# Supporting Materials

## Mechanically robust, exceptionally recyclable and shape memory cross-linked network based on reversible dynamic urea bonds

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**Characterization:**

Fourier transform infrared (FTIR) spectra were conducted by using infrared spectrophotometer (Nicolet-560, Nicolet Co., USA) in the wavenumber range of 400-4000 $cm^{-1}$ with a resolution setting of 4 $cm^{-1}$. The morphologies were observed by using a scanning electronic microscope (SEM, JEOLJSM-5900LV, Japan) under an accelerated voltage of 15 kV. Dynamic mechanical analysis (DMA) was conducted by using a TA Instruments Q800 apparatus (USA) from -80 to 190 °C at a heating rate of 5 °C $min^{-1}$. DMA can also be characterized the stress relaxation, creep and recovery experiments, and dilatometry experiments in a stress relaxation mode at the setting strain of 5%, in a creep mode held stress for 10 min and removed stress for 20 min, in a controlled force at 0.08 N, respectively. Shape memory effect was quantitatively surveyed by DMA in a strain rate mode at the setting stress of 1.8 MPa. The differential scanning calorimetry (DSC) curve was measured via 204 instrument (NETZSCH, Germany) from -70 to 150 °C under a nitrogen atmosphere at a heating rate of 10 °C $min^{-1}$. Thermogravimetric analysis (TGA) was performed on a TA Instruments SDT-Q600 thermal analyzer from 25 to 600 °C under a nitrogen atmosphere at a heating rate of 10 °C $min^{-1}$. The transmittance of HTPUs films was measured by an ultraviolet visible light photometer (UV3600, Shimadzu, Japan). Rheological measurements were performed on flat melt-pressed disks using a HAKKE-MARS Ⅲ rheometer equipped with 20 mm plate-plate geometries and disk-shaped

specimens (20 mm diameter; 1 mm thick). Frequency sweeps from 100 to 0.01 rad $s^{-1}$ were performed at various temperature with a strain of 0.5%, which is in the linear viscoelastic regime. Mechanical properties were tested by using an Instron-4302 mechanical tester (USA) at a constant tensile rate of 50 mm $min^{-1}$ under room temperature. Solvent resistance experiment was conducted via soaking a wafer sample in different solvent that replaced by a new solvent every day. Gel contents were obtained by Soxhlet extraction experiment in THF at 90 °C.

Table S1 The recipes of hindered thermoset polyurea (HTPUs) elastomers.

| Samples | PTMG1000 | IPDI | DPA | THDI | Molar ratio [a] |
|---|---|---|---|---|---|
| HTPU-1 | 10 g (10 mmol) | 4.45 g (20 mmol) | 2.29 g (20 mmol) | 4.00 g (6.67 mmol) | 3:6:6:2 |
| HTPU-2 | 10 g (10 mmol) | 4.45 g (20 mmol) | 1.53 g (13.33 mmol) | 1.33 g (2.22 mmol) | 9:18:12:2 |
| HTPU-3 | 10 g (10 mmol) | 4.45 g (20 mmol) | 1.31 g (11.43 mmol) | 0.57 g (0.95 mmol) | 21:42:24:2 |

[a] The molar ratio of PTMG1000 : IPDI : DPA : THDI.

In addition the crosslink density ν can be defined as the number of moles of elastically effective network chains per cubic centimeter of sample and calculated by the equation provided by Scanlan (eqn (1))[1, 2]:

$$\nu = \sum_{f=3}^{\infty} \frac{f}{2} C_f \qquad (1)$$

Where $f$ is the functionality of the reactants and $C_f$ is the concentration of the reactant with functionality f, expressed as moles per volume of fully cured polymer. Therefore, crosslink density ν of the prepared HTPU-1, HTPU-2 and HTPU-3 is 0.5 mmol $cm^{-3}$, 0.2 mmol $cm^{-3}$ and 0.09 mmol $cm^{-3}$ respectively.

