TP}[3, 15] was heated for 2 h and PpRH_{TP}[3, 15]₁₈ was heated for 18 h.

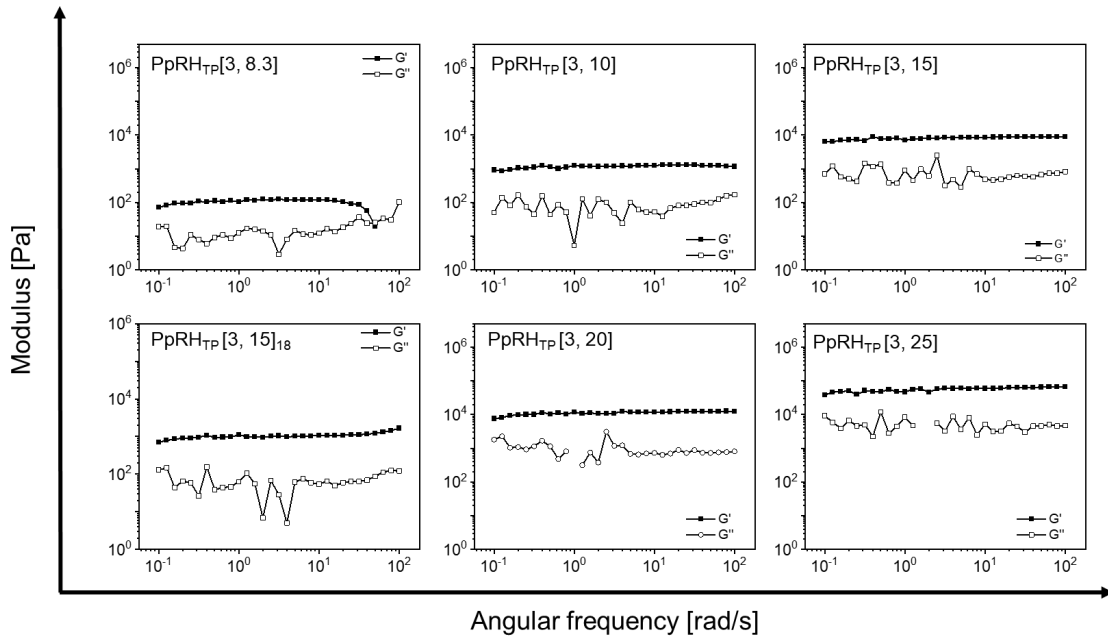


Figure S23. Angular frequency sweep profiles of PpRH_{TP}[3, x] (x = 8.3, 10, 15, 20, 25). PpRH_{TP}[3, 15] was heated for 2 h and PpRH_{TP}[3, 15]₁₈ was heated for 18 h.

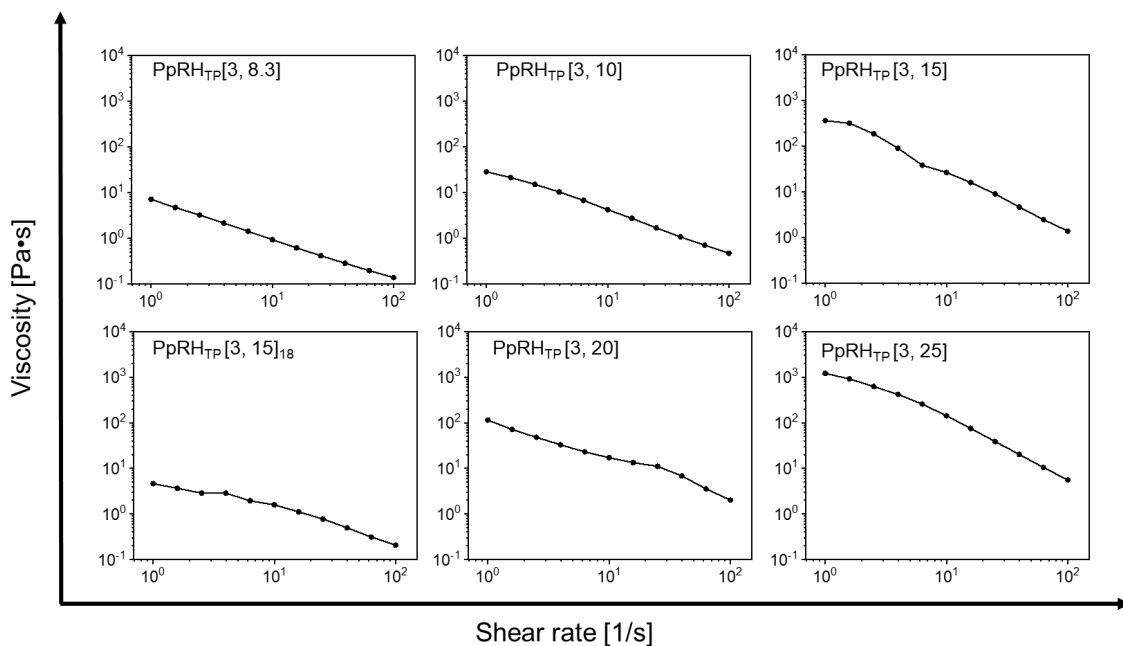


Figure S24. Steady shear rate sweep profiles of PpRH_{TP}[3, x] (x = 8.3, 10, 15, 20, 25). PpRH_{TP}[3, 15] was heated for 2 h and PpRH_{TP}[3, 15]₁₈ was heated for 18 h.

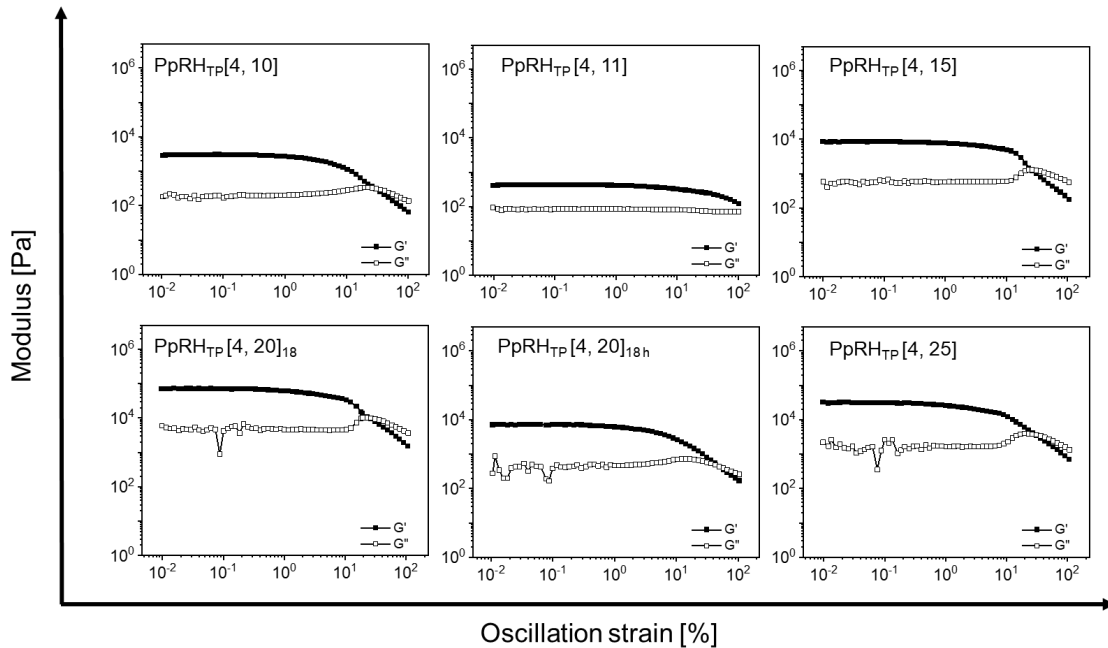


Figure S25. Oscillation strain sweep profiles of PpRH_{TP}[4, x] (x = 10, 11, 15, 20, 25). PpRH_{TP}[4, 20] was heated for 2 h and PpRH_{TP}[4, 20]₁₈ was heated for 18 h.

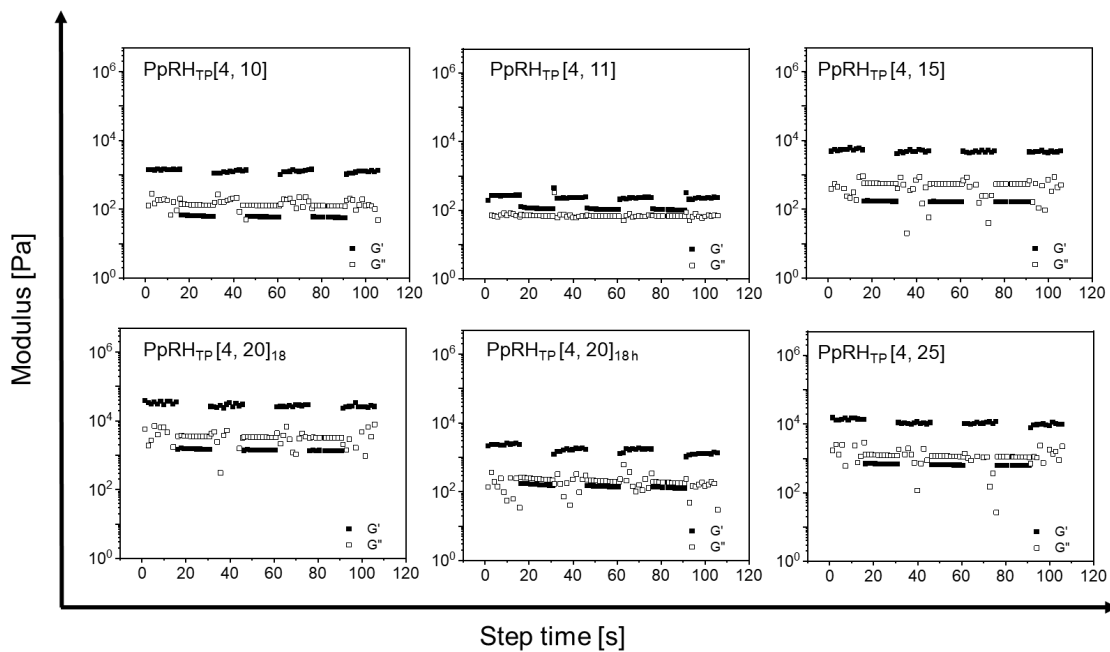


Figure S26. Dynamic step-strain amplitude test profiles of PpRH_{TP}[4, x] (x = 10, 11, 15, 20, 25). PpRH_{TP}[4, 20] was heated for 2 h and PpRH_{TP}[4, 20]₁₈ was heated for 18 h.

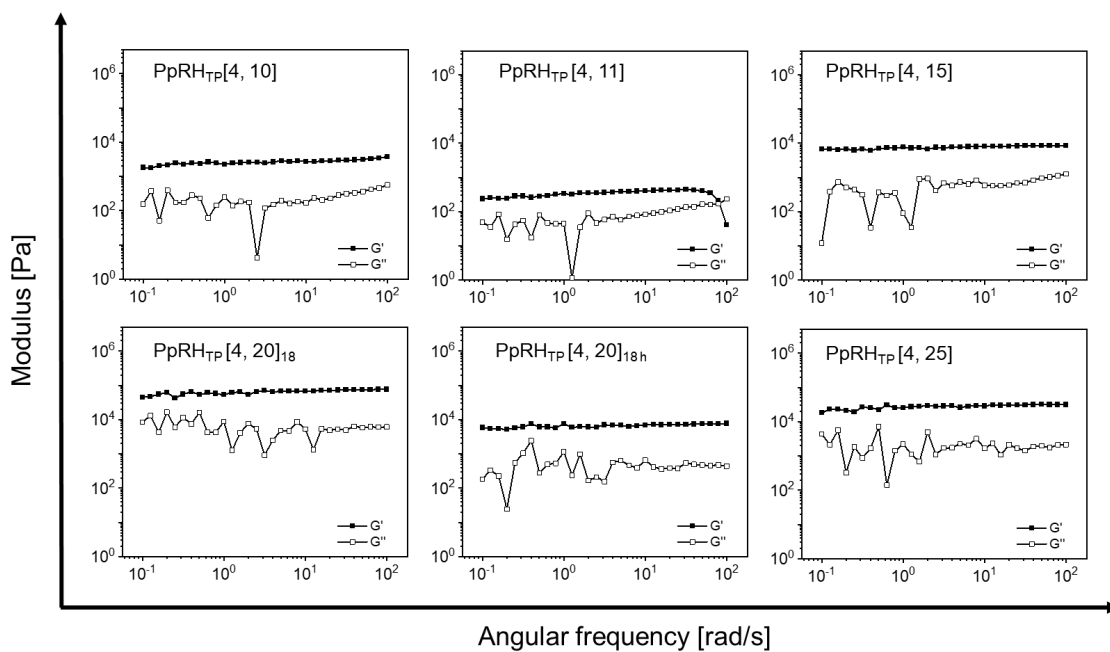


Figure S27. Angular frequency sweep profiles of PpRH_{TP}[4, x] (x = 10, 11, 15, 20, 25). PpRH_{TP}[4, 20] was heated for 2 h and PpRH_{TP}[4, 20]₁₈ was heated for 18 h.

