

Dynamic covalent polymer networks with mechanical and mechanoresponsive properties reinforced by strong hydrogen bonding

Wenli Gao,^a Rui Tang,^a Minghao Bai,^a Hengzhe Yu,^a Yonghong Ruan,^a Jinli Zheng,^a Yinjun Chen*^b and Wengui Weng*^a

^aDepartment of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian 361005, China

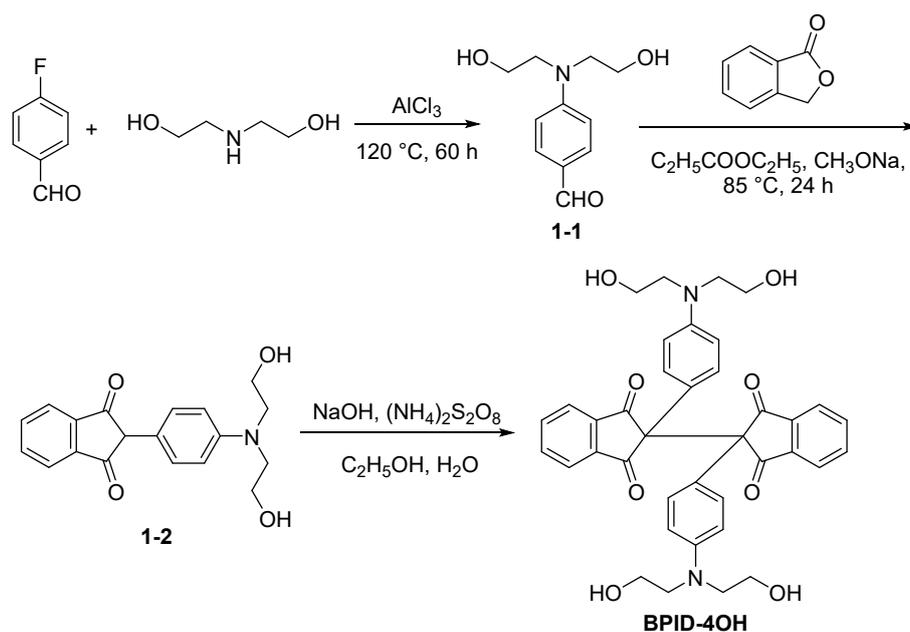
^bState Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

Experimental details

1. Materials

Reagents and solvents were used as received without purification unless otherwise stated. All reagents, chemicals, and solvents were purchased from Energy Chemical, Heowns, and Sinopharm. Poly(tetra methylene ether glycol) (PTMG, $M_n = 1000$ g/mol) was dried at 100 °C under vacuo for 3 h before use.

1.1 Synthesis of BPID-tetrahydroxy (BPID-4OH) mechanophore

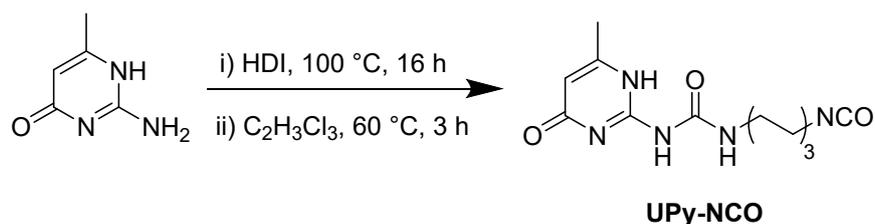


Scheme S1. Synthesis route for tetrahydroxy crosslinker **BPID-4OH**.

Tetrahydroxy crosslinker **BPID-4OH** was synthesized as our previous reports.¹ Anhydrous aluminum chloride (1.0 g, 7.50 mmol) and diethanolamine (67.5 g, 0.64 mmol) were mixed in a 250 mL flask, and then p-fluorobenzaldehyde (20 g, 0.16 mmol) was added and the reaction was conducted at 120 °C for 60 h. The reaction mixture was diluted with 120 mL water at room temperature and neutralized by 10% hydrochloric acid. Subsequently, the mixture was extracted 6 times with n-butanol at 65 °C. The organic phase was dried in vacuum. The crude product was purified by silica column chromatography and afford an orange red solid, compound **1-1** (14.0 g, 41.5% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 9.50 (s, 1H), 7.56-7.55 (d, *J* = 8.45 Hz, 2H), 6.63-6.62 (d, *J* = 8.5 Hz, 2H), 4.67 (s, 2H), 3.80-3.78 (t, *J* = 4.7 Hz, 4H), 3.59-3.57 (t, *J* = 4.7 Hz, 4H).

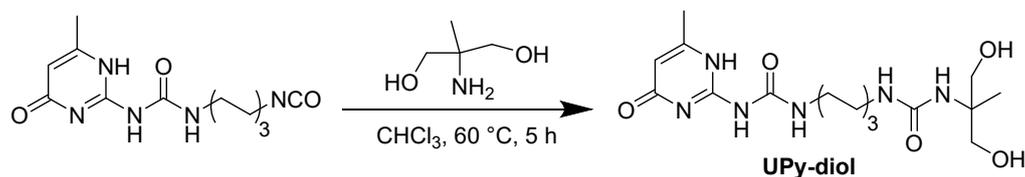
Compound **1-1** (5.61 g, 0.0268 mmol) and benzophthalide (4.314 g, 0.0322 mmol) were dissolved into 24 mL ethyl propionate in a flask. The solution was then mixed with a newly prepared sodium methoxide solution in ice bath. The solution was refluxed at 85 °C for 24 h, and then cooled down to room temperature. The solvent was removed under reduced pressure to afford a black powder. The powder was dispersed in water and extracted with dichloromethane (DCM). The aqueous phase was collected. 10% hydrochloric acid was added dropwise into the aqueous phase and offered a solution with a pH value of 4. Deep red precipitation was collected and dried in vacuum to offer the compound **1-2** (5.0 g, 38.6% yield). Next, 3.25 g compound **1-2** (10 mmol) was dissolved in 50 mL anhydrous ethanol at 50 °C. After 10 min, 100 mL NaOH (1.72 g, 75 mmol) solution was added. (NH₄)₂S₂O₈ (4.56 g, 420 mmol) was dissolved in 150 mL deionized water at 90 °C, and then slowly added dropwise into the solution above. After 5 min, a bright yellow powder was obtained by filtration. The powder was purified by recrystallization to offer 1 g of **BPID-4OH** compound with a yield of 30.8%. ¹H NMR (500 MHz, (CD₃)₂CO): δ (ppm) = 7.89 (m, 8H), 6.95-6.94 (d, *J* = 8.4 Hz, 4H), 6.59-6.58 (d, *J* = 8.4 Hz, 4H), 4.19 (s, 4H), 3.71 (m, 8H), 3.53 (m, 8H).