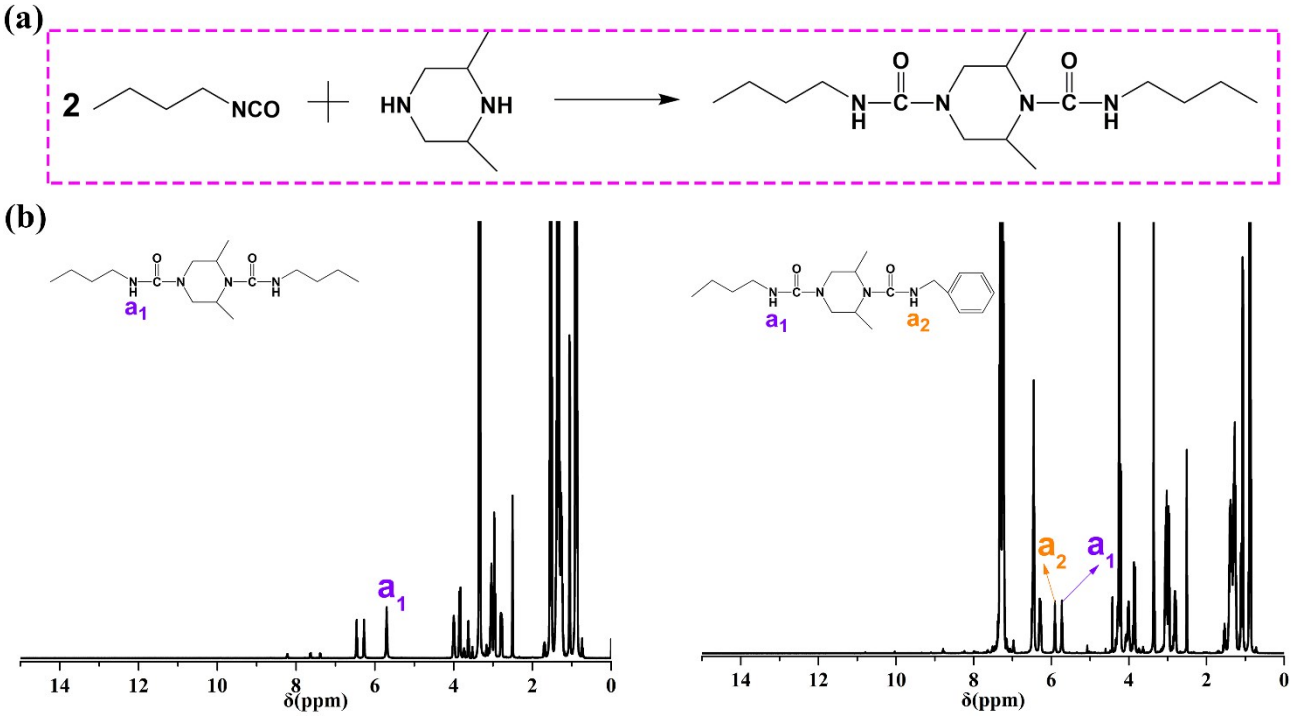


Fig. S1 (a) Schematic synthesis route of a secondary amine (AA), *N,N*$^4$-dibutyl-2,6-dimethylpiperazine-1,4-dicarboxamide. (b) $^1$H NMR spectra of AA and *N*$^1$-benzyl-*N*$^4$-butyl-2,6-dimethylpiperazine-1,4-dicarboxamide (CC).