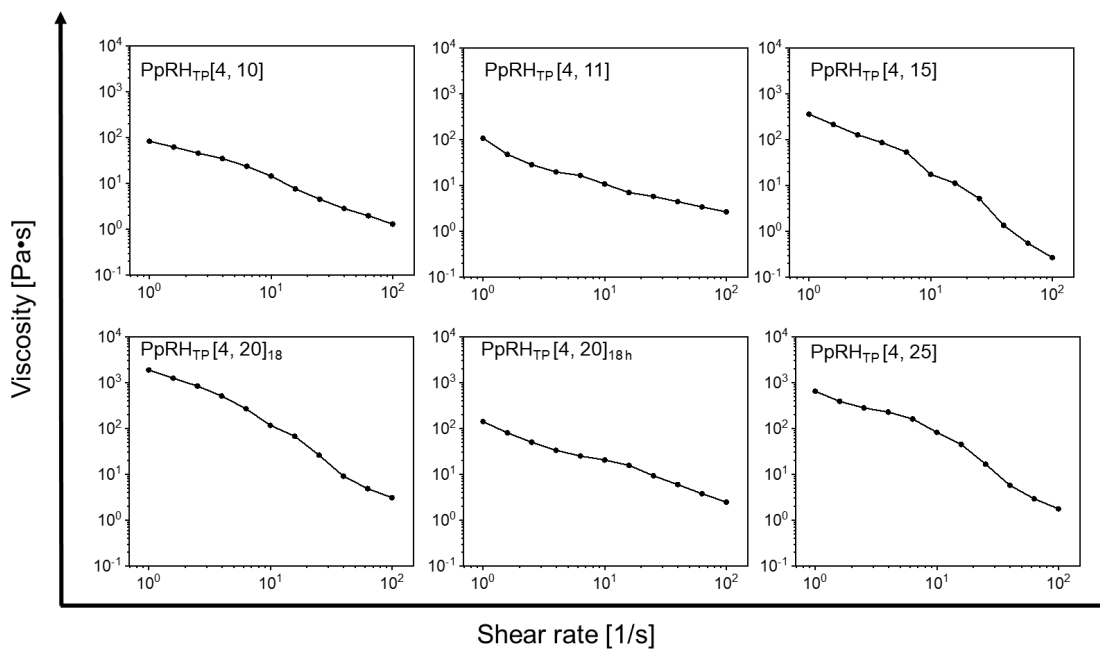


Figure S28. Steady shear rate sweep profiles of PpRH_{TP}[4, x] (x = 10, 11, 15, 20, 25). PpRH_{TP}[4, 20] was heated for 2 h and PpRH_{TP}[4, 20]₁₈ was heated for 18 h.

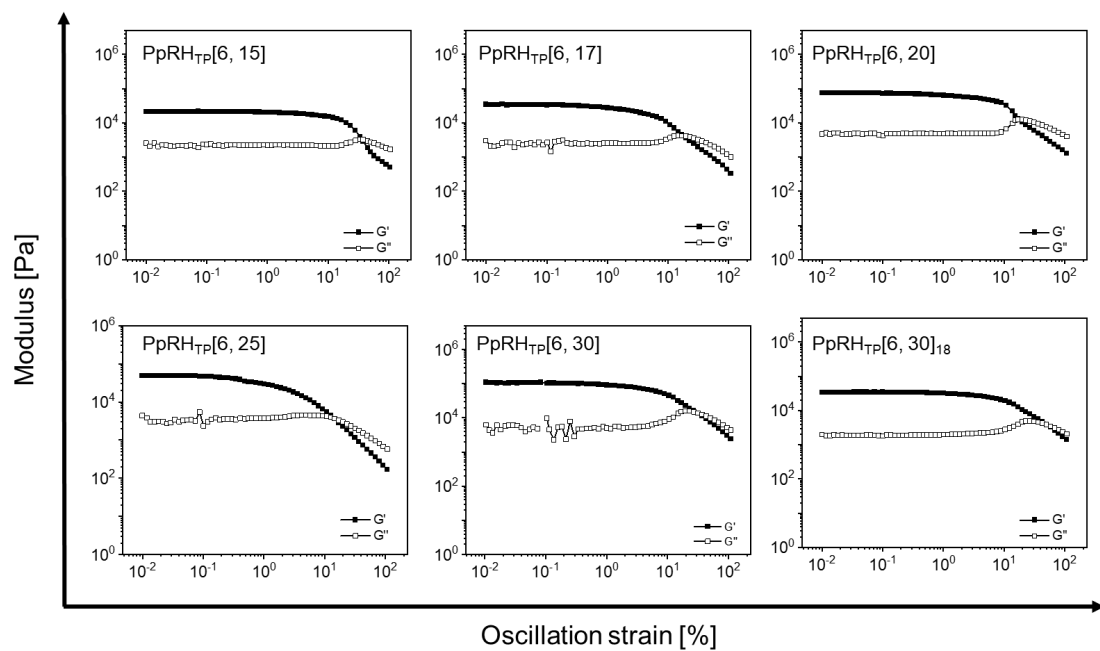


Figure S29. Oscillation strain sweep profiles of PpRH_{TP}[6, x] (x = 15, 17, 20, 25, 30). PpRH_{TP}[6, 30] was heated for 2 h and PpRH_{TP}[6, 30]₁₈ was heated for 18 h.

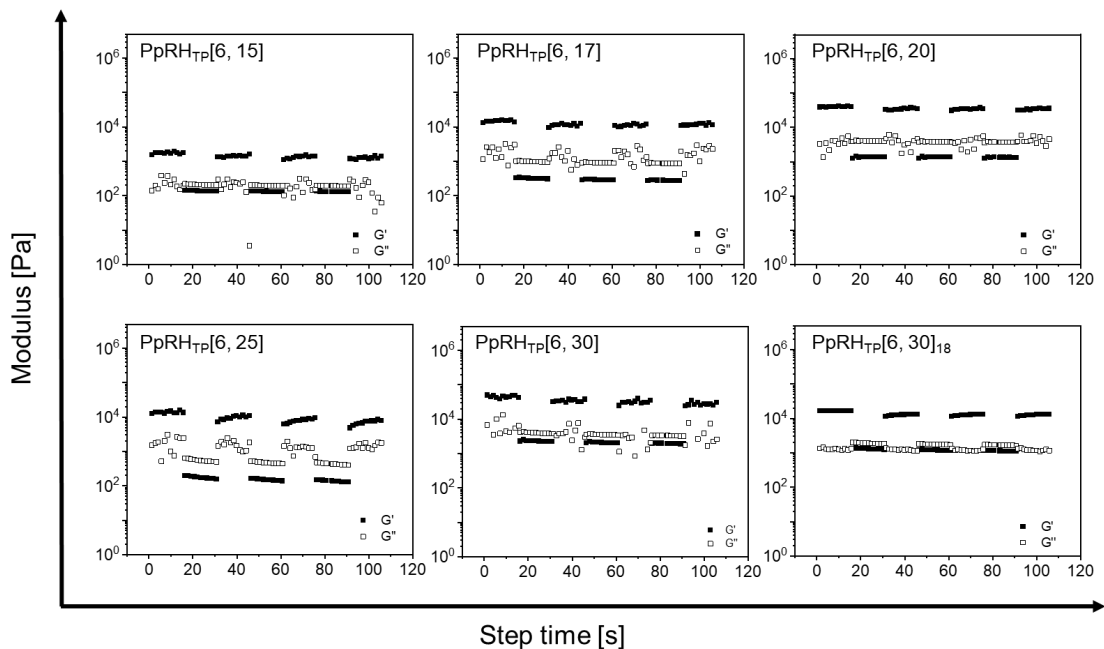


Figure S30. Dynamic step-strain amplitude test profiles of PpRH_{TP}[6, x] (x = 15, 17, 20, 25, 30). PpRH_{TP}[6, 30] was heated for 2 h and PpRH_{TP}[6, 30]₁₈ was heated for 18 h.

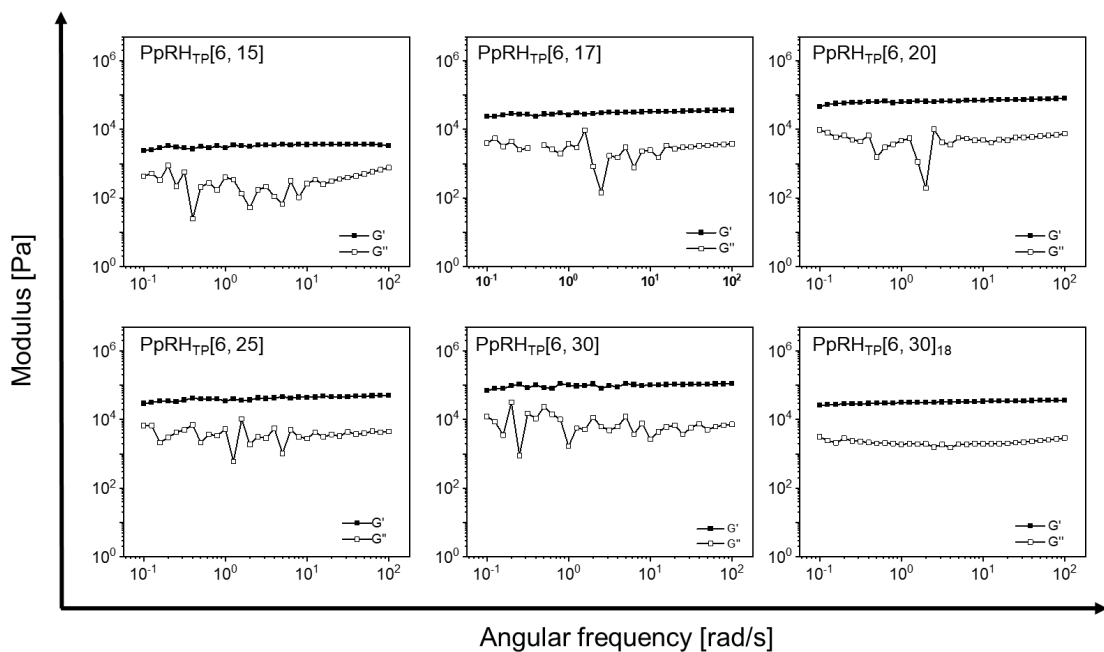


Figure S31. Angular frequency sweep profiles of PpRH_{TP}[6, x] (x = 15, 17, 20, 25, 30). PpRH_{TP}[6, 30] was heated for 2 h and PpRH_{TP}[6, 30]₁₈ was heated for 18 h.

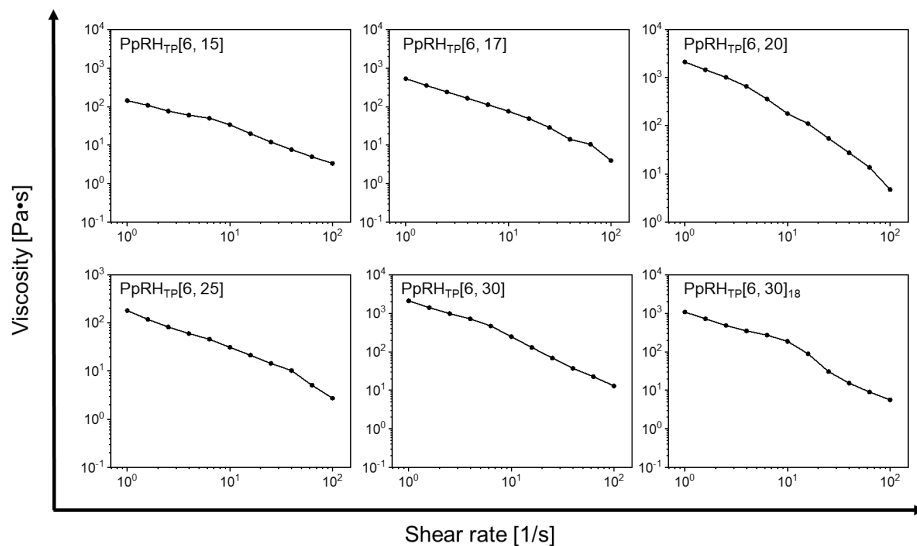


Figure S32. Steady shear rate sweep profiles of PpRH_{TP}[6, x] (x = 15, 17, 20, 25, 30). PpRH_{TP}[6, 30] was heated for 2 h and PpRH_{TP}[6, 30]₁₈ was heated for 18 h.

Table S2. The summary of the preparation of **BD** crosslinked PpRH_{BD} hydrogels.

| PEG _{4k} -(NH ₂) ₂ | | α -CD | | BD | | Reaction time at 60 °C | Fed EG:CD |
|--|------|--------------|-----|------|------|------------------------|-----------|
| wt% | mM | wt% | mM | wt% | mM | h | |
| 3 | 7.5 | 25.0 | 257 | 0.08 | 5.0 | 2 | 2.7:1 |
| | | 20.0 | 206 | | | 2 | 3.3:1 |
| | | 15.0 | 154 | | | 2 | 4.4:1 |
| | | 15.0 | 154 | | | 18 | 4.4:1 |
| | | 10.0 | 103 | | | 2 | 6.6:1 |
| | | 8.3 | 85 | | | 2 | 8.0:1 |
| | | 5.0 | 52 | | | 2 | 8.8:1 |
| 4 | 10.0 | 25.0 | 257 | 0.11 | 6.7 | 2 | 3.5:1 |
| | | 20.0 | 206 | | | 2 | 4.4:1 |
| | | 20.0 | 206 | | | 18 | 4.4:1 |
| | | 15.0 | 154 | | | 2 | 6.0:1 |
| | | 11.0 | 113 | | | 2 | 8.0:1 |
| | | 10.0 | 103 | | | 2 | 8.8:1 |
| 6 | 15.0 | 30.0 | 257 | 0.16 | 10.0 | 2 | 4.4:1 |
| | | 30.0 | 257 | | | 18 | 4.4:1 |
| | | 16.6 | 171 | | | 2 | 8.0:1 |