1.2 Synthesis of UPy-hexyl isocyanate (**UPy-NCO**)



UPy-NCO was synthesized according to our literature method previously.² 2-Amino-4-hydroxy-6-methylpyrimidine (2.5 g, 20 mmol) and hexamethylene diisocyanate (HDI) (23.75 mL, 148 mmol) were mixed into a flask. The mixture was heated at 100 °C for 16 h in a nitrogen atmosphere and cooled down to 60 °C. Trichloroethane was injected into the solution above, and the reaction was conducted at 60 °C for 3 h. After filtration, a white powder was obtained and pure **UPy-NCO** was gained (5.6 g, 95.2% yield) by washing the white powder with a mixed solvent of n-hexane and ether (6:1 in volume). ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 13.11 (s, 1H), 11.86 (s, 1H), 10.15 (d, *J* = 34.1 Hz, 1H), 5.82 (s, 1H), 3.321-3.224 (m, 2H), 2.23 (s, 2H), 1.68-1.54 (m, 3H).

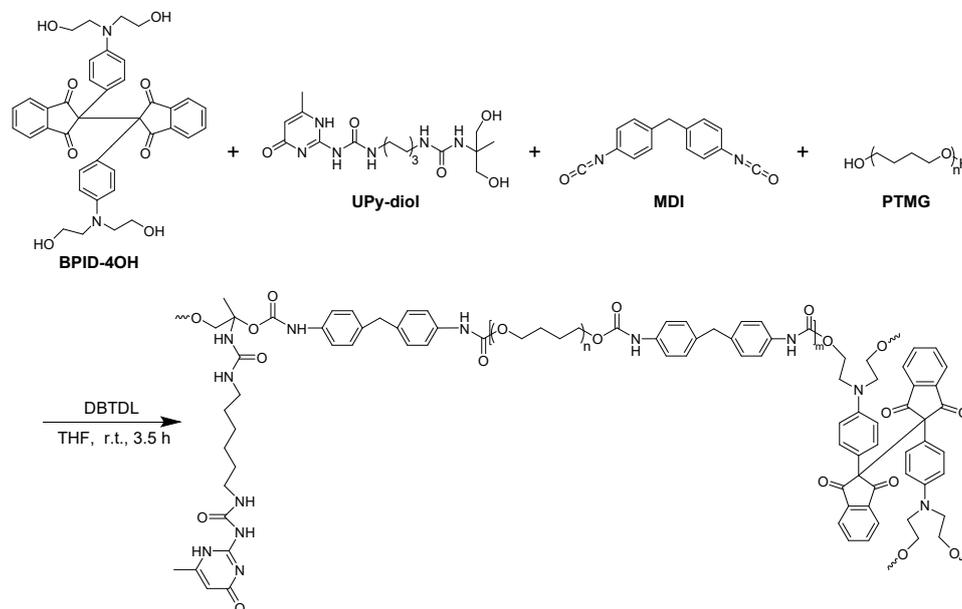
1.3 Synthesis of tetra hydrogen bonding moiety (**UPy-diol**)



UPy-diol was prepared by the reaction between **UPy-NCO** and 2-amino-2-methyl-1,3-propanediol (**AMPD**).³ **UPy-NCO** (5 g, 17.1 mmol) and **AMPD** (2.44 g, 23.2 mmol) were mixed in 20 mL anhydrous CHCl₃ at 60°C. After 5 h, the white solid was filtrated, washed with CHCl₃, and dissolved in DMF. The solution was centrifuged with a rotate speed of 3000 rpm for 5 min. Liquid phase was collected and added dropwise into large amount of diethyl ether and white precipitate generated. The precipitate was filtrated and washed with acetone and diethyl ether for 3 times, respectively. After drying in vacuum, 5.89 g white solid of **UPy-diol** was afforded (5.98 g, 88% yield). ¹H NMR (500 MHz, DMSO-*d*₆): δ (ppm) = 7.51 (s, 1H), 6.18 (t, *J* = 5.3 Hz, 1H), 5.78 (s, 1H), 5.65 (s, 1H), 5.10 (t, *J* = 5.5 Hz, 1H), 3.45-3.24 (m, 3H), 3.12 (dd, *J* = 12.8, 6.5 Hz, 1H),

2.92 (dt, $J = 22.2, 11.0$ Hz, 1H), 2.63-2.44 (m, 1H), 1.37 (ddd, $J = 43.7, 25.3, 4.9$ Hz, 3H), 1.09 (s, 1H).

1.4 Synthesis of labelled polyurethane networks:



Scheme S2. Synthetic route of dual dynamic crosslinking network polyurethane **PU-H₅**.

PTMG was heated to 90 °C and dried in vacuum for 4 h before polymerization. Subsequently, PTMG (1 g, 1.0 mmol), methylene diphenyl diisocyanate (MDI) (360 mg, 1.5 mmol), **UPy-diol** (70 mg, 0.18 mmol) and dibutyltin dilaurate (DBTDL) (5 μ L) were mixed in 5 mL DMF at 30 °C under N₂ atmosphere. After 2 h, **BPID-4OH** (65 mg, 0.1 mmol) in 3 mL DMF was added into the mixture above. After that, DBTDL (5 μ L) was fed into the mixture. After 2 h, the viscosity of mixture significantly increased. The viscous polymers were poured into Teflon mold and centrifuged at 3000 rpm for 3 min to remove the bubble in mixture. The polymerization was continued at 80 °C for 24 h and then dried at 60 °C for 48 h in vacuum to afford a polymer film.

To verify the reinforcement of mechanical properties by hydrogen bond, another two polymer networks were synthesized by tailoring the mole ratio of UPy motif. The detailed information for the polymerization were shown in Table S1 and the synthesized procedure was described above as the synthesis of **PU-H₅**. Then **PU-H_{2.5}** and **PU-H₀** were afforded.

Table S1. Parameter of different compounds used for polymerization

Polymers	BPID-4OH	PTMG	MDI	Catalyst (DBTDL)	UPy-diol	Weight percent (UPy-diol, wt%)
PU-H₅	64.8 mg	1.0 g	350 mg	5 μ L	70 mg	5
PU-H_{2.5}	64.8 mg	1.0 g	325 mg	5 μ L	35 mg	2.5
PU-H₀	64.8 mg	1.0 g	300 mg	5 μ L	0	0

2. Measurement

2.1 NMR

NMR spectra were recorded in CDCl₃ (δ = 7.26 ppm), (CD₃)₂CO (δ = 2.05 ppm), or DMSO-*d*₆ (δ = 2.49 ppm) and referenced to the residual solvent signals on a 500 MHz Bruker Avance III spectrometer with tetramethylsilane (TMS) as an internal standard.

2.2 Uniaxial tensile tests

'Dog-bone' shaped specimens were punched from polymer films with a cutter. Uniaxial tensile tests were carried out on the Instron 3343 machine with a strain rate of 0.05 s⁻¹. Additional two small pieces of the same specimen were localized on each side of the samples to minimize slippage. To get more accurate data, two black markers were labeled on the surface of specimen, and videos were made to record the variation of the two-marker positions. Images extracted out from videos were used to monitor the deformation of materials. Positions of black marks in each image was obtained by Image J and the value of engineering strain of samples was the variation of two-marker position. To ensure the credibility of data, tensile tests were repeated at least three times for each sample.