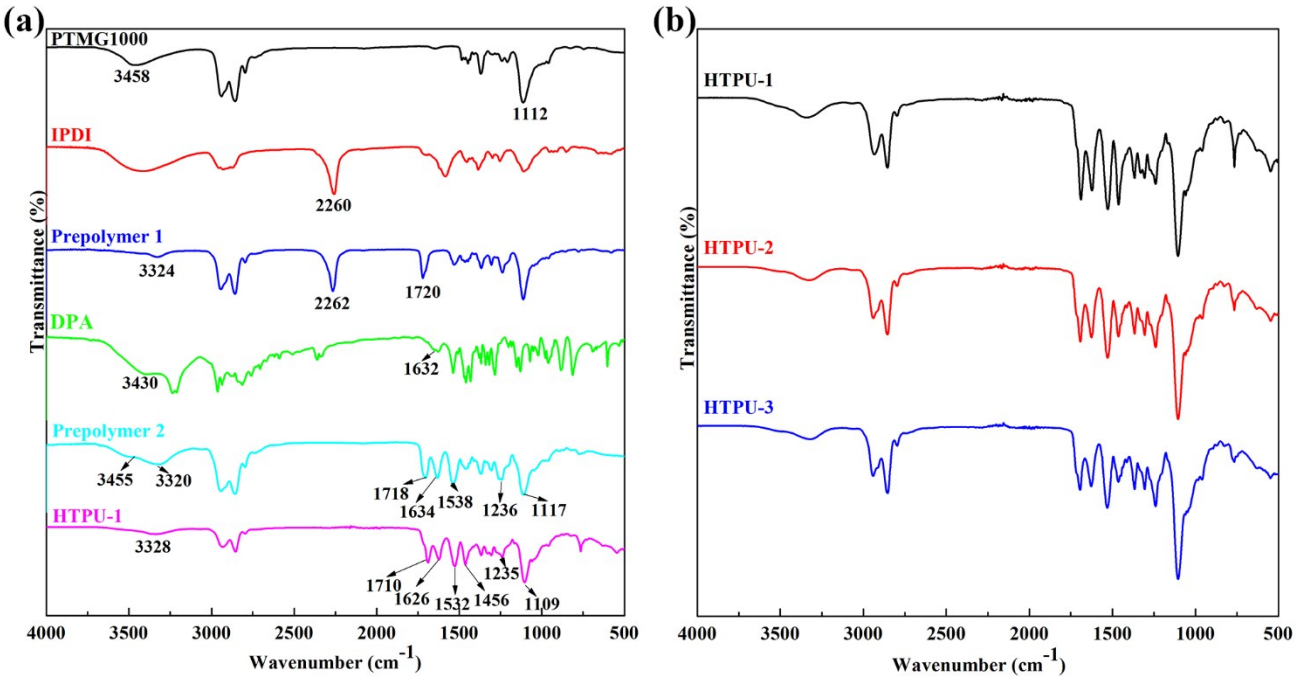


Fig. S2 (a) FTIR spectra of PTMG1000, IPDI, DPA, Prepolymer 1, Prepolymer 2 and HTPU-1; (b) FTIR spectra of HTPU-1, HTPU-2 and HTPU-3.

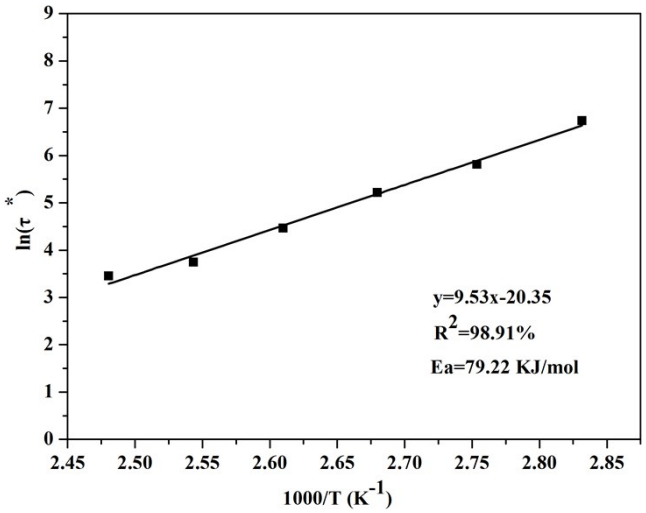


Fig. S3 Fitting of relaxation time-temperature to an Arrhenius equation.