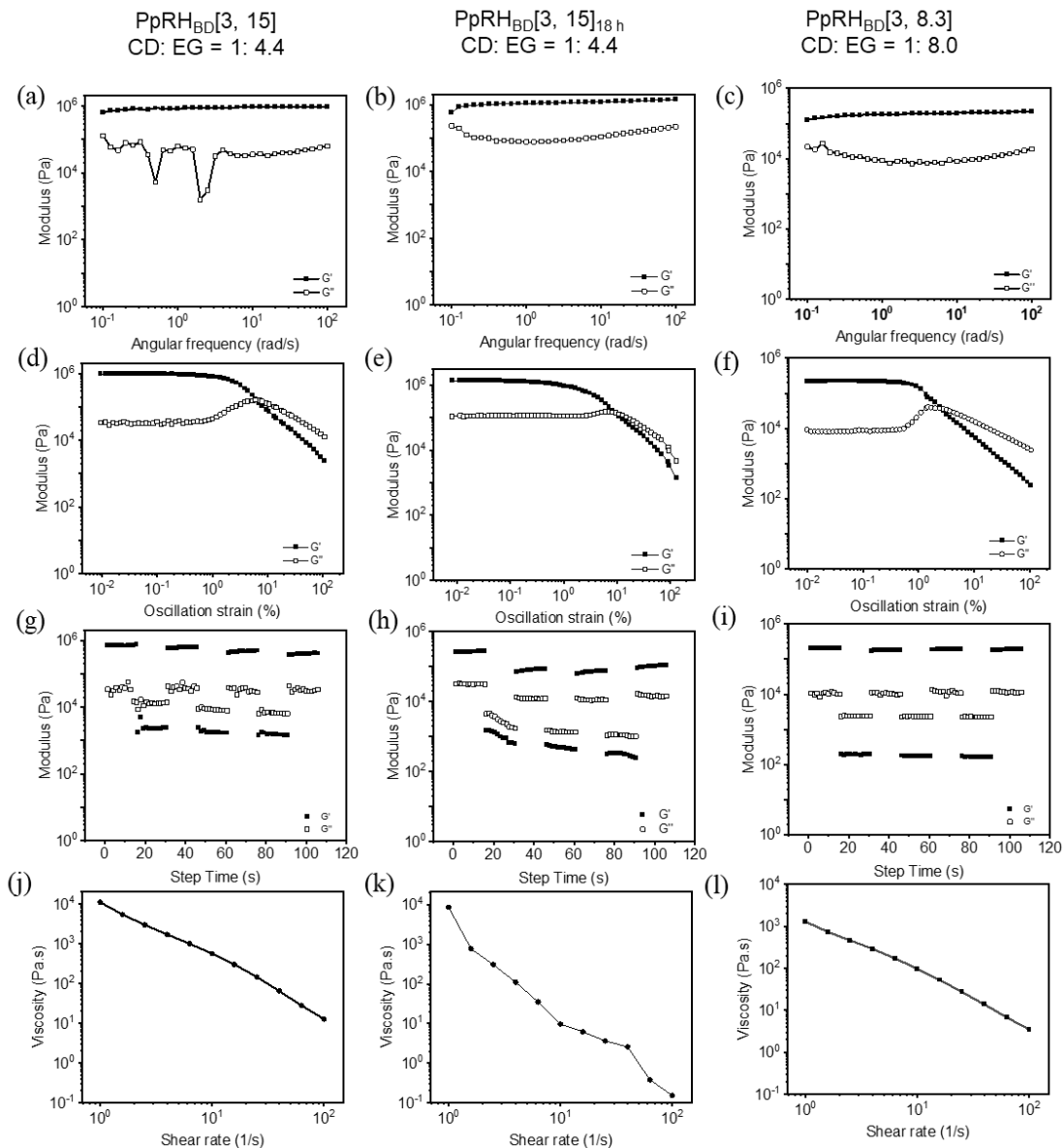


Figure S33. Rheological analysis of PpRH_{BD}[3, 15], PpRH_{BD}[3, 15]_{18h} and PpRH_{BD}[3, 8.3] at 25 °C. (a-c) Oscillation strain sweeps of the hydrogels at the oscillation strain from 0.01% to 100%. (d-f) Angular frequency sweeps of the hydrogels at the angular frequency from 0.1 rad/s to 100 rad/s. (g-i) Dynamic step-strain amplitude sweeps of the hydrogels. The applied oscillation strain was alternated between 1% and 100% every 15 s at 1 rad/s angular frequency. (j-l) Steady rate sweeps of the hydrogels at the shear rate from 1 s⁻¹ to 100 s⁻¹.

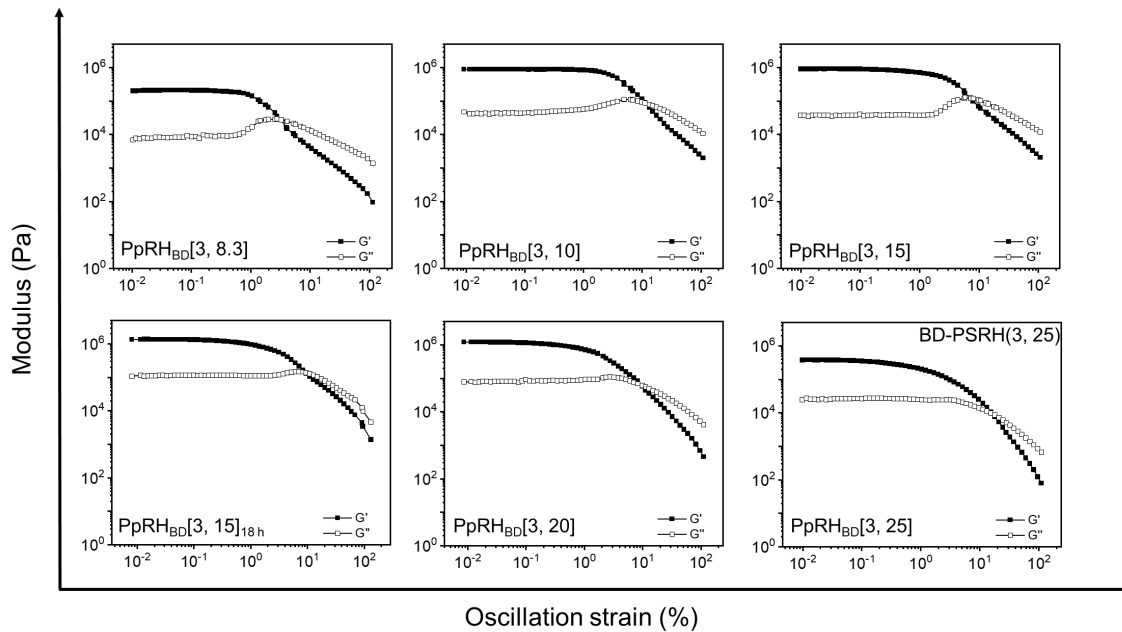


Figure S34. Oscillation strain sweep profiles of PpRH_{BD}[3, x] (x = 8.3, 10, 15, 20, 25). PpRH_{BD}[3, 15] was heated for 2 h and PpRH_{BD}[3, 15]₁₈ was heated for 18 h.

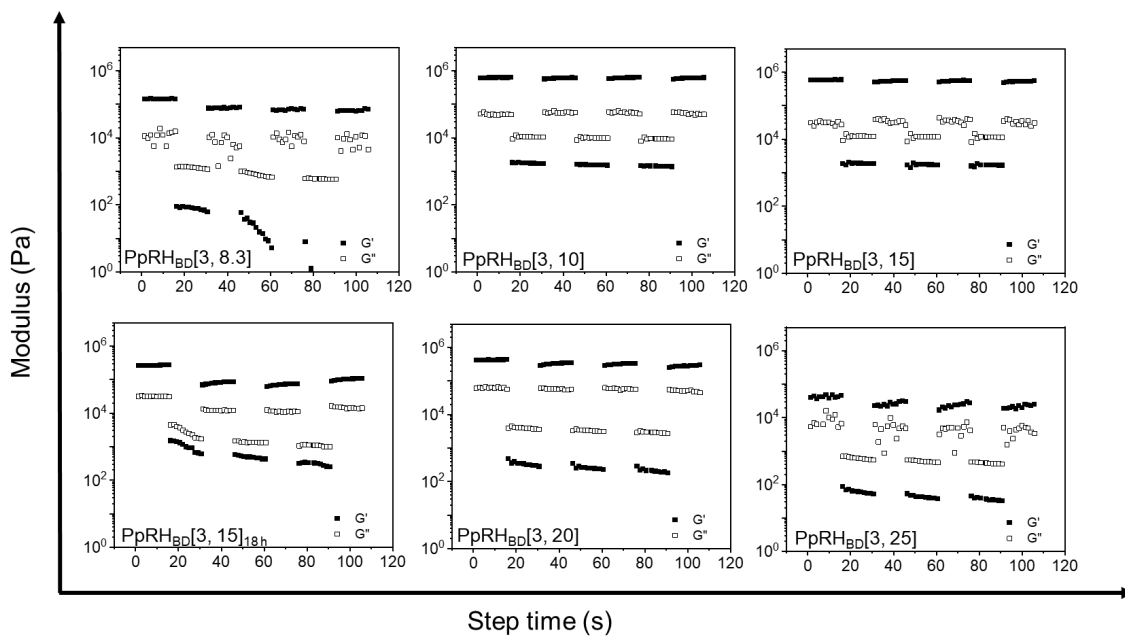


Figure S35. Dynamic step-strain amplitude test profiles of PpRH_{BD}[3, x] (x = 8.3, 10, 15, 20, 25). PpRH_{BD}[3, 15] was heated for 2 h and PpRH_{BD}[3, 15]₁₈ was heated for 18 h.

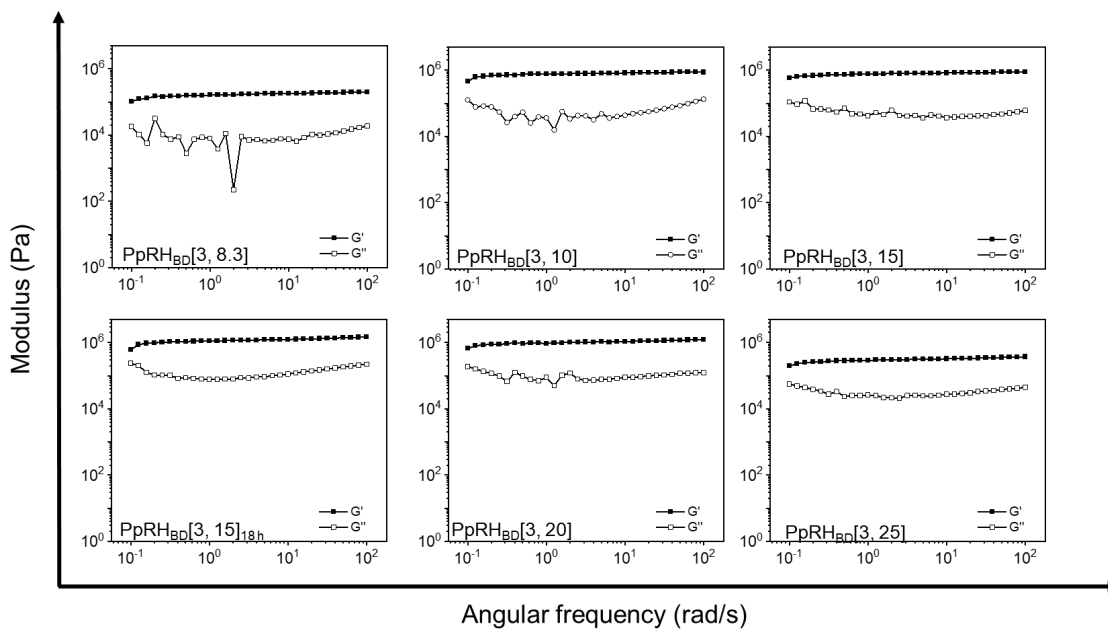


Figure S36. Angular frequency sweep profiles of PpRH_{BD}[3, x] (x = 8.3, 10, 15, 20, 25). PpRH_{BD}[3, 15] was heated for 2 h and PpRH_{BD}[3, 15]_{18h} was heated for 18 h.

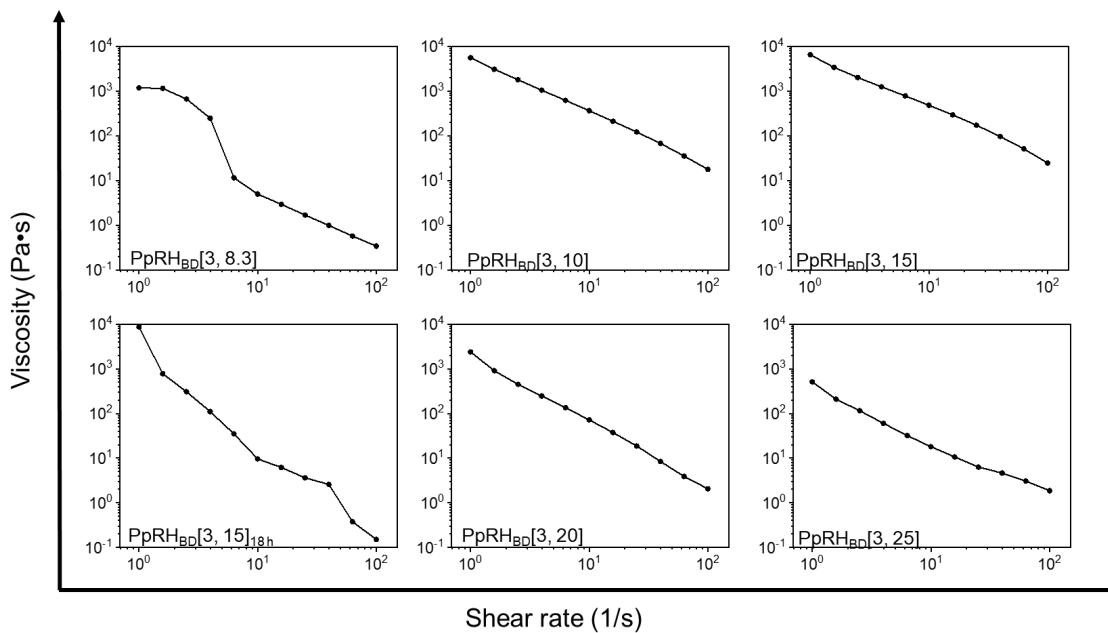


Figure S37. Steady shear rate sweep profiles of PpRH_{BD}[3, x] (x = 8.3, 10, 15, 20, 25). PpRH_{BD}[3, 15] was heated for 2 h and PpRH_{BD}[3, 15]_{18h} was heated for 18 h.