2.3 Dynamic Mechanical Analysis (DMA)

Creep tests were carried out on a TA Instruments DMA 850. Rectangle samples with a dimension of 20 mm \times 3 mm (length \times width) were performed measurements. A

stress of 0.1 N was applied to the sample for 600 s, and strain was detected. **PU-H₅**, **PU-H_{2.5}** and **PU-H₀** were heated to desired temperatures ranging from -10 °C to 100 °C, 10 °C to 100 °C, and 10 °C to 90 °C, respectively.

2.4 Small angle X-ray scattering (SAXS)

All scattering tests were carried out with an Anton-Paar SAXSess mc² platform equipped with slit collimation (slit dimensions: 20 mm × 0.33 mm). The scattering vector is defined as $q = 4\pi/\lambda\sin(\theta)$, where λ is the wavelength of the X-ray beam (0.1542 nm) and 2θ is the scattering angle. The camera length was calibrated to be 260 mm using silver behenate standard with (001) peak position at $q = 1.076 \text{ nm}^{-1}$. For strain-dependent SAXS tests (SD-SAXS), specimens were slowly stretched until the distance between the two black markers achieved the expected values. They were then tightened into sample clamps. For variable temperature SAXS tests (VT-SAXS), films were heated to desired temperatures ranging from 25 °C to 145 °C. At each temperature, films were first equilibrated for 5 min to ensure thermal equilibration. Typical exposure time was 20 min for both SD-SAXS and VT-SAXS.

2.5 Self-healing experiment

A notch was made on the polymer films of **PU-H₅**, **PU-H_{2.5}** and **PU-H₀** by a razor blade, respectively. Notched samples were spliced with force and heated to 100 °C for 1 h in oven. The damaged area was recorded by a VHX-600 digital microscope before and after self-healing treatment. The specimens with varying self-healing treatment time ranging from 1 h to 24 h were then performed uniaxial tensile tests to quantify the self-healing properties.

2.6 RGB analysis

Videos (25 FPS) were made by a SONY camera (HDR-CX210) during tensile tests to record the deformation and mechanochromics of polyurethane networks. Videos then were used for RGB analysis. To begin, images were extracted out from videos and imported into Image J to measure the distance between two black marks, which were

labeled on one of the surfaces of specimen. Then the precise deformation was calculated by dividing the original length of two marks into their distance. Subsequently, images alternating with 100% deformation were chosen for RGB analysis. Images were imported into Image J software again and the average values of R, G and B were detected directly in Image J software by selecting the interest region of samples. Here, R, G and B represent the average chromatic values of red, green and blue channels in the interest region of samples. The chromatic ratio of G/R was used to evaluate the color change of materials. To obtain the critical strain of color change, CIE was performed based on the values of chromatic ratio and corresponding strain.

2.7 Reprocessing experiment

Polymer films of **PU-H₅** were cut into small pieces by scissors, and then dissolved into DMF with a concentration of 15 mg/mL. The polymer solution was heated to 80 °C for 5 h, and then poured into a Teflon mold, centrifuged at 3000 rpm for 3 min to remove air bubbles in solution and dried at 80 °C for 24 h. The residual solvent was gradually evaporated in vacuum at 70 °C for 24 h to afford a new polymer film. The reprocessed films were then performed uniaxial tensile test to ensure the stability of mechanical properties before and after reprocessibility.

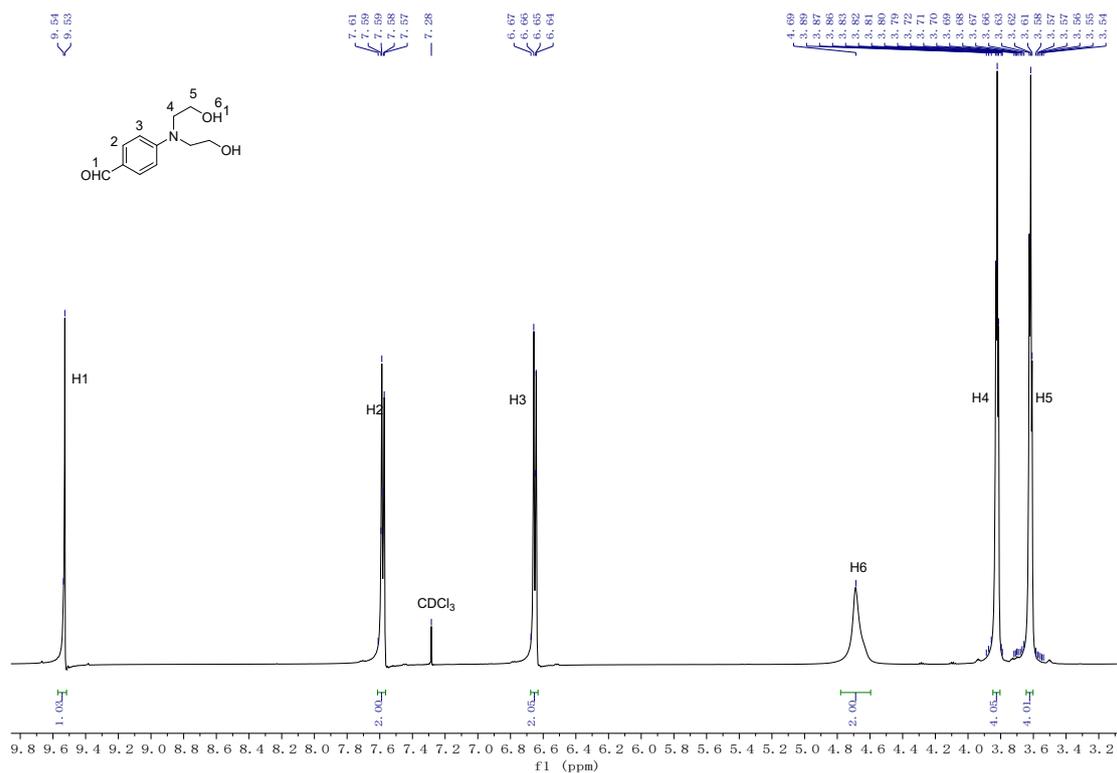


Figure S1. ¹H-NMR spectrum of Compound 1-1.