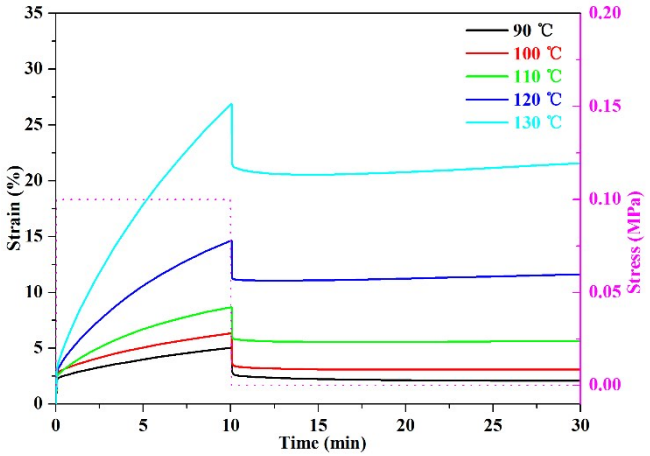


Fig. S4 Creep and recovery curves of HTPU-2 at various temperature.

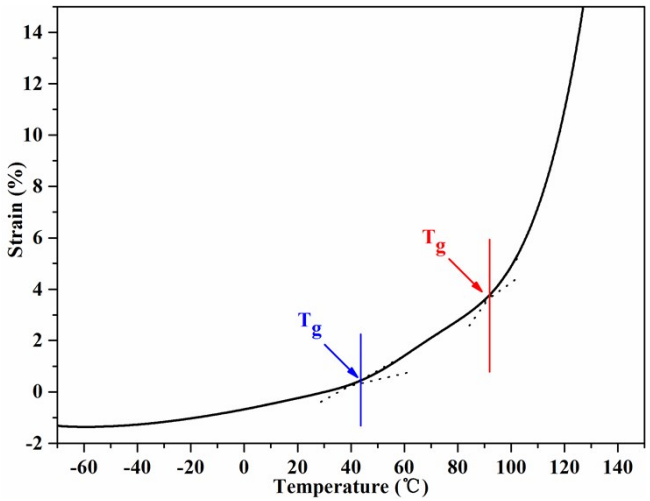


Fig. S5 Temperature dependence of thermal expansion curve of HTPU-2 networks.

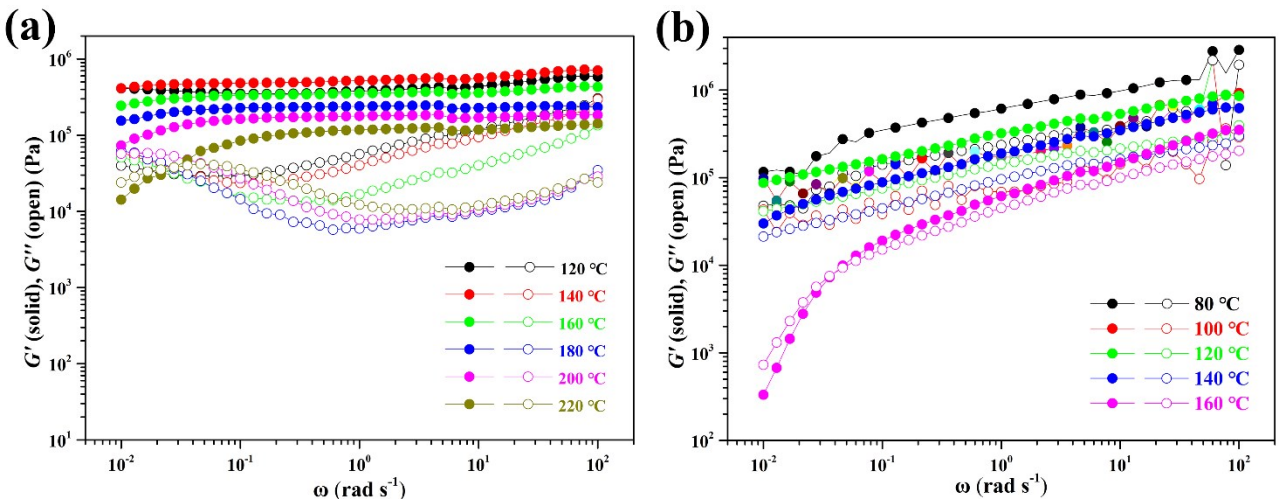


Fig. S6 (a) and (b) Storage (*G′*, solid) and loss (*G″*, open) moduli of HTPU-1 and HTPU-3 versus frequency at temperatures from 100 to 180 °C with a strain amplitude of 0.5%.