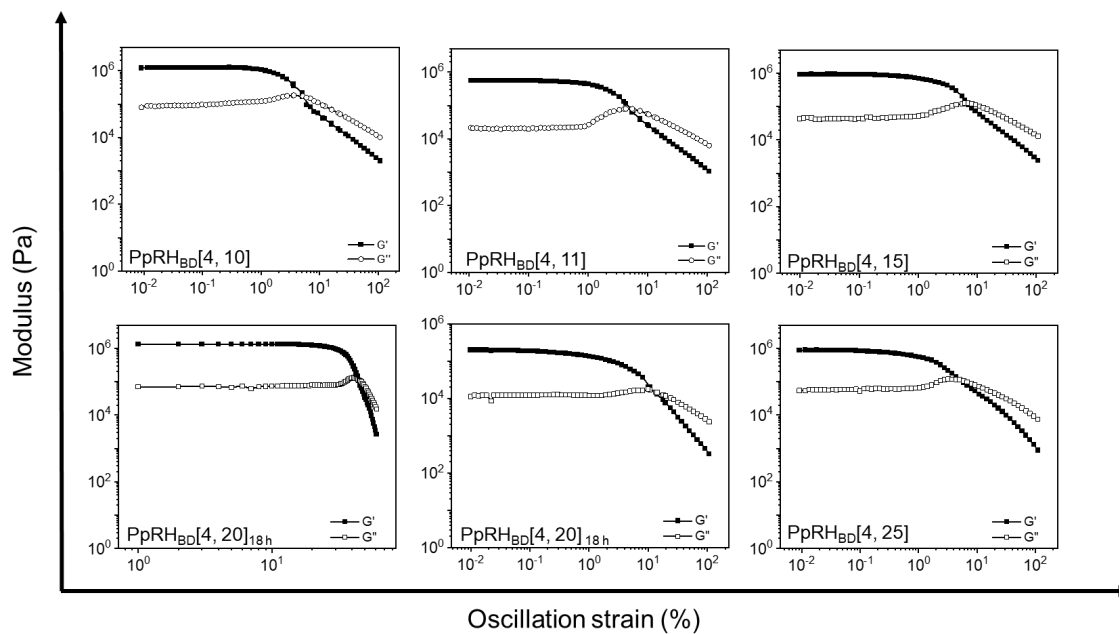


Figure S38. Oscillation strain sweep profiles of PpRH_{BD}[4, x] (x = 10, 11, 15, 20, 25). PpRH_{BD}[4, 20] was heated for 2 h and PpRH_{BD}[4, 20]_{18h} was heated for 18 h.

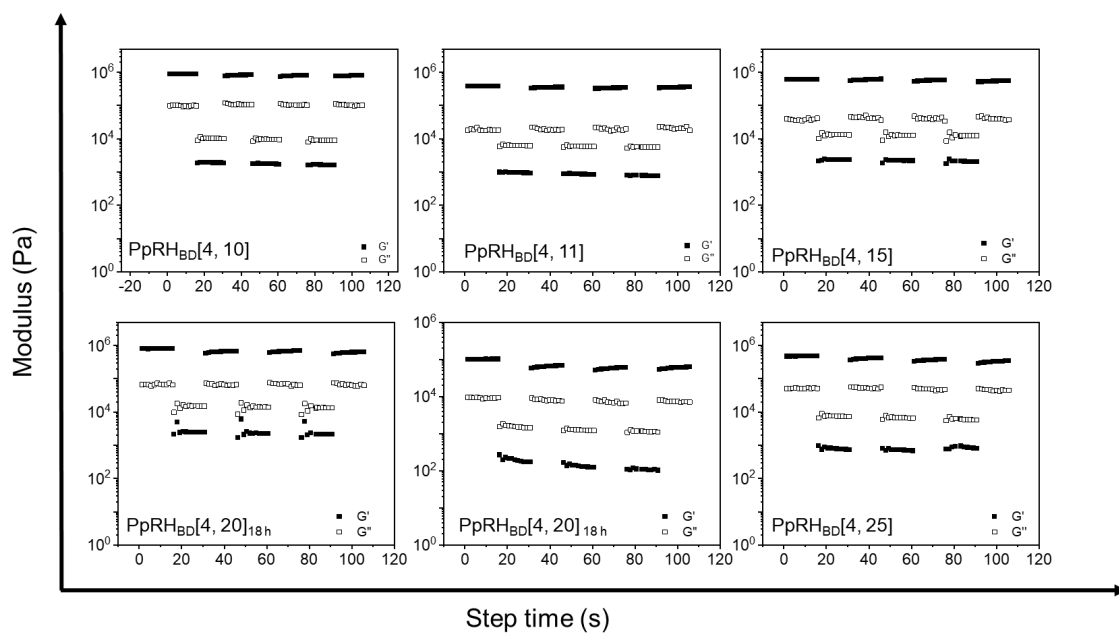


Figure S39. Dynamic step-strain amplitude test profiles of PpRH_{BD}[4, x] (x = 10, 11, 15, 20, 25). PpRH_{BD}[4, 20] was heated for 2 h and PpRH_{BD}[4, 20]_{18h} was heated for 18 h.

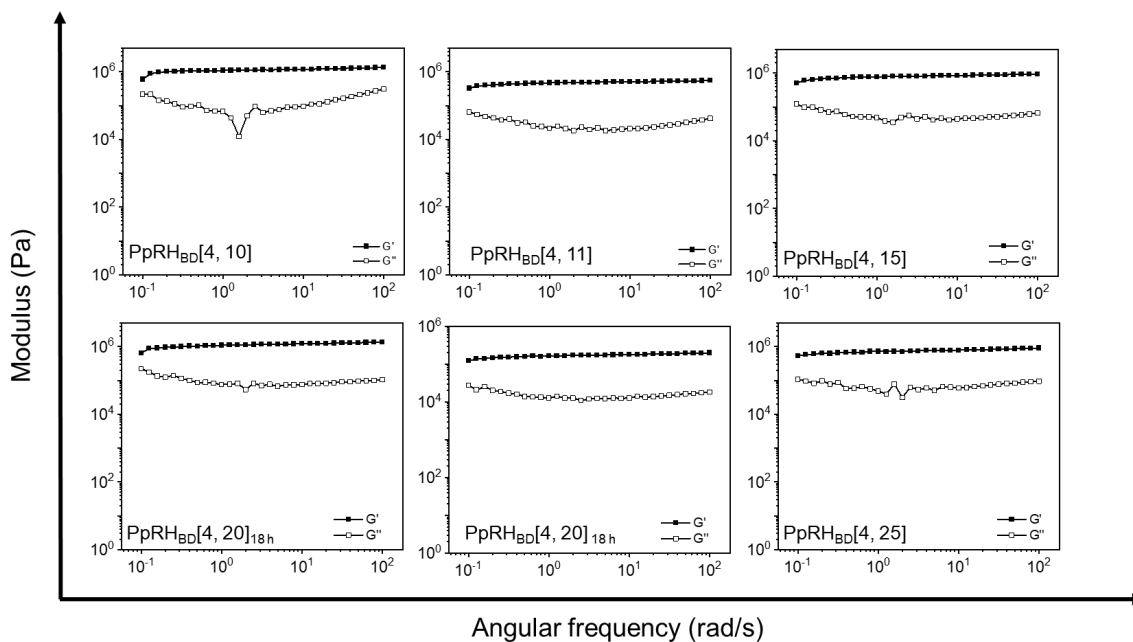


Figure S40. Angular frequency sweep profiles of PpRH_{BD}[4, x] (x = 10, 11, 15, 20, 25). PpRH_{BD}[4, 20] was heated for 2 h and PpRH_{BD}[4, 20]_{18h} was heated for 18 h.

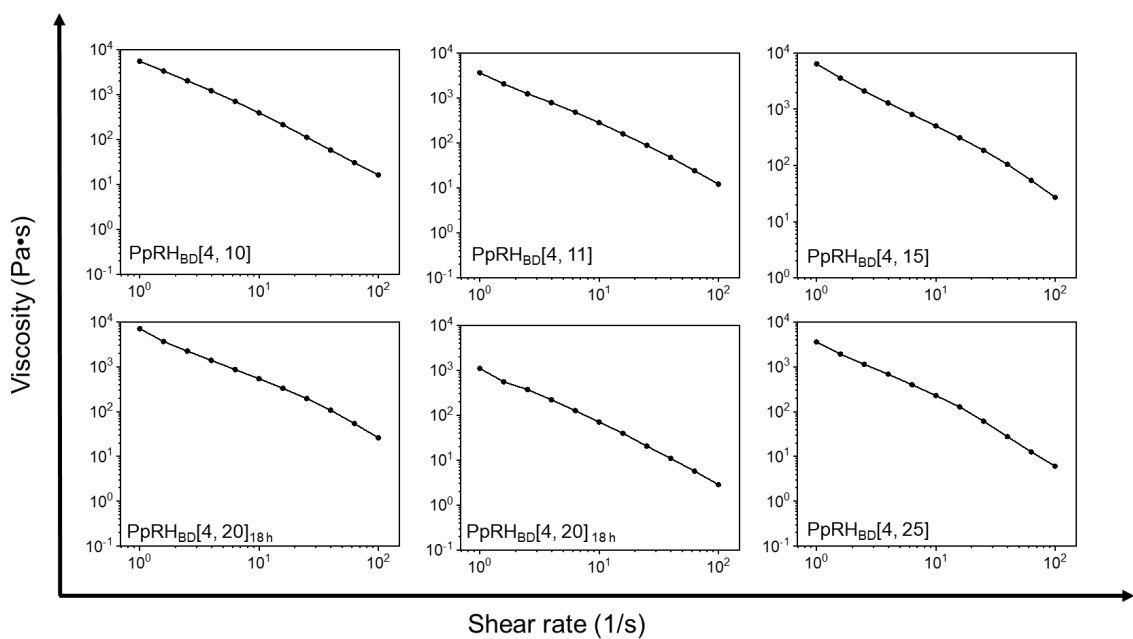


Figure S41. Steady shear rate sweep profiles of PpRH_{BD}[4, x] (x = 10, 11, 15, 20, 25). PpRH_{BD}[4, 20] was heated for 2 h and PpRH_{BD}[4, 20]_{18h} was heated for 18 h.

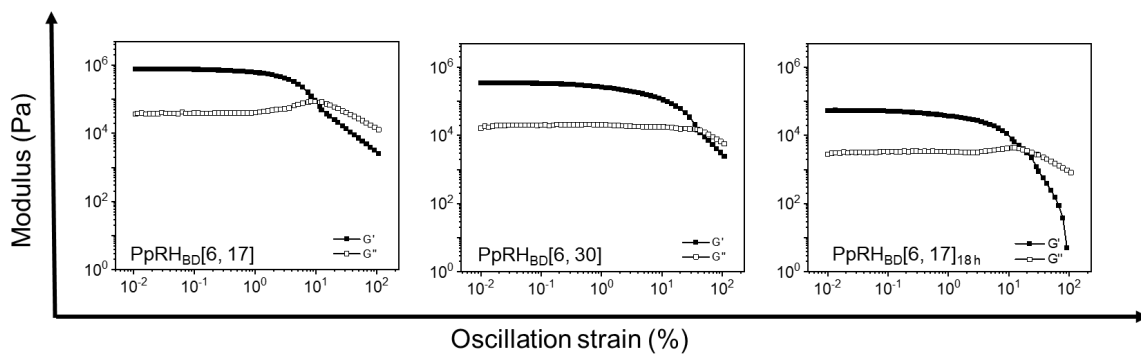


Figure S42. Oscillation strain sweep profiles of PpRH_{BD}[6, x] (x = 17, 30). PpRH_{BD}[6, 17] was heated for 2 h and PpRH_{BD}[6, 17]_{18h} was heated for 18 h.

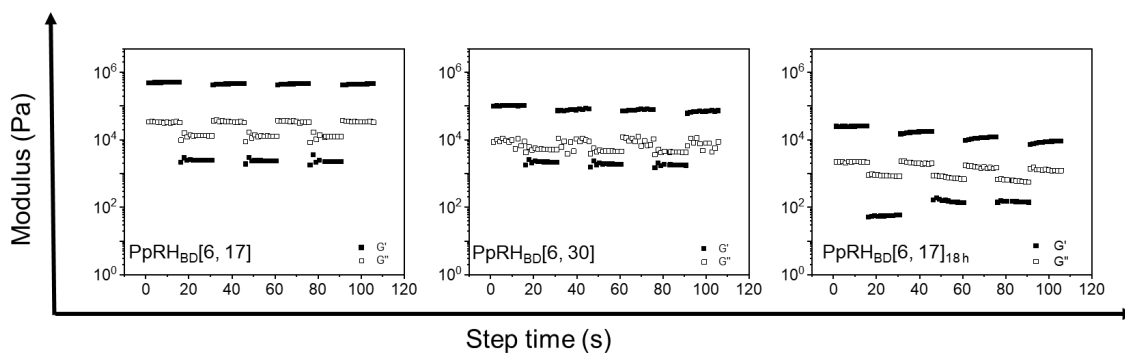


Figure S43. Dynamic step-strain amplitude test profiles of PpRH_{BD}[6, x] (x = 17, 30). PpRH_{BD}[6, 17] was heated for 2 h and PpRH_{BD}[6, 17]_{18h} was heated for 18 h.

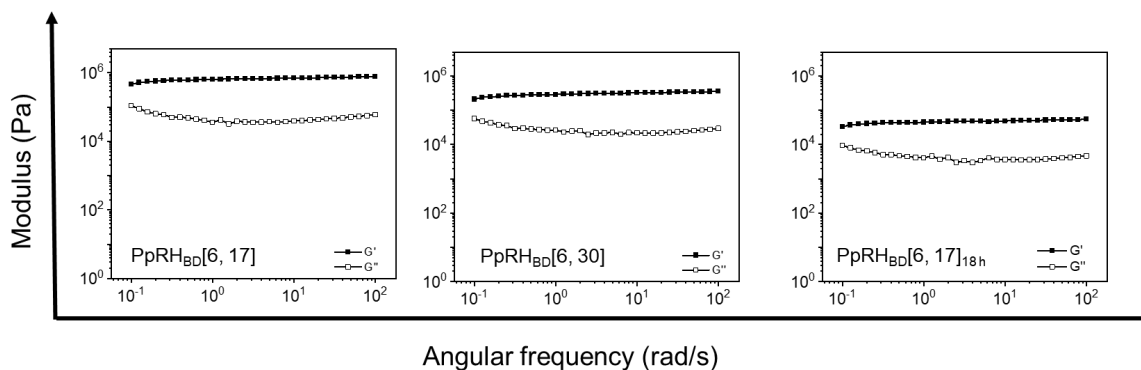


Figure S44. Angular frequency sweep profiles of PpRH_{BD}[6, x] (x = 17, 30). PpRH_{BD}[6, 17] was heated for 2 h and PpRH_{BD}[6, 17]_{18h} was heated for 18 h.