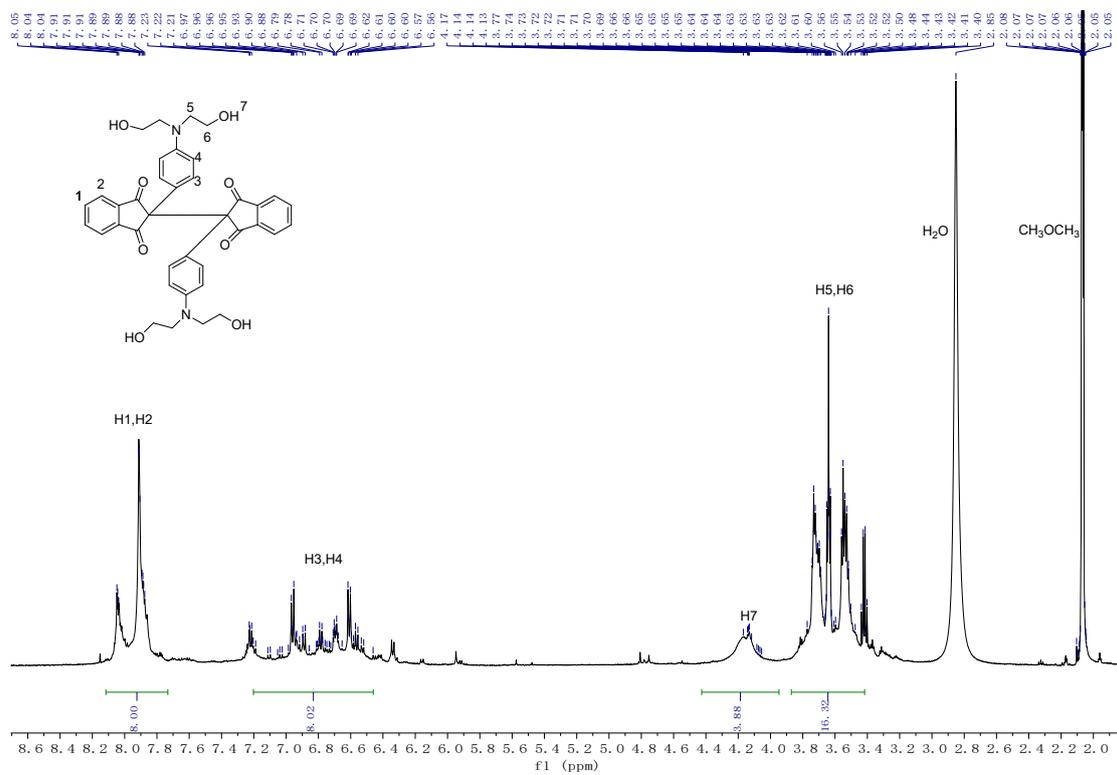


Figure S2. ¹H-NMR spectrum of BPID-4OH mechanophore.

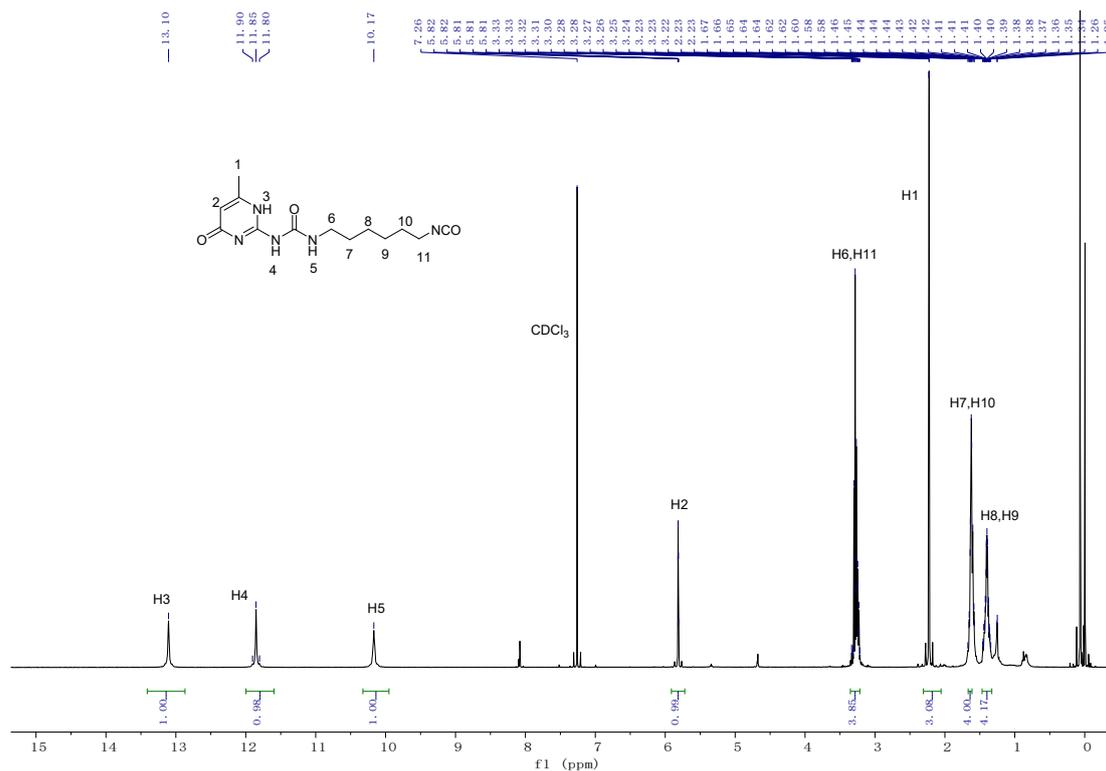


Figure S3. $^1\text{H-NMR}$ spectrum of UPy-NCO compound.

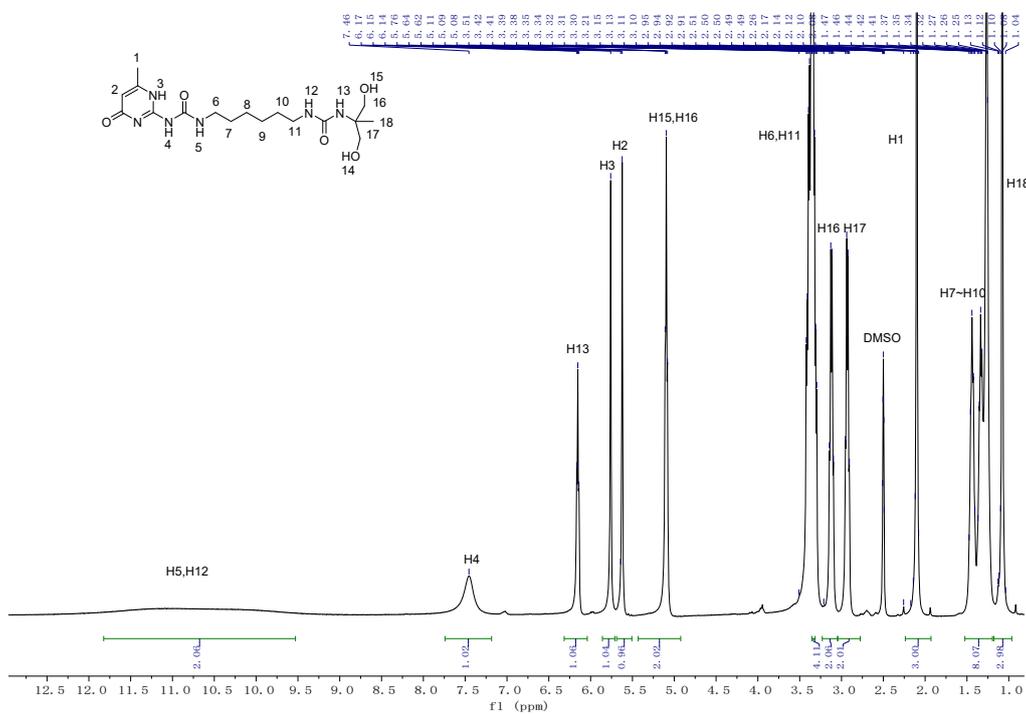


Figure S4. $^1\text{H-NMR}$ spectrum of UPy-diol compound.