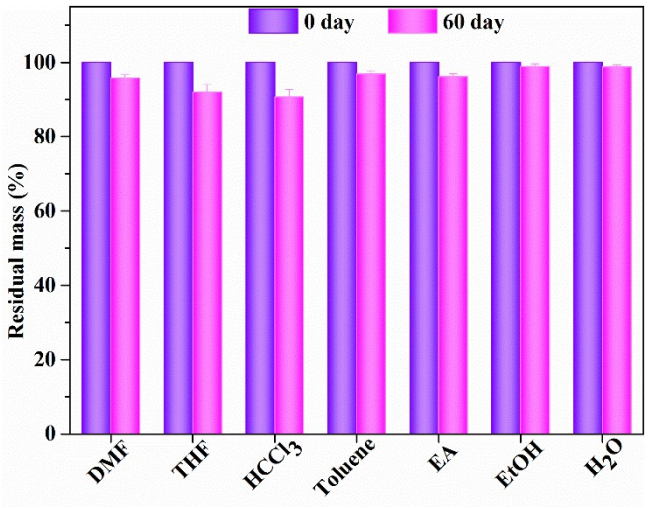


Fig. S7 Residual mass of HTPU-2 soaked in various solvents after 60 days.

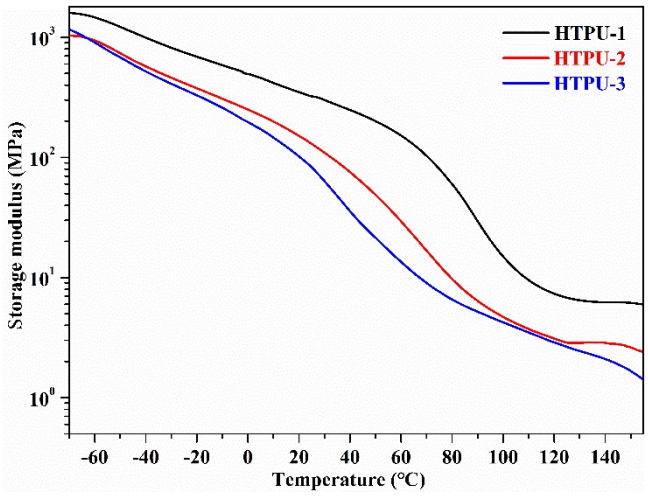

Fig. S8 Storage modulus of HTPU-1, HTPU-2 and HTPU-3.

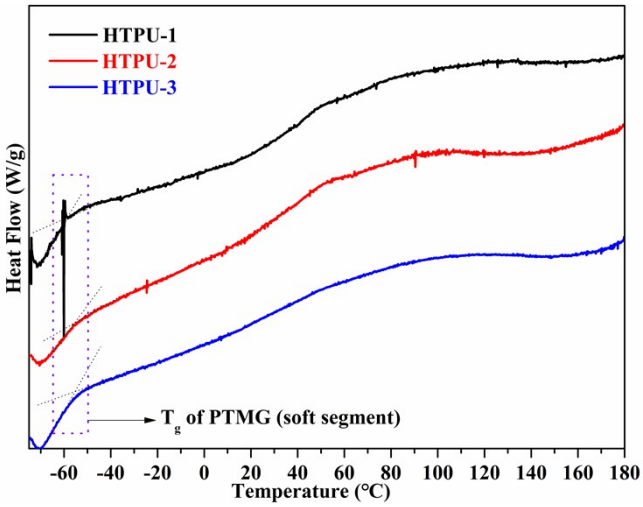


Fig. S9 DSC curves of HTPU-1, HTPU-2 and HTPU-3 from -80 to 190 °C.