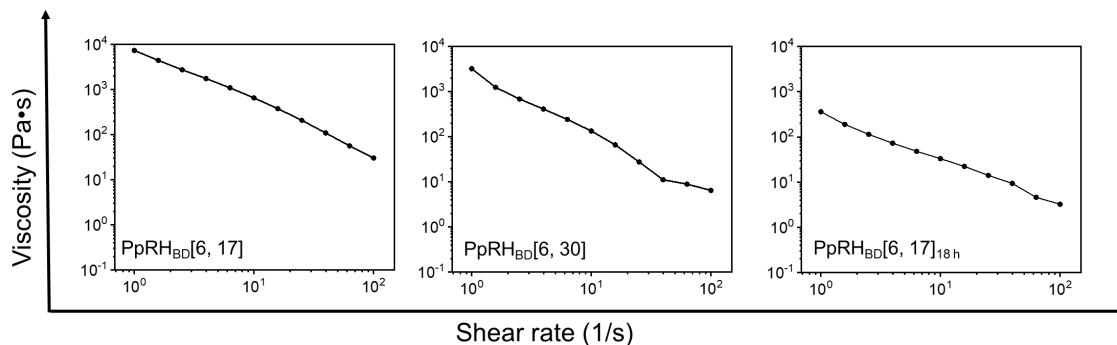


Figure S45. Steady shear rate sweep profiles of PpRH_{BD}[6, x] (x = 17, 30). PpRH_{BD}[6, 17] was heated for 2 h and PpRH_{BD}[6, 17]_{18h} was heated for 18 h.

S5. Investigation of threaded α -CD numbers on each PEG chain

To study the α -CD threading numbers and threading ratios in **TP** or **BD** crosslinked PpRH hydrogels, digestion experiments were performed. The crosslinked hydrogels were washed with DMSO three times, followed by solvent exchanges with acetone for 24 h. The acetone-gels were dried at 70 °C for 24 h to obtain the xerogel samples. The xerogels were hydrolyzed in NaOD/D₂O (5% w/v) for ¹H NMR analysis at 70 °C until all the samples were dissolved. The threaded α -CD numbers were calculated based on the integration of proton peaks of α -CD and PEG backbones. The maximum number of threaded α -CDs (N_{\max}) was calculated as 45 per PEG axle, based on the maximum threading ratio of EG/ α -CD = 2:1 and 90 repeating EG units per PEG axle.

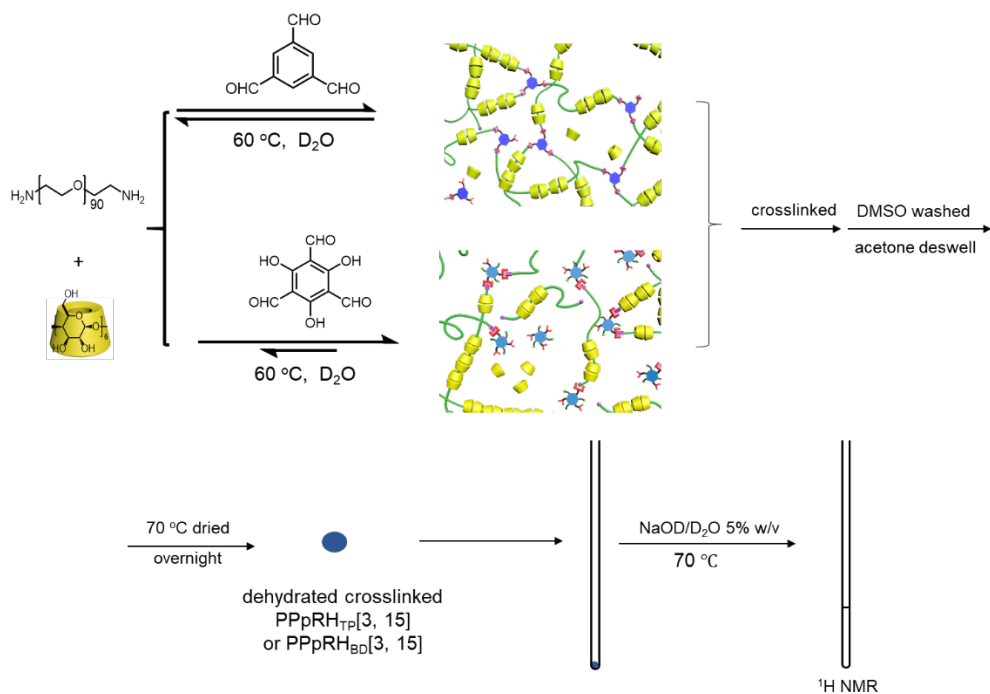


Figure S46. Illustration of the digestion experiment.

Table S3. Summary of threaded α -CD numbers in the TP crosslinked hydrogels from PpRH_{TP} samples. The results were measured using ¹H NMR digestion experiments.

| PEG _{4k} -(NH ₂) ₂ | | α -CD | | TP | | reaction time at 60 °C | fed EG:C D | found EG:CD ¹ | threaded α -CD per PEG (N) | threading ratio N/N _{max} ² (%) |
|--|------|--------------|-----|------|------|------------------------|------------|--------------------------|-----------------------------------|---|
| wt % | mM | wt % | mM | wt % | mM | h | | | | |
| 2.0 | 5.0 | 25.0 | 257 | 0.08 | 3.5 | 2 | 1.8:1 | 5.7:1 | 16 | 36 |
| | | 20.0 | 206 | | | 2 | 2.2:1 | 6.5:1 | 14 | 31 |
| | | 15.0 | 154 | | | 2 | 3.0:1 | 8.3:1 | 11 | 24 |
| 3 | 7.5 | 25.0 | 257 | 0.11 | 5.0 | 2 | 2.7:1 | 7.0:1 | 13 | 29 |
| | | 20.0 | 206 | | | 2 | 3.3:1 | 8.3:1 | 11 | 24 |
| | | 15.0 | 154 | | | 2 | 4.4:1 | 9.1:1 | 10 | 22 |
| | | 15.0 | 154 | | | 18 | 4.4:1 | 22.5:1 | 4 | 9 |
| | | 10.0 | 103 | | | 2 | 6.6:1 | 15.2:1 | 6 | 13 |
| | | 8.3 | 85 | | | 2 | 8.0:1 | 30.3:1 | 3 | 7 |
| 4 | 10.0 | 20.0 | 206 | 0.14 | 6.7 | 2 | 4.4:1 | 4.8:1 | 19 | 42 |
| | | 25.0 | 257 | | | 2 | 3.5:1 | 7.6:1 | 12 | 27 |
| | | 20.0 | 206 | | | 2 | 4.4:1 | 9.1:1 | 10 | 27 |
| | | 20.0 | 206 | | | 18 | 4.4:1 | 11.2:1 | 8 | 18 |
| | | 15.0 | 154 | | | 2 | 6.0:1 | 15.2:1 | 6 | 13 |
| | | 11.0 | 113 | | | 2 | 8.0:1 | 15.2:1 | 6 | 13 |
| | | 10.0 | 103 | | | 2 | 8.8:1 | 18.2:1 | 5 | 11 |
| 6 | 15.0 | 30.0 | 308 | 0.21 | 10.0 | 2 | 4.4:1 | 8.2:1 | 11 | 24 |
| | | 30.0 | 308 | | | 18 | 4.4:1 | 8.2:1 | 10 | 24 |
| | | 25.0 | 257 | | | 2 | 5.3:1 | 10.1:1 | 9 | 20 |
| | | 20.0 | 206 | | | 2 | 8.8:1 | 11.4 | 8 | 18 |
| | | 16.6 | 171 | | | 2 | 8.0:1 | 7.5:1 | 6 | 15 |
| | | 15.0 | 154 | | | 2 | 12.1:1 | 18.2:1 | 5 | 11 |
| | | 10.0 | 103 | | | 2 | 13.3:1 | 30.3:1 | 3 | 7 |

¹calculated with the integration of proton resonances of α -CD and the -CH₂CH₂O- of PEG_{4k}-(NH₂)₂.

²maximum number of threaded α -CDs (N_{max}) was calculated as 45 per PEG_{4k}-(NH₂)₂ based on the repeating unit of EG in PEG_{4k}-(NH₂)₂ as 90 and the binding stoichiometry EG/CD as 2: 1.

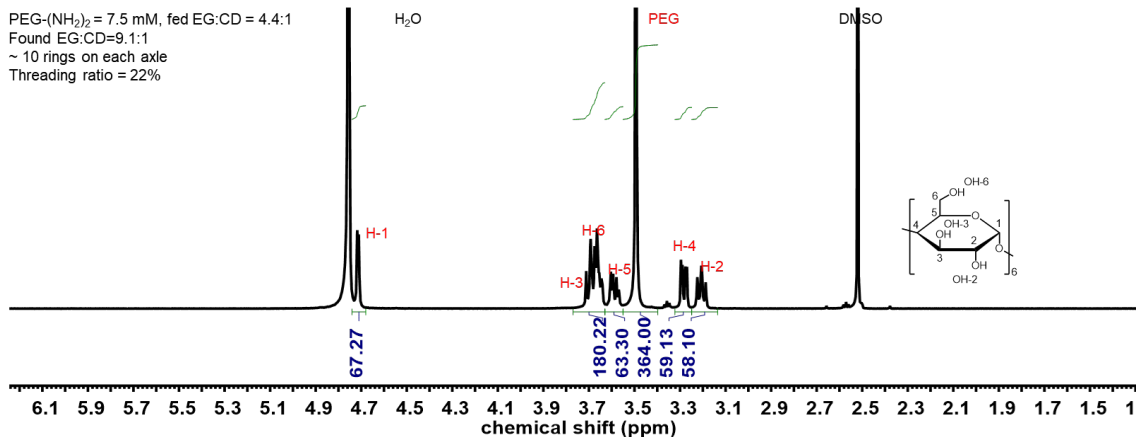


Figure S47. ¹H NMR spectrum of digested kPH-1 (NaOD/D₂O (5 w/v %), 500 MHz, 298K).

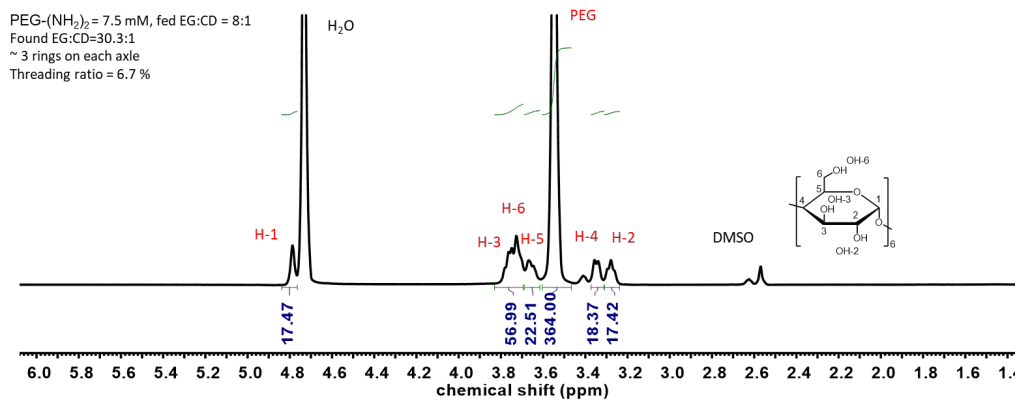


Figure S48. ¹H NMR spectrum of digested sample from PpRH_{TP}[3, 8.3] (NaOD/D₂O (5 w/v %), 500 MHz, 298K).

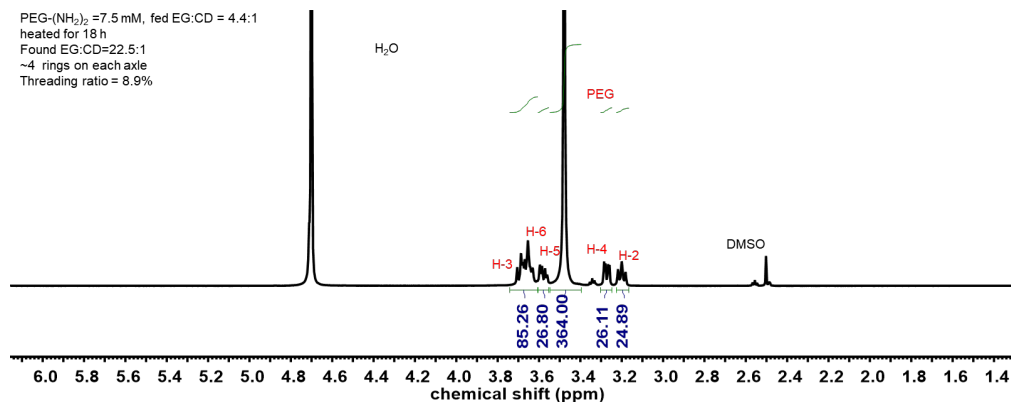


Figure S49. ¹H NMR spectrum of digested sample from PpRH_{TP}[3, 15]_{18h} (NaOD/D₂O (5 w/v %), 500 MHz, 298 K).

Table S4. Summary of threaded α -CD numbers in the **BD** crosslinked PpRH_{BD} hydrogels.

| PEG _{4k} -(NH ₂) ₂ | | α -CD | | BD | | reaction time at 60 °C | fed EG:C D | found EG:CD ¹ | threaded α -CD per PEG (N) | threading ratio N/N _{max} ² (%) |
|--|------|--------------|-----|-------|------|------------------------|------------|--------------------------|-----------------------------------|---|
| wt % | mM | wt % | mM | wt % | mM | h | | | | |
| 3 | 7.5 | 25.0 | 257 | 0.14 | 6.7 | 2 | 2.7:1 | 5.0:1 | 18 | 40 |
| | | 20.0 | 206 | | | 2 | 3.3:1 | 5.4:1 | 17 | 38 |
| | | 15.0 | 154 | | | 2 | 4.4:1 | 7.0:1 | 13 | 29 |
| | | 15.0 | 154 | | | 18 | 4.4:1 | 6.5:1 | 14 | 31 |
| | | 10.0 | 103 | | | 2 | 6.6:1 | 9.1:1 | 10 | 22 |
| | | 8.3 | 85 | | | 2 | 8.0:1 | 11.3:1 | 8 | 18 |
| 4 | 10.0 | 25.0 | 257 | 0.105 | 5.0 | 2 | 3.5:1 | 4.1:1 | 22 | 49 |
| | | 20.0 | 206 | | | 2 | 4.4:1 | 5.0:1 | 18 | 40 |
| | | 20.0 | 206 | | | 18 | 4.4:1 | 6.9:1 | 18 | 29 |
| | | 15.0 | 157 | | | 2 | 6.0:1 | 7.6:1 | 12 | 27 |
| | | 11.0 | 113 | | | 2 | 8.0:1 | 10.0:1 | 9 | 20 |
| | | 10.0 | 103 | | | 2 | 8.8:1 | 11.4:1 | 8 | 18 |
| 6 | 15.0 | 30.0 | 308 | 0.21 | 10.0 | 2 | 4.4:1 | 6.9:1 | 13 | 29 |
| | | 30.0 | 308 | | | 18 | 4.4:1 | 6.9:1 | 13 | 29 |
| | | 16.6 | 171 | | | 2 | 8.0:1 | 11.3:1 | 8 | 18 |

¹ calculated with the integration of proton resonances of α -CD and the -CH₂CH₂O- of PEG_{4k}-(NH₂)₂.