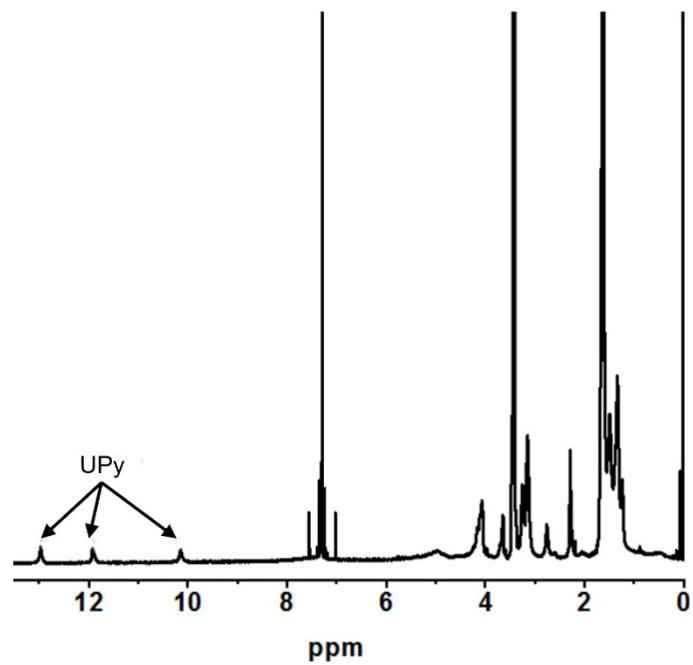


Figure S5. $^1\text{H-NMR}$ spectrum of PU-H_5 .

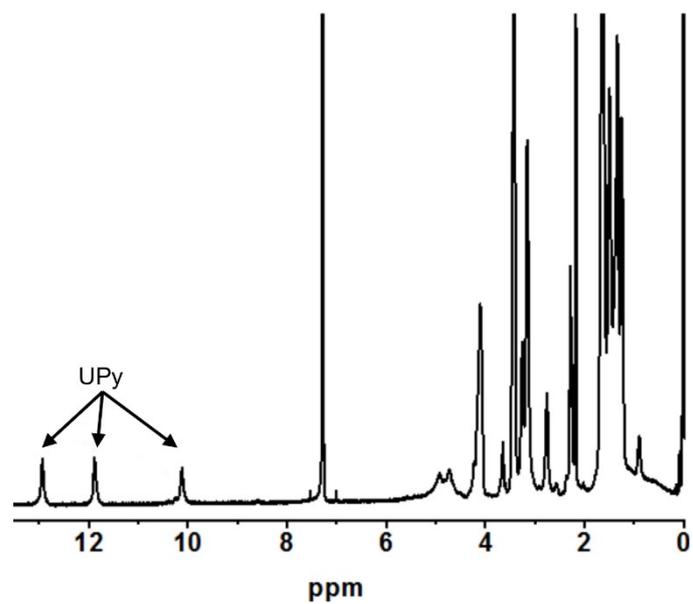


Figure S6. $^1\text{H-NMR}$ spectrum of $\text{PU-H}_{2.5}$.

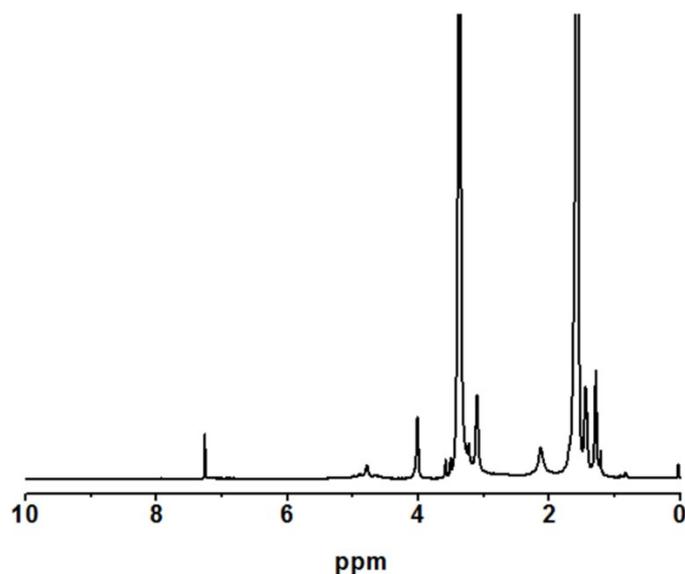


Figure S7. $^1\text{H-NMR}$ spectrum of PU-H_0 .

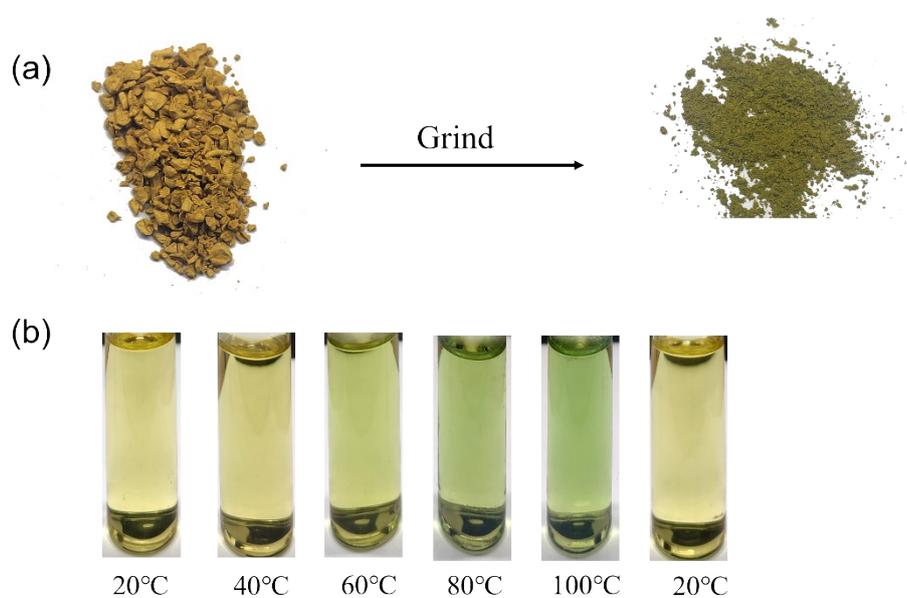


Figure S8. **BPID-4OH** can be activated by mechanical force and heating. (a) Powder of **BPID-4OH** was grinded and dissociated into two radical motifs accompany with a color change from yellow to green. (b) **BPID-4OH** was dissolved into *N,N*-dimethylformamide and then was heated up to 100 °C. The color of solution gradually changed from yellow to green and when cooling down it returned to yellow. It illustrated the reversible dissociation of **BPID** mechanophore.