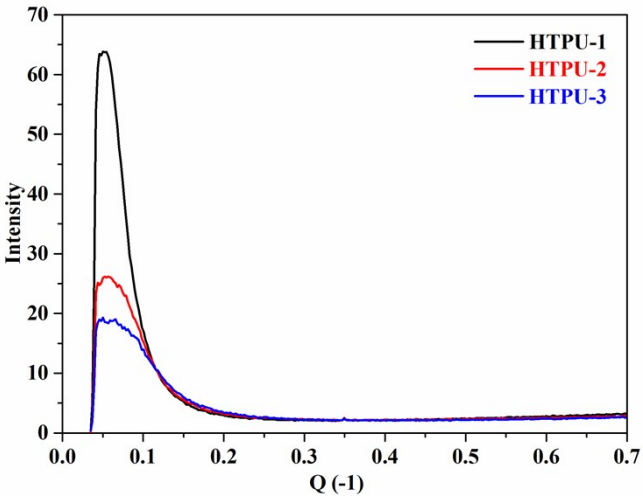


Fig. S10 SASX curves of HTPU-1, HTPU-2 and HTPU-3.

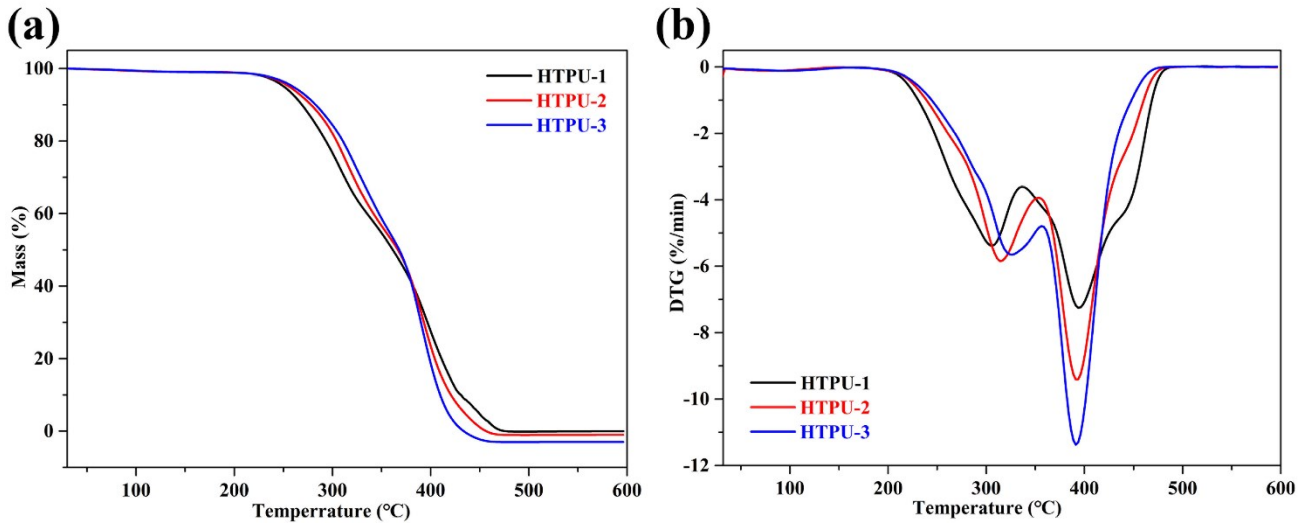


Fig. S 11 (a) TG and (b) DTG curves of HTPU-1, HTPU-2 and HTPU-3.

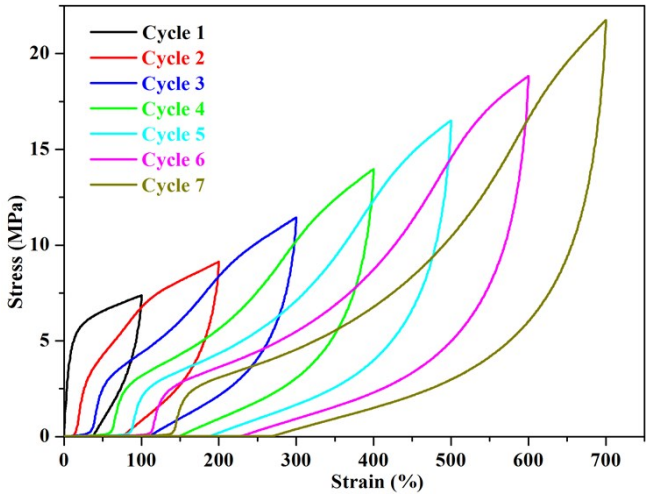


Fig. S12 Successive loading-unloading curves with increasing strains from 100% to 700% of HTPU-2 for seven cycles.