² maximum number of threaded α -CDs (N_{max}) was calculated as 45 per PEG_{4k}-(NH₂)₂ based on the repeating unit of EG in PEG_{4k}-(NH₂)₂ as 90 and the binding stoichiometry EG/CD as 2: 1.

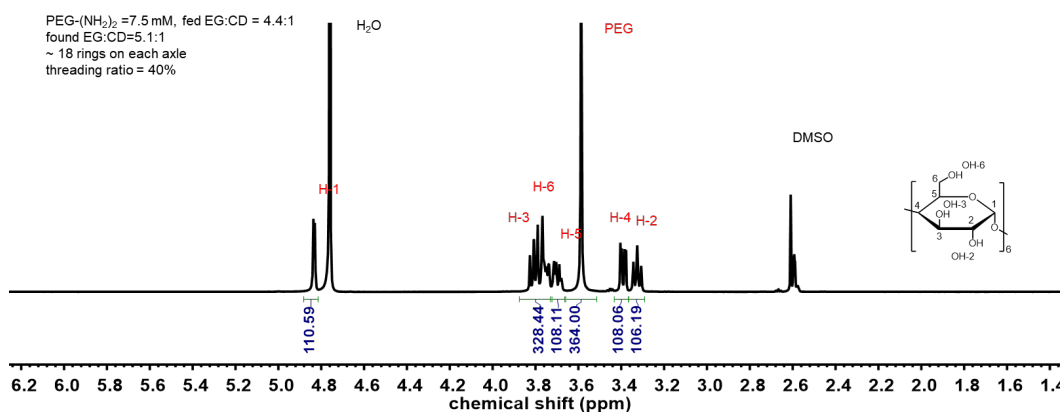


Figure S50. ¹H NMR spectrum of digested sample from PpRH_{BD}[3, 15] (NaOD/D₂O (5 w/v %), 500 MHz, 298 K).

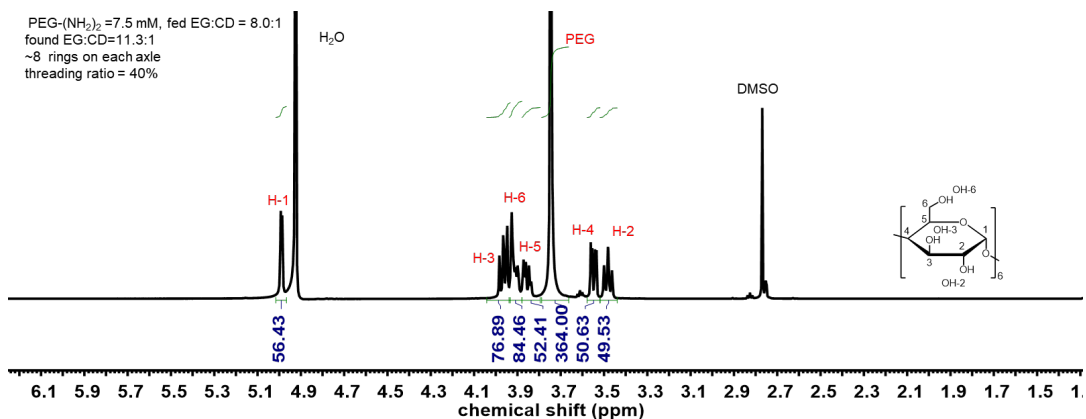


Figure S51. ¹H NMR spectrum of digested sample from PpRH_{BD}[3, 8.3] (NaOD/D₂O (5 w/v %), 500 MHz, 298 K).

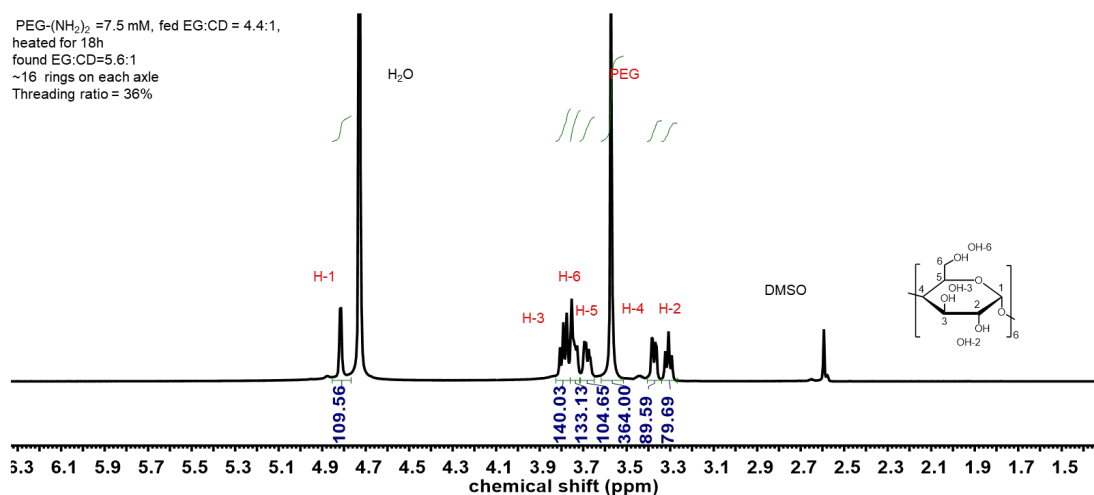


Figure S52. ¹H NMR spectrum of digested sample from PpRH_{BD}[3, 15]_{18h} (NaOD/D₂O (5% w/v), 500 MHz, 298 K).

S6. Comparison of PpRH_{TP} and PpRH_{BD}

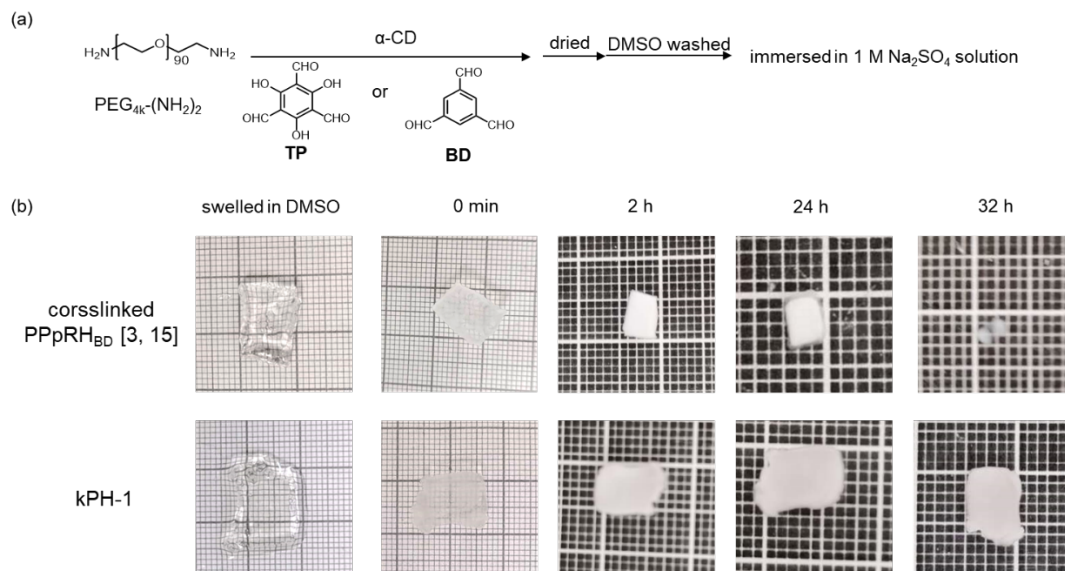


Figure S53. Chemical stability comparison between kPH-1 and the treated PpRH_{BD}[3, 15] sample. (a) The scheme of the experiment method. (b) Images of crosslinked PpRH_{BD}[3, 15] (up) and kPH-1 (bottom) washed with DMSO and solvent exchanged to water (1M Na₂SO₄) for 32 h. PpRH_{BD}[3, 15] degraded in water gradually while kPH-1 was chemically stable in water.

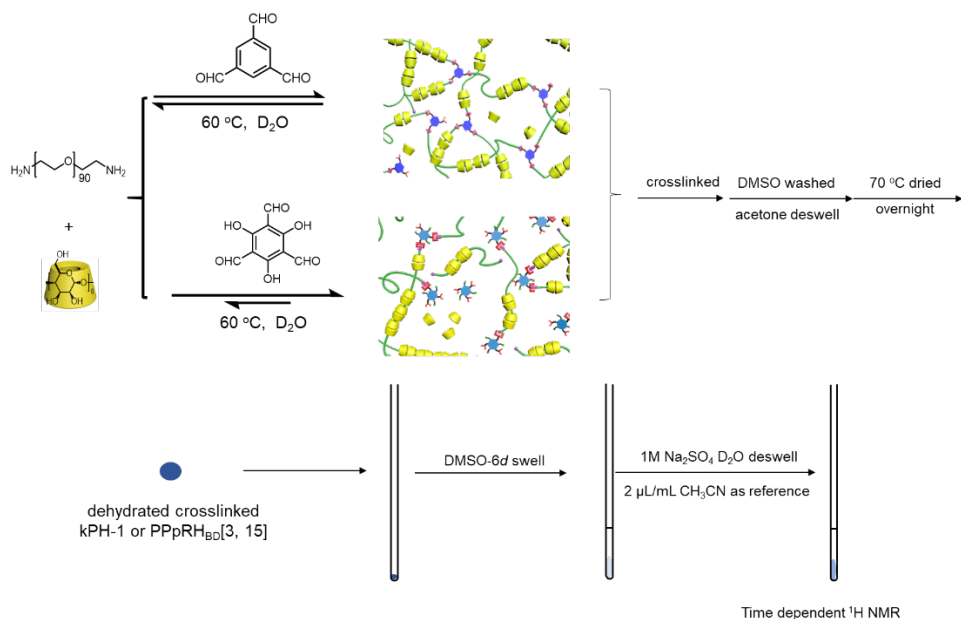


Figure S54. Scheme of the ¹H NMR investigation of the chemical stability of the crosslinked kPH-1 and sample from PpRH_{BD}[3, 15].

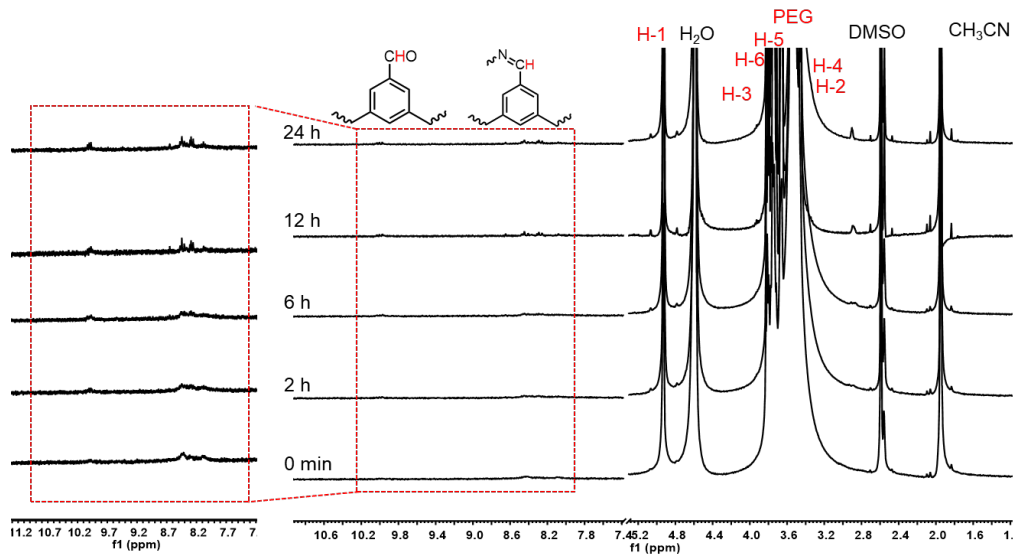


Figure S55. Time-dependent ^1H NMR spectra to monitor the dissolution process of PpRH_{BD}[3, 15] in D_2O (1 M NaSO_4 , 298 K, 600 MHz).

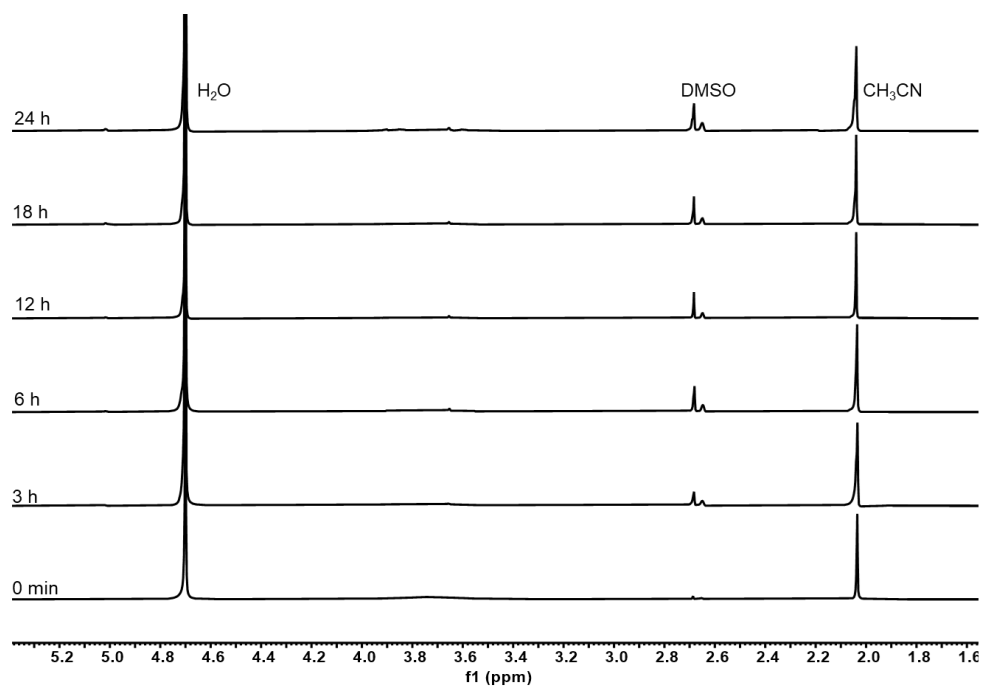


Figure S56. Time-dependent ^1H NMR spectra to confirm the stability of kPH-1 in D_2O (1 M NaSO_4 , 298 K, 600 MHz).