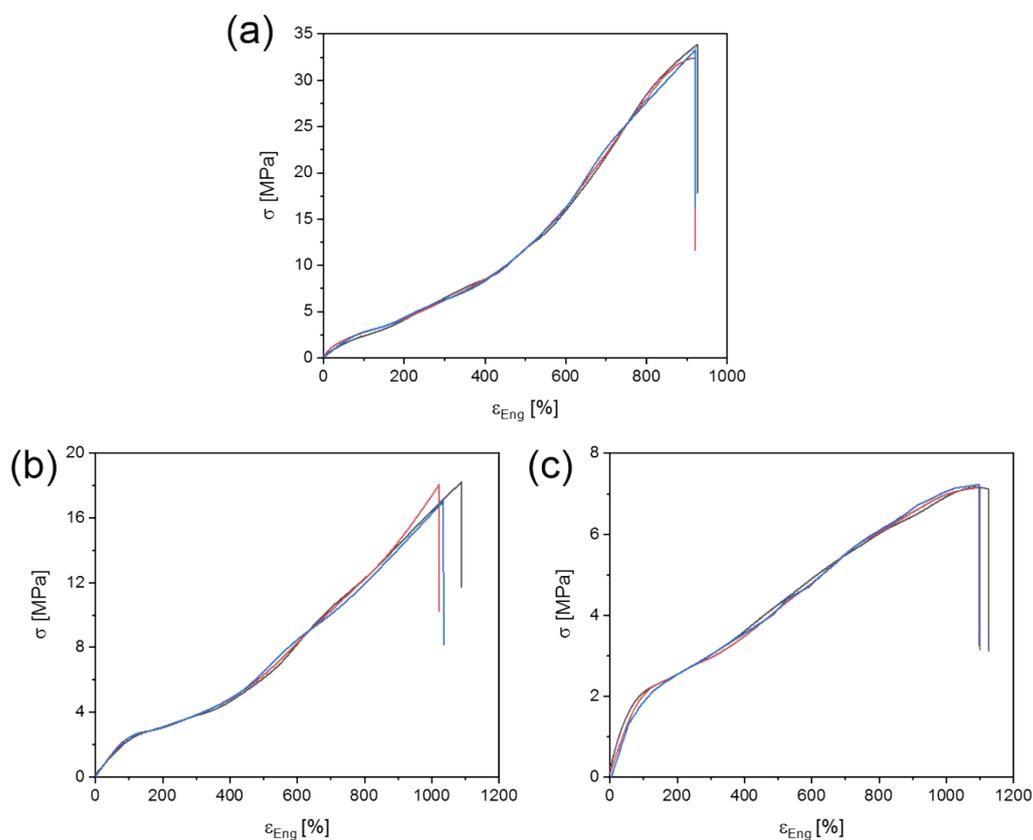


Figure S9. The stress-strain curves of (a) **PU-H₅**, (b) **PU-H_{2.5}** and (c) **PU-H₀** samples at room temperature. Uniaxial tensile tests were performed with dog-bone shape of specimens and three specimens were measured for each type of materials.

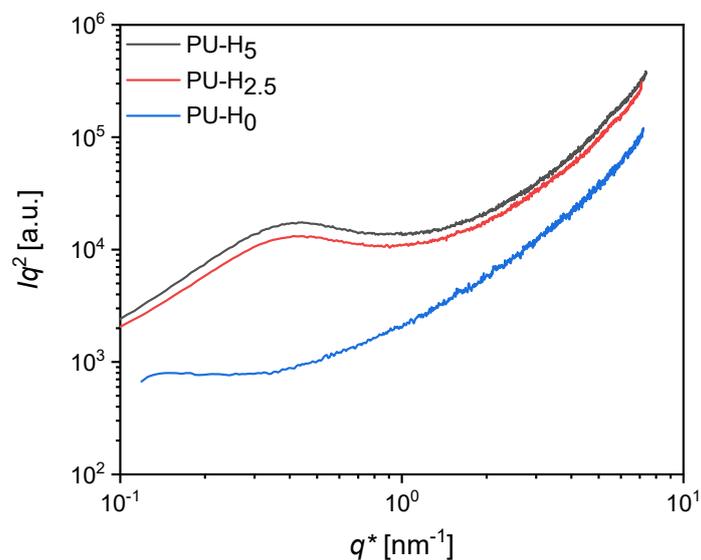


Figure S10. SAXS data of polyurethane networks at room temperature after Lorentz correction.

Table S2. Mechanical properties of polyurethane networks

Polymers	PU-H ₅	PU-H _{2.5}	PU-H ₀
Young's modulus (E/MPa)	3.21±0.55	3.06±0.48	2.54±0.39
Strain at break (%)	921±24	1047±26	1105±33
Ultimate stress (MPa)	33.09±3.4	17.76±2.6	7.20±1.3
Toughness (MPa)	123.6±10.6	87.2±8.8	49.6±5.0

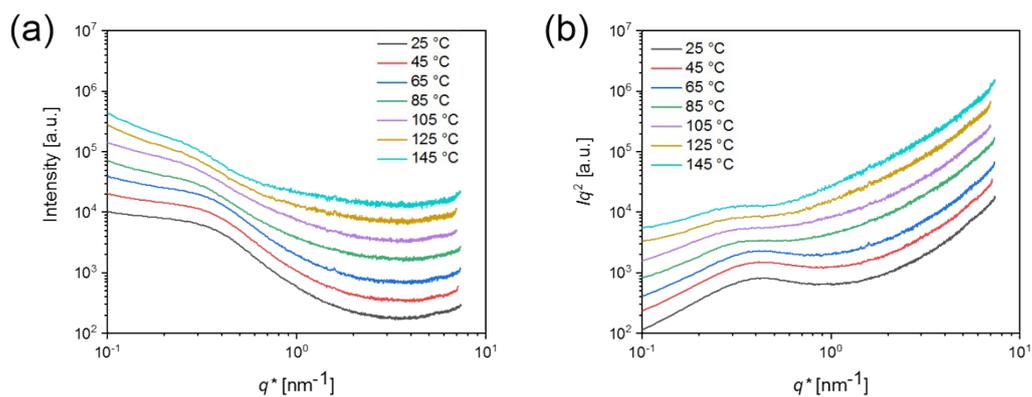


Figure S11. The SAXS data of PU-H₅ at varying temperatures (a) before and (b) after Lorentz transformation.