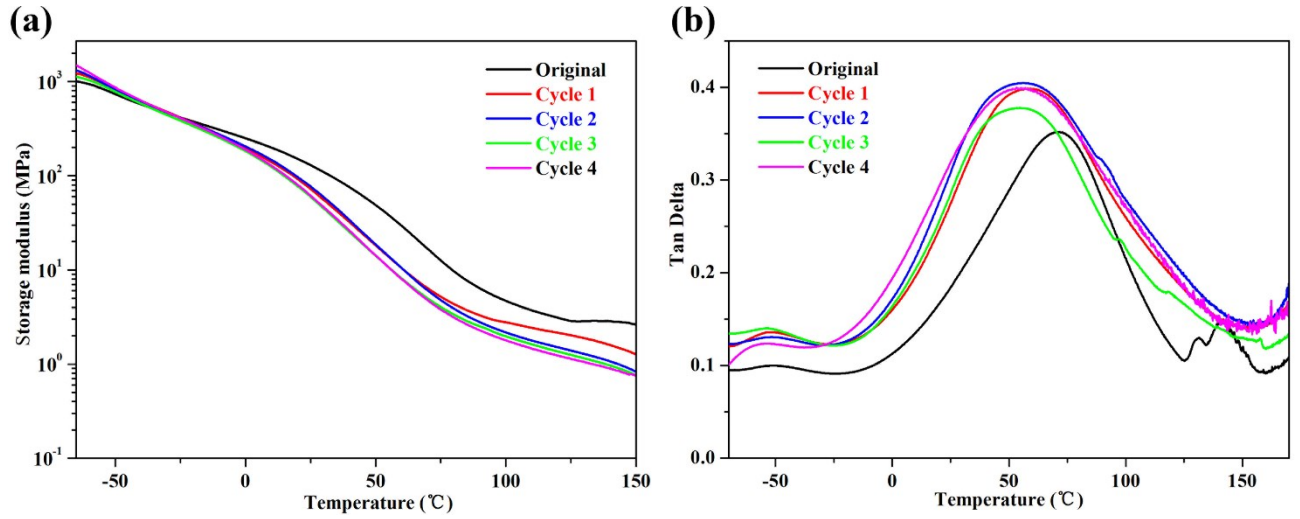

Fig. S13 DMA curves of original synthesized HTPU-2 and the recycled HTPU-2 after reprocessing multiple times by hot press: (a) Storage Modulus and (b) Tan Delta.

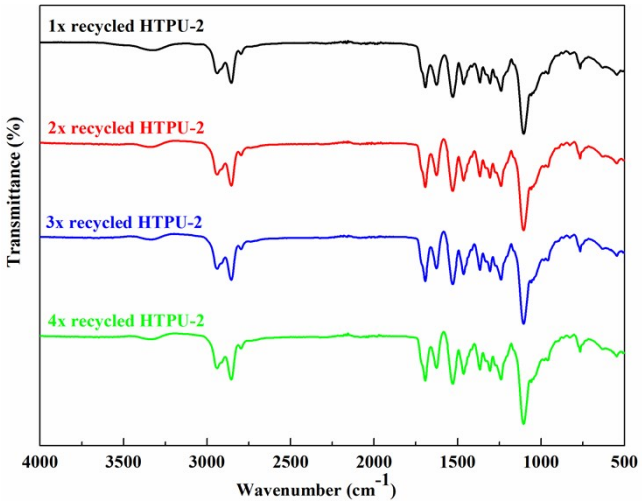


Fig. S14 FTIR spectra of the recycled HTPU-2 after reprocessing four times by hot press.