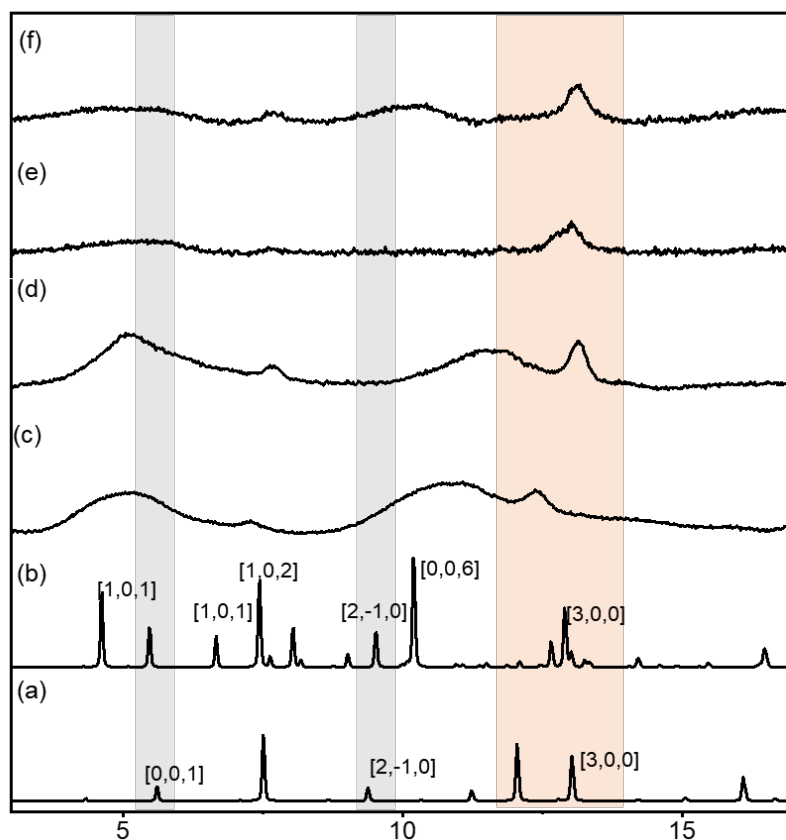


Figure S57. Simulated WAXS profiles of (a) $[(EG)_4/2(\alpha\text{-CD})]_n$ and (b) $\text{PEG}_{600}\text{-(OH)}_2/\alpha\text{-CD}$ samples.^{S4} PXR profiles of (c) kPH-1, (d) dehydrated PpRH_{BD}[3, 15], (e) PpRH_{TP}[3, 15] hydrogel and (d) PpRH_{BD}[3, 15] hydrogel.

S7. Mechanical property investigation

The tensile tests were performed on a DHR2 system (TA instruments®, New Castle, DE) with a 50 N load cell. All the specimens were cut into rectangular pieces with 5.0 mm to 8.0 mm width and 0.5 mm to 1.0 mm thickness. The loading length of the samples was 3 mm with a tensile rate of 1.5 mm/min.

The compressive tests were carried out on an Instron 5543 universal testing system equipped with a 500 N load cell. All the specimens were cut into cylinders of 8.0 mm to 10.0 mm in diameter and 7.0 mm to 10.0 mm in height. The compressive rate is 1.0 mm/min.

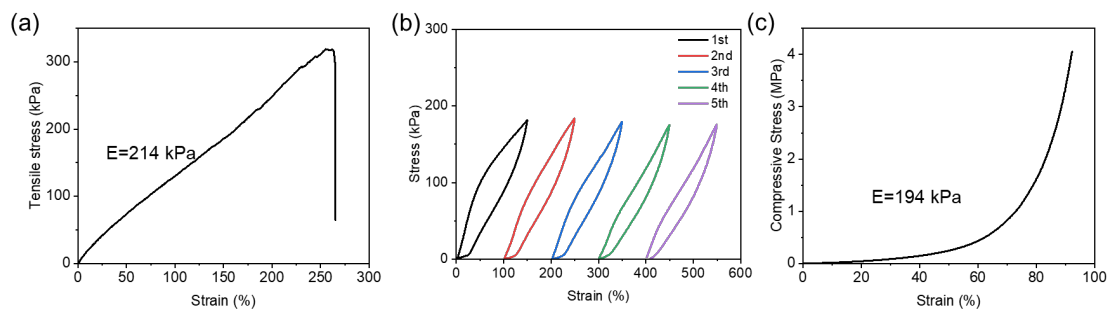


Figure S58. Mechanical property investigation of kPH-1. (a) Uniaxial tensile stress-strain profile, (b) multi-cyclic (un)loading stress-strain profiles, and (c) uniaxial compressive stress-strain profile. Tensile rate=1.5 mm/min; compressive rate =1.0 mm/min.

Table S5. The summary of mechanical properties of kPH-1

| Sample | Young's modulus kPa | Strain % | Work of rupture $\text{kJ}\cdot\text{m}^{-3}$ | Compressive modulus kPa |
|--------|------------------------|-------------|--|-------------------------------|
| kPH-1 | 214 | 262 | 439 | 194 |

S8. 3D Printing

Direct ink writing and post-printing crosslinking. The prepared hydrogel ink was firstly loaded into a syringe barrel, centrifuged to remove the air bubbles, and transferred into a Nordson EFD syringe barrel (3 mL) for 3D-printing. DIW was performed using extrusion-based 3D printers (Tabletop, nScript) equipped with Nordson EFD precision smooth flower tapered tips (i.d. = 400 μm). Printing paths were manually written. Typically, the printed monoliths were stored in a humid box with a cap on it to prevent deform of 3D structures. The humid box was then stored at 70 °C overnight, followed by an additional 5h annealing at 70 °C to remove water. The dehydrated hydrogel was washed with DMSO three times. The crosslinked hydrogels were obtained after a solvent exchange process in Na_2SO_4 (1 M) aqueous solution for 48 h.

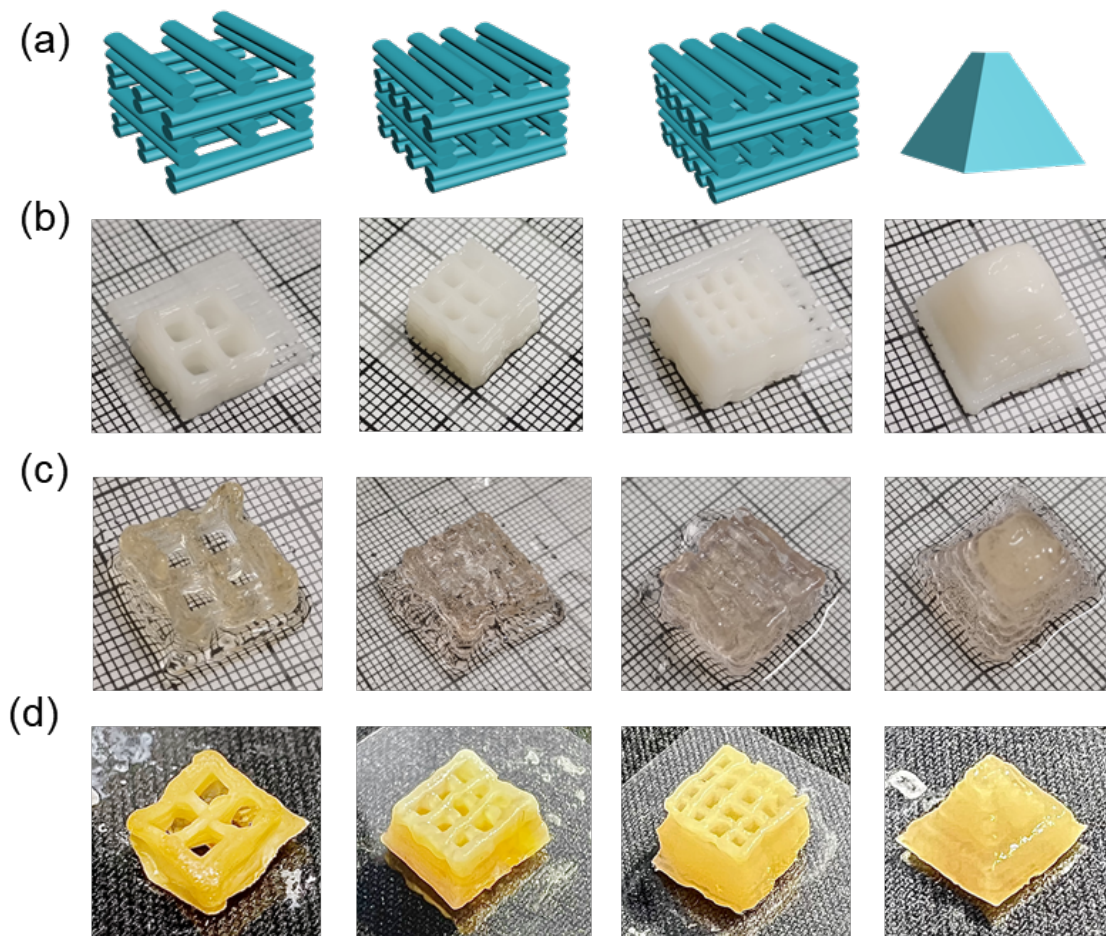
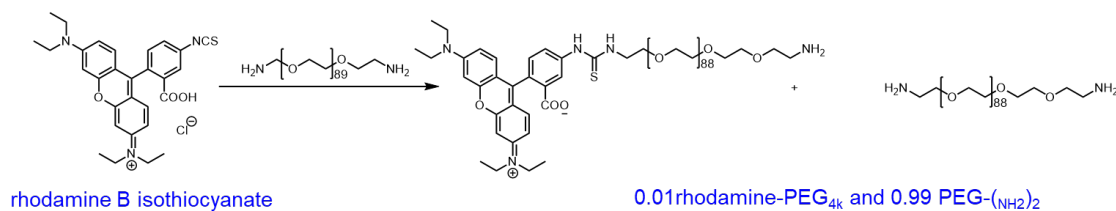


Figure S59. Designed and 3D-printed PpRH_{TP}[3,15] and kPH-1 monoliths. (a) Computer-aided designs of 3D-printed objects (cubic lattices, and pyramid); 3D printed monolith of PpRH_{TP}[3,15] after (b) printing, (c) after washed with DMSO and (d) kPH-1 hydrogels.

S9. Mechanochromic responsiveness



0.01rhodamine-PEG_{4k}: In a 50-mL round bottom flask, PEG_{4k}-(NH₂)₂ (1.0 g, 0.25 mmol) and rhodamine B isothiocyanate (1.34 mg, 2.5 × 10⁻³ mmol) were dissolved in 20 mL ethanol in an ice bath. The reaction solution was allowed to warm up and stirred in N₂ for 24 h. After the solvent was removed under vacuum, the desired polymer was obtained as a pink solid by precipitating in diethyl ether three times.

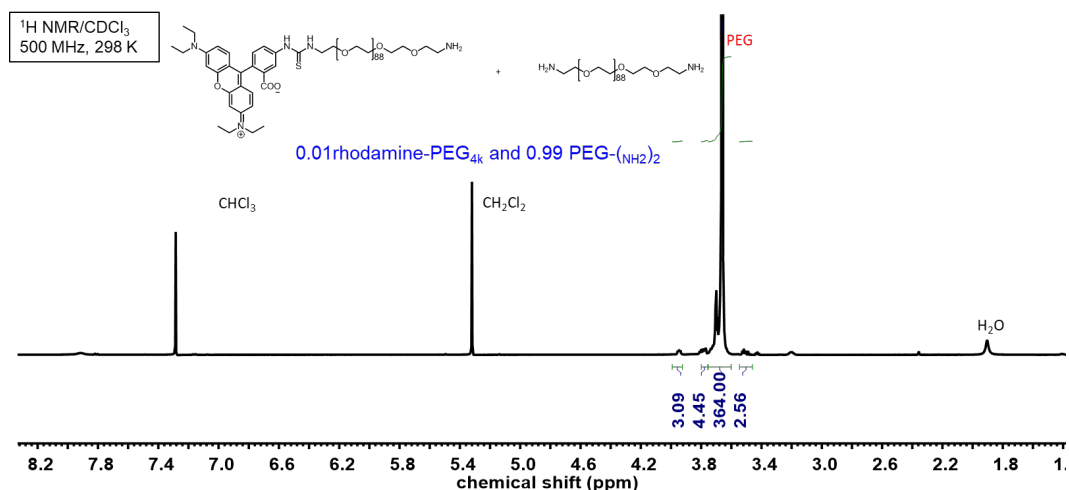
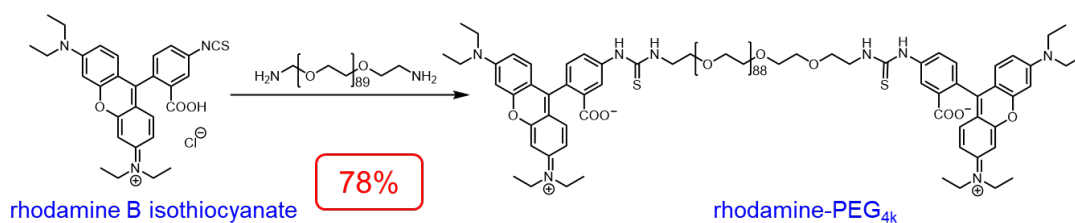


Figure S60. ¹H NMR of 0.01 Rhodamine-PEG_{4k} (500 MHz, CDCl₃, 298 K).