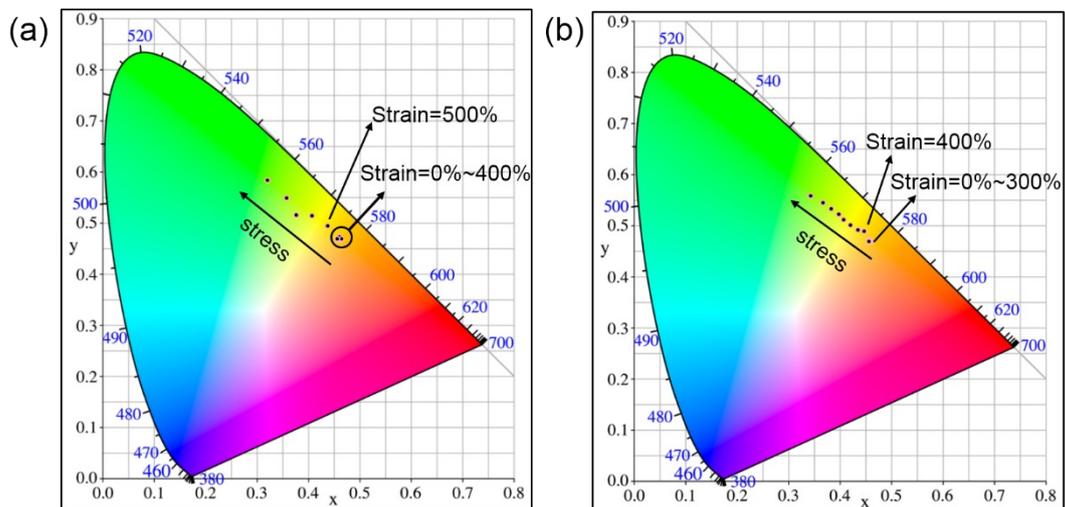


Figure S12. Videos were made during tensile tests to record the color change of samples. Images extracted out from the videos were used to do RGB analysis, then RGB values were used to plotted CIE images. (a) and (b) were the CIE image of PU-H₅ and PU-H₀ samples, respectively.

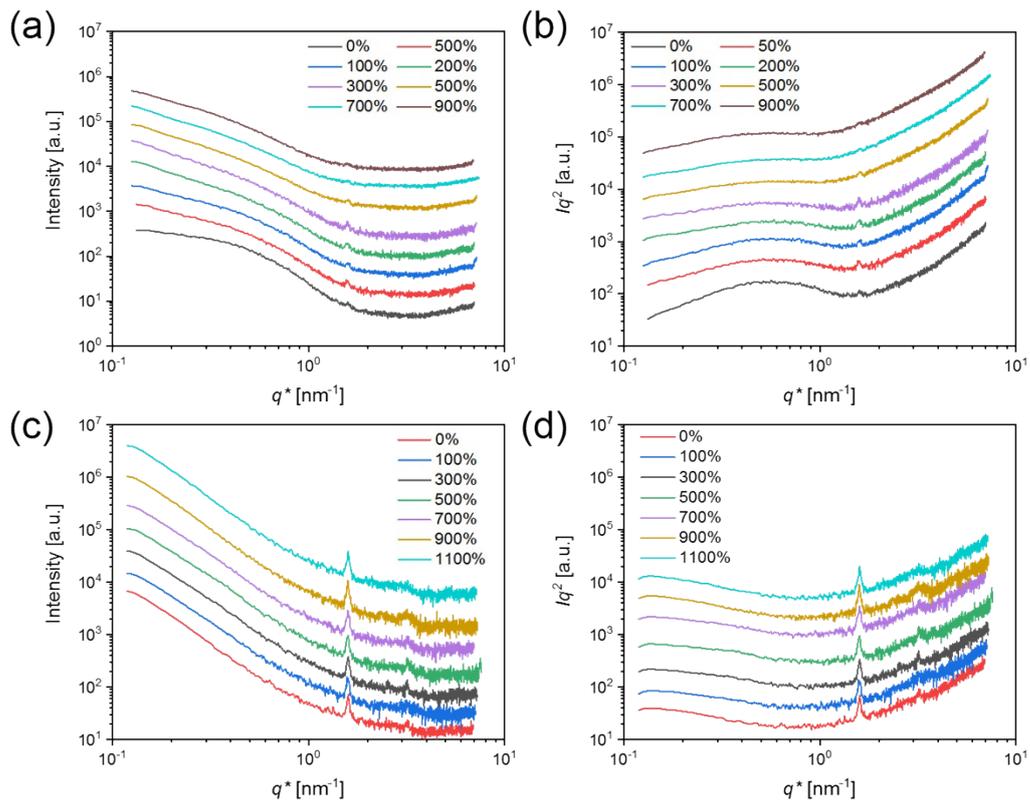


Figure S13. The SAXS data of $PU-H_5$ samples (a) before and (b) after Lorentz transformation at varying deformations, and the SAXS data of $PU-H_0$ samples (c) before and (d) after Lorentz transformation.

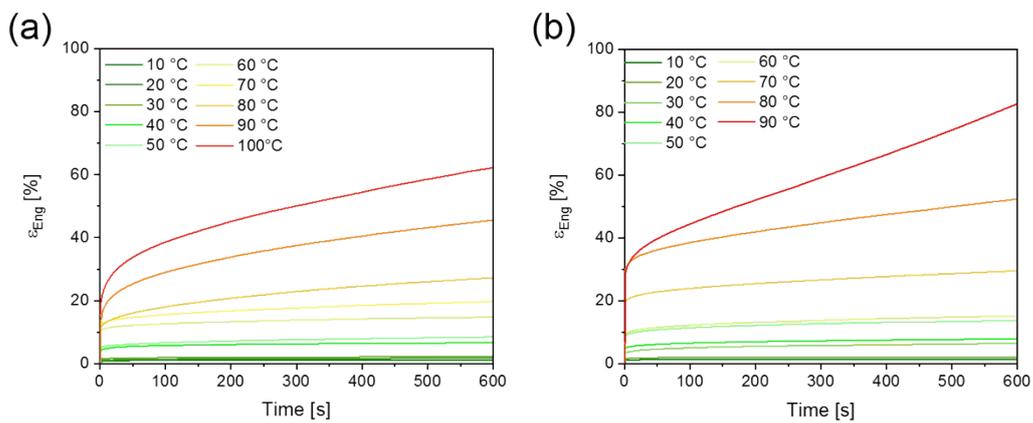


Figure S14. (a) $PU-H_{2.5}$ and (b) $PU-H_0$ samples were performed creep measurement.