**Elastic shape memory and permanent shape reconfigurability of HTPUs.**

Demonstration of macroscopic shape manipulation: In elasticity step (a typical shape memory experiment), the original plane shape was heated in oven at 60 °C for 5 min and then was immediately deformed into a 3D "petals" shape and cooled at 0°C with the deformation force maintained. It can release the deformation force after the temporary shape completely fixing. The original plane shape can recover by heating under the stress-free condition. In plasticity step, the original plane shape was plastically fixed into the newly permanent shape of 3D "petals" shape with the aid of external force by annealing at 115 °C for 30 min. A typical shape memory experiment can be conducted from the new permanent shape.

Characterization of the elastic and plastic shape memory[3, 4]: The shape fixity ratio ($R_f$) and shape recovery ratio ($R_r$) were calculated using equation (2) and (3):

$$R_f = \varepsilon_{unload}/\varepsilon_{load} \times 100\% \quad (2)$$

$$R_r = [\varepsilon_{unload} - \varepsilon_{rec}]/ \varepsilon_{unload} \times 100\% \quad (3)$$

Where $\varepsilon_{unload}$, $\varepsilon_{load}$ and $\varepsilon_{rec}$ are the fixed strain after the stress is completely relaxed, maximum strain under load and the strain after shape recover, respectively.

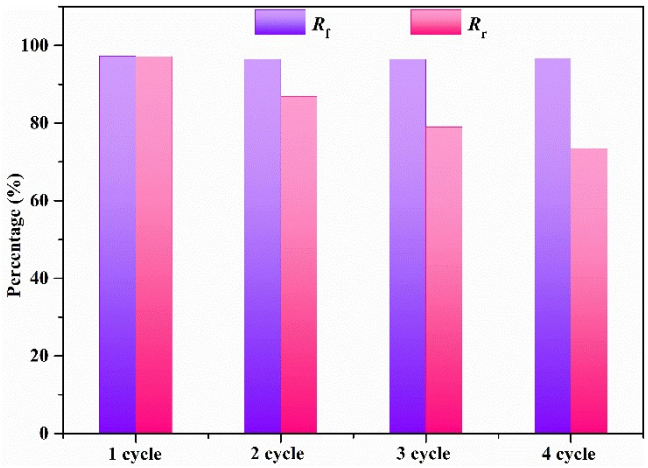


Fig. S15 Shape fixity ratio ($R_f$) and shape recovery ratio ($R_r$) after consecutive shape memory cycles of the synthesized HTPU-2 with the fixity and recovery temperature of 0 °C and 60 °C.

Video S1 Permanent shape reconfigurability for shape memory of fixity and recovery from 3D "petals" shape to original plane shape.

Table S2 Physical properties of the cross-linked HTPUs elastomers.

| Sample | Breaking strength (MPa) | Elongation at break (%) | Young's modulus (MPa) |
|---|---|---|---|
| EHTPU-1 | 25.25 | 329.03 | 179.85 |
| EHTPU-2 | 31.65 | 873.66 | 6.82 |
| EHTPU-3 | 38.04 | 1104.77 | 8.90 |

Table S3 Physical properties of the original and recycled HTPU-2.

| Sample | Breaking strength (MPa) | Elongation at break (%) | Young's modulus (MPa) |
|---|---|---|---|
| Original | 31.65 | 873.66 | 6.82 |
| 1x recycled | 29.25 | 1148.66 | 5.14 |
| 2x recycled | 28.57 | 1203.65 | 4.46 |
| 3x recycled | 25.08 | 1240.88 | 3.12 |
| 4x recycled | 24.15 | 1295.31 | 2.89 |

**References**


1. T. L. Smith and A. B. Magnusson, *J. Polym. Sci.*, 1960, **42**(140), 391-416.
2. B.-S. Chiou and P. E. Schoen, *J. Appl. Polym. Sci.*, 2002, **83**(1), 212-223.
3. N. Zheng, Z. Fang, W. Zou, Q. Zhao, and T. Xie, *Angew. Chem. Int. Ed.*, 2016, **128**(38), 11593-11597.
4. R. Liu, X. Kuang, J. Deng, Y.-C. Wang, A. C. Wang, W. Ding, Y.-C. Lai, J. Chen, P. Wang, Z. Lin, H. J. Qi, B. Sun, and Z. L. Wang, *Adv. Mater.*, 2018, **30**(8), 1705195.