Rhodamine-PEG_{4k}: In a 50-mL round bottom flask, PEG_{4k}-(NH₂)₂ (100 mg, 0.025 mmol) and rhodamine B isothiocyanate (29.00 mg, 0.055 mmol) were dissolved in 20 mL ethanol in an ice bath. The reaction solution was allowed to warm up and stirred in N₂ for 24 h. After the solvent was removed under vacuum, the polymer was obtained as a violet solid by precipitating in diethyl ether three times with a yield of 78%. ¹H NMR (500 MHz, DMSO-*d*₆) δ = 8.28 – 8.03 (m, 2H), 7.94 (dd, *J* = 8.6, 5.8 Hz, 1H), 7.80 (s, 5H), 7.22 – 7.02 (m, 2H), 7.02 – 6.75 (m, 2H), 6.20 (d, *J* = 14.6 Hz, 1H), 6.13 – 6.02 (m, 1H), 3.61 (s, 364H), 2.98 (p, *J* = 5.7 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 5H), 1.15 – 0.98 (m, 7H).

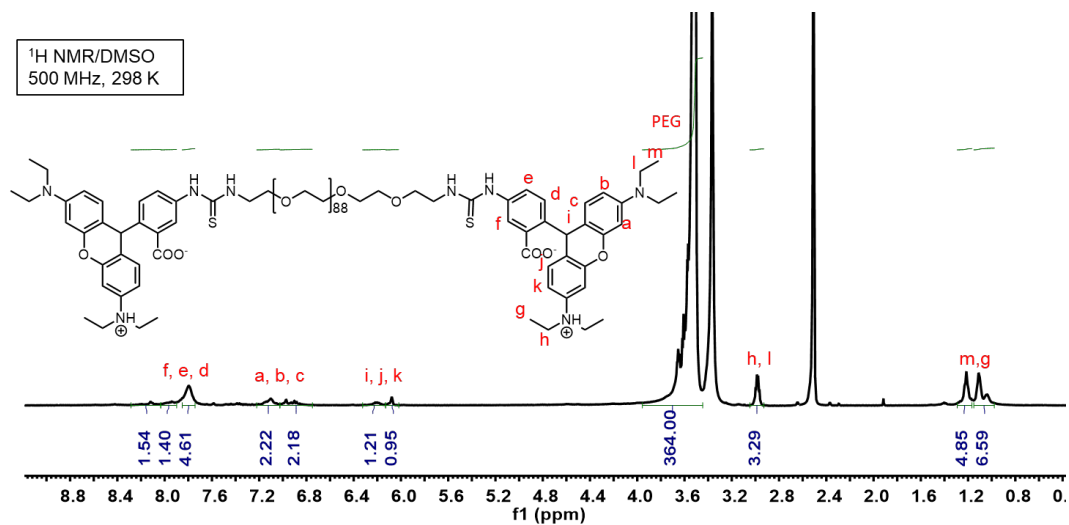
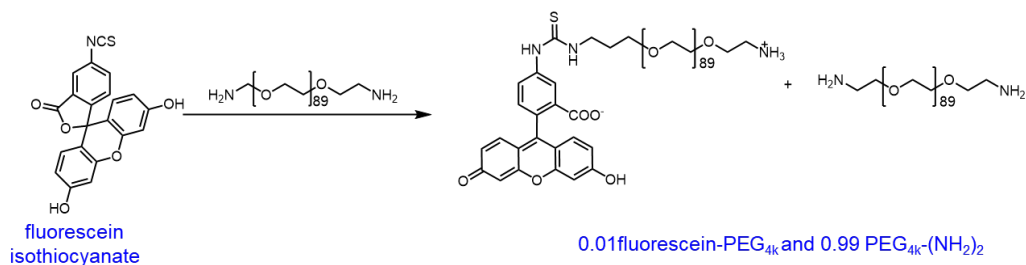


Figure S61. ¹H NMR of rhodamine-PEG_{4k} (500 MHz, DMSO-*d*₆, 298 K).



0.01 Fluorescein-PEG_{4k}: PEG_{4k}-(NH₂)₂ (1.0 g, 0.25 mmol) and fluorescein isothiocyanate (0.97 mg, 0.0025 mmol) were mixed in a 50 mL flask and dissolved in 20 mL methanol. The solution was refluxed in N₂ for 24 h. After the solution was cooled to room temperature and the solvent was removed under vacuum, the yellow polymer was obtained by precipitating in diethyl ether three times.

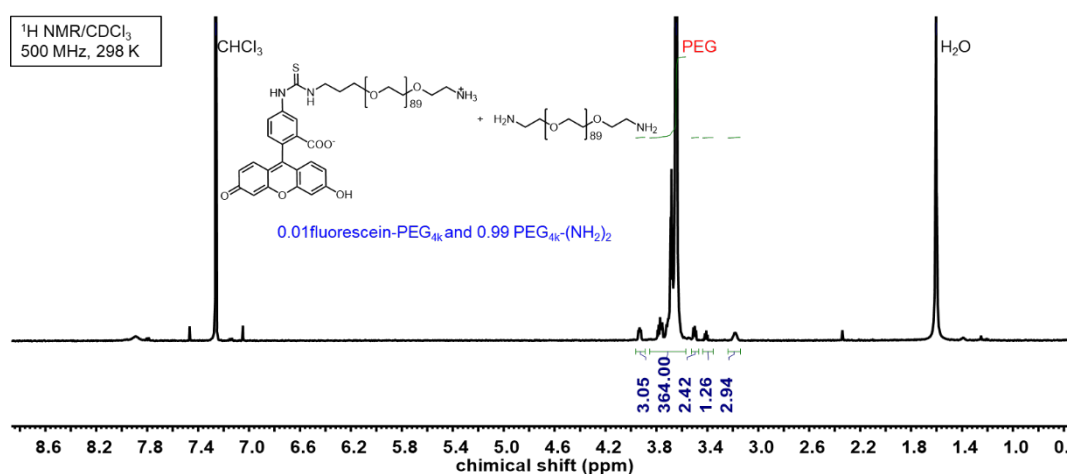
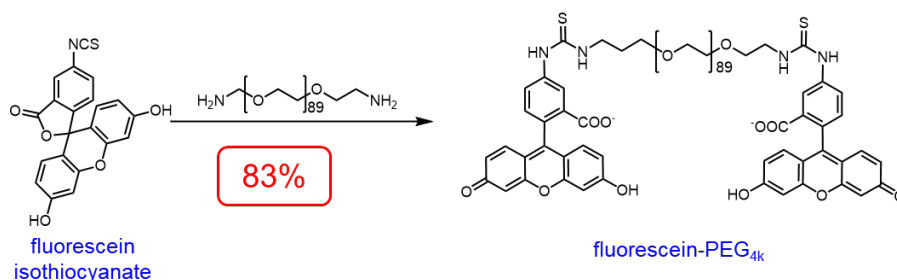


Figure S62. ¹H NMR of 0.01 fluorescein-PEG_{4k} (500 MHz, CDCl₃, 298 K).



Fluorescein-PEG_{4k}: PEG_{4k}-(NH₂)₂ (100 mg, 0.025 mmol) and fluorescein isothiocyanate (21.42 mg, 0.055 mmol, 2.2 eq.) were mixed in a 50 mL flask and dissolved in 20 mL methanol. The solution was refluxed in N₂ for 24 h. After the solution was cooled to room temperature and the solvent was removed under vacuum, the polymer was obtained by precipitating in diethyl ether three times (yield = 83%). ¹H NMR (500 MHz, DMSO-*d*₆) δ = 8.28 (s, 1H), 8.10 (s, 1H), 7.75 (d,

$J = 8.1$ Hz, 1H), 7.18 (d, $J = 8.3$ Hz, 1H), 6.68 (d, $J = 2.4$ Hz, 2H), 6.61 (d, $J = 8.7$ Hz, 2H), 6.57 (d, $J = 8.8$ Hz, 2H), 3.52 (s, 364H).

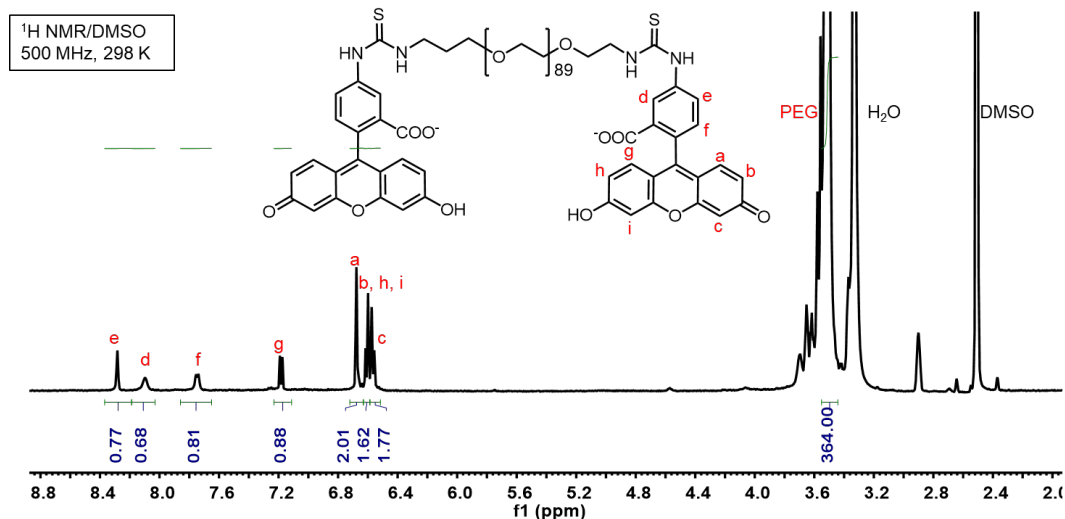


Figure S63. ^1H NMR of fluorescein-PEG_{4k} (500 MHz, DMSO-*d*₆, 298 K).

Mechanochromic hydrogel preparation: The preparation of PpRH_{TP} with 0.01 equivalent FRET pairs modified PEG_{4k}-(NH₂)₂ is described as follows. An aqueous solution (16 mL) of 0.01Flu-PEG_{4k} (3.75 wt%), 0.01Flu-PEG_{4k} (3.75 wt%) and TP (2.65 wt%) were added to the aqueous solution of α -CD (25 wt%, 24 mL). The mixture was stirred at 60 °C for 2 h to form PpRH_{TP}. Next, the mixture was cooled down and transferred into a 12-well plate for 24 h. After crosslinking at 70 °C, the crosslinked PpRH_{TP} was washed with DMSO, and the solvent was exchanged with water (1 M Na₂SO₄) for 24 h. The hydrogels were cut into cylinders with diameters of 8~10 mm and heights of 5~6 mm for further investigations.

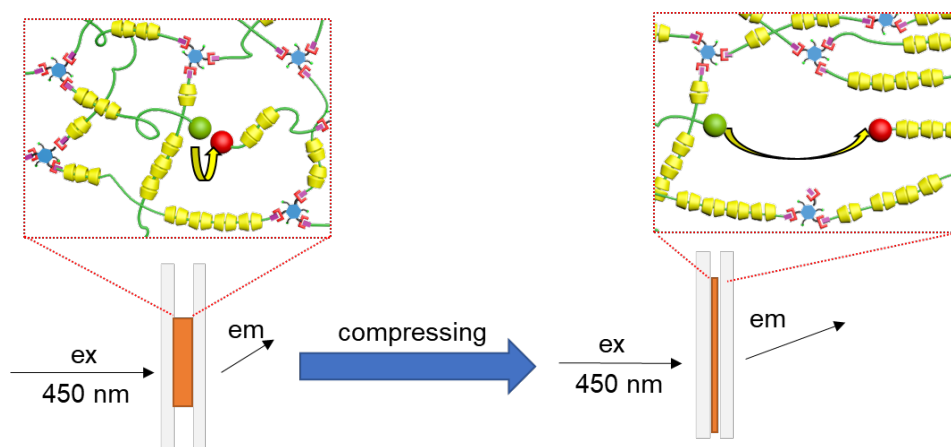


Figure S64. Schematic illustration of the fluorescence emission measurements of kPH-1 doped with FRET pairs at different compressive strains.

Mechanochromic responsive experiment: The prepared kPH-1_{REFT} hydrogels were sandwiched between two glass slides and compressed to different strains for fluorescent measurements. Fluorescent measurements were performed on the Horriba QuantaMaster Fluorescence System with a solid sample holder to clamp the prepared samples. The excitation wavelength is 450 nm, and the incidence angle is about 45°.

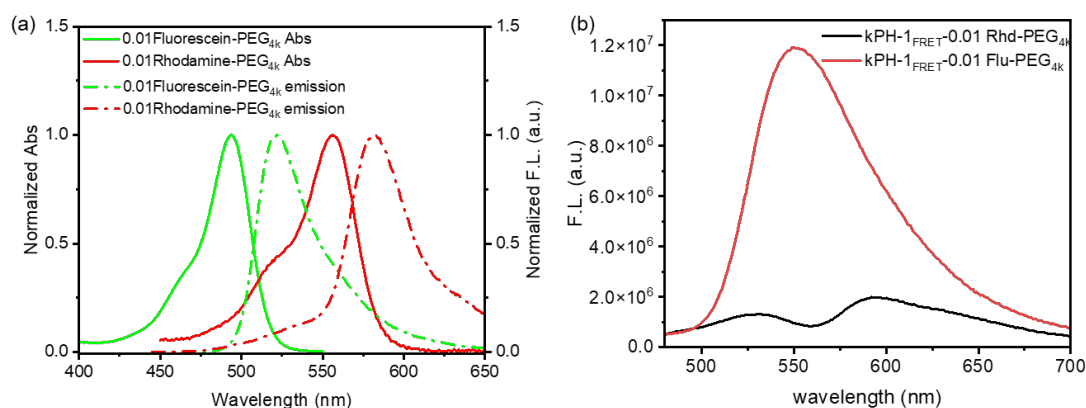


Figure S65. (a) Normalized absorption and emission spectra of the aqueous solutions of 0.01 Rhod-PEG_{4k} and 0.01 Flu-PEG_{4k}. (b) Emission spectra of kPH-1_{REFT} with 0.01 Rhod-PEG_{4k} and Flu-PEG_{4k}. $\lambda_{\text{ex}} = 450 \text{ nm}$.

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