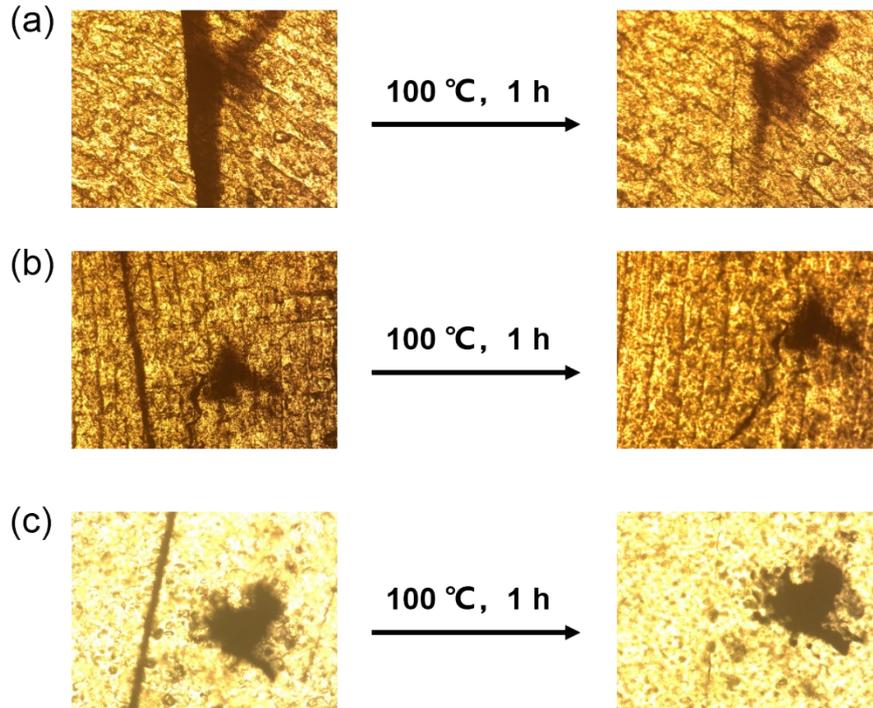


Figure S15. Self-healing properties of polyurethane networks were detected at 100 °C. When a notch on a specimen was spliced at 100 °C. The gap disappeared after 1 h. (a), (b) and (c) were the images of **PU-H₅**, **PU-H_{2.5}** and **PU-H₀** samples before and after self-healing treatment.

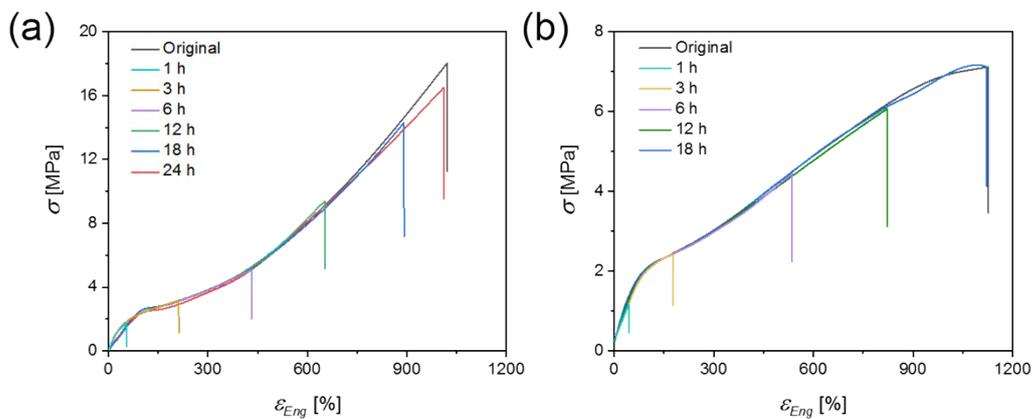


Figure S16. After self-healing in different times, (a) **PU-H_{2.5}** and (b) **PU-H₀** samples were measured by uniaxial tensile tests.

Table S3. Comparison of the healing efficiency of this work and other reports

Sample	Healing condition	Healing efficiency (%)	Ref.
PU-H₀	100 °C, 24 h	97.91±17.08	This work
PU-H_{2.5}	100 °C, 24 h	88.24±15.87	This work

PU-H ₅	100 °C, 24 h	93.99±14.44	This work
PT-HM-U0	100 °C, 24 h	41.8±11.6	3
PT-HM-U10	100 °C, 24 h	86.2±15.5	3
PT-HM-U20	100 °C, 24 h	92.7±12.3	3



Figure S17. Reprocessing procedure of **PU-H₅** samples: small pieces of polyurethane network were immersed in DMF and heated to 80 °C for 5 h to form a homogenous solution. Subsequently, the solution was poured into Teflon mold for recasting and a new polyurethane film was afforded after drying in vacuo.

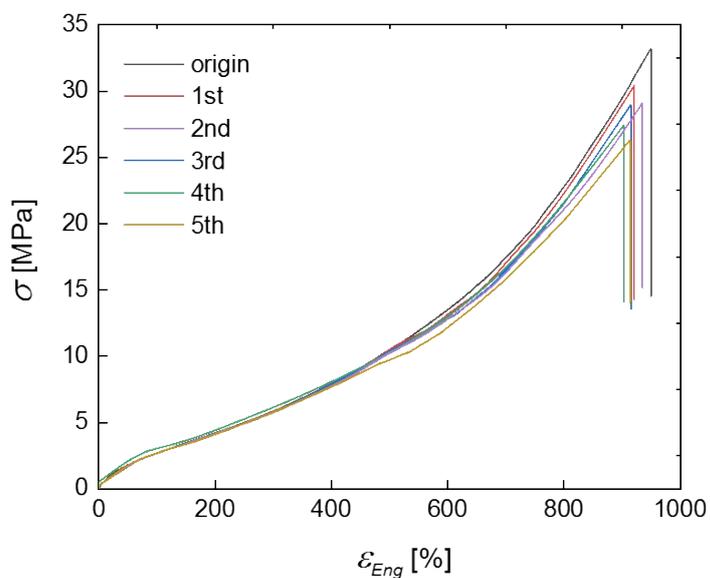


Figure S18. Stress-strain curves of **PU-H₅** samples after performing different cycles of reprocessing.

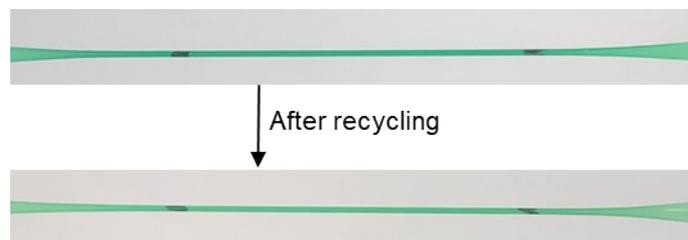


Figure S19. Mechanochromism of a **PU-H₅** at the same strain before and after recycling. Little difference in the color change was observed before and after recycling.

3. References

- 1 L. Yang, P. Ouyang, Y. Chen, S. Xiang, Y. Ruan, W. Weng, X. He and H. Xia, *Giant*, 2021, **8**, 10069.
- 2 H. Zhang, Y. Chen, Y. Lin, X. Fang, Y. Xu, Y. Ruan and W. Weng, *Macromolecules*, 2014, **47**, 6783-6790.
- 3 Y. Song, Y. Liu, T. Qi and G. L. Li, *Angew Chem Int Edit*, 2018, **57**, 13838-13842.