Supporting Information

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Reconfigurable Poly(urea-urethane) Thermoset Based on Hindered Urea Bonds with Triple-Shape-Memory Performance

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Materials

1,1,1-tris(hydroxymethyl)propane (TMP), 1,3-bis(isocyanatomethyl)cyclohexane (BIMCH), dibutyltin dilaurate (DBTDL) and polyethylene glycol (PEG) (molecular weight, 1500) were purchased from sigma-aldrich. *N,N*'-di-tert-butylethylenediamine (DTBEA) was purchased from TCI America. Polycaprolactone diol (PCL diol) (molecular weight, 2000) was purchased from polyscience. Chloroform ($CHCl_3$, purity＞99.8%) was purchased from VWR chemicals.

Synthesis

The samples were synthesized according to the molar ratio of the raw materials (listed in Figure 1b). Typically, for PUU-1, the PCL diol (4.00g) and TMP (1.25g) were dissolved in $CHCl_3$ (10.50g) at 59 ^{o}C under mild magnetic stirring and DTBEA (2.06g) was added into the solution after it cooled down. Next the BIMCH (5.43g) was slowly dropped into the solution and the fast reaction between BIMCH and DTBEA released lots of heat. After the solution cooled down, DBTDL (0.25g (2phr)) was added. Then the solution was rotary evaporated to remove the $CHCl_3$ and finally viscous liquid was obtained. After that, the liquid was carefully cast onto an explanate polytetrafluoroethylene (PTFE) film (10×10×0.5mm) and the system was pre-cured at 40 ^{o}C for 2h and fully cured at 60 ^{o}C for 12h. After that, the PUU film can be easily peeled off from PTFE film. The poly (BIMCH-DTBEA) (PBD) was synthesized as follows: the DTBEA (2.15g) was dissolved in $CHCl_3$ (9.15g) and BIMCH (2.43g) was

added by drops. The system was fully reacted under 60°C for 12h and after this the $CHCl_3$ was removed by vacuum oven under 60 °C for 12h.

Characterization

Gel content

About 100 mg of PUU sample was soaked in $CHCl_3$ (15 mL) for three days. After that, the residual PUU sample was dried in a 70 °C vacuum oven until the weight reached a constant value. Then the gel content was calculated as the weight ratio of the PUU sample after and before the soaking. The eventual gel content is calculated as the average of the values of three tests.

Stress relaxation and Arrhenius analysis.

The stress relaxation was performed using dynamic mechanical analyzer (DMA Q800, TA instruments). First a 30×5×1mm specimen was heated up and equilibrate at desired temperature, then the specimen was stretched to a constant strain of 10% and the relative stress was monitored.

The temperature dependent τ* was then plotted versus 1000/T and fitted by the Arrhenius equation (Relation 1) [1].

$$\ln(\tau^*) = \ln(\tau_0) + E_a/RT \qquad 1$$

Where τ_0 is the characteristic relaxation time at infinite T, E_a is the activation energy, R is the universal gas constant and T is the temperature.

Mechanical property

The stress-strain curve of PUU-1 was obtained via DMA under a controlled-force mode in which the force was ramped from 0 to 18N with a rate of 3N/min. The specimen size is 30×5×1mm.

Temperature dependent creep and dynamic mechanical test

The temperature dependent creep was tested via heating (5°C/min) the specimen (30×5×1mm) under a constant force of 0.5N under controlled force DMA mode. The dynamic mechanical test was performed under multi-frequency strain mode and the heating rate, frequency, and oscillation amplitude were 3°C /min, 1 Hz, and 10μm, respectively. The sample size was 30×5×1mm.

Shape memory performance

Shape memory performance of was investigated by the DMA Q800 under the controlled-force mode. The test processes include equilibrating at a constant temperature, applying constant force, cooling, unloading force and reheating. For dual-shape memory performance, the fixity ratio (R_f) and recovery ratio (R_r) could be calculated from relations 2 and 3, respectively.

$$R_f = \varepsilon_2/\varepsilon_1 \times 100\% \qquad 2$$

$$R_r = (1- \varepsilon_r /\varepsilon_2) \times 100\% \qquad 3$$

Where ε_1 is the maximum engineering strain achieved during uniaxial stretching. ε2 is the engineering strain of the temporary shape after unloading, and ε_r is the engineering strain of the recovered shape (Figure S1).

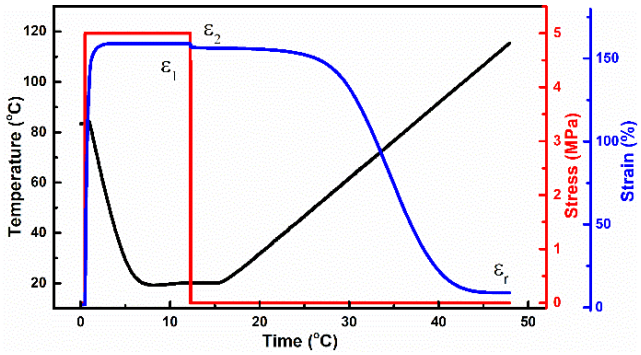

Figure S1 Quantitative test of dual-shape memory performance of PUU

For triple-shape memory performance, the fixity ratio (R_f) and recovery ratio (R_r) could be calculated from relations 4,5,6 and 7, respectively [2].

$$R_f \text{ (first temporary shape)} = \varepsilon_2/\varepsilon_1 \times 100\% \qquad 4$$

$$R_r\,(\text{first temporary shape}) = (\varepsilon_5-\varepsilon_6)/\varepsilon_5 \times 100\% \qquad 5$$

$$R_f\,(\text{second temporary shape}) = \varepsilon_4/\varepsilon_3 \times 100\% \qquad 6$$

$$R_r\,(\text{second temporary shape}) = (\varepsilon_4-\varepsilon_5)/(\varepsilon_4-\varepsilon_2) \times 100\% \qquad 7$$

ε_1 -ε_6 are marked out in Figure 3b.

DSC test of PCL diol and poly (BIMCH-DTBEA) (PBD)

The endothermic temperatures of PCL diol and PBD were measured using a TA differential scanning calorimeter (DSC-2500). Experiments were performed with about 5 mg samples under nitrogen atmosphere. The samples were firstly heated to 125°C at a rate of 10°C/min to eliminate thermal history and then held at 125°C for 1 min. Subsequently, the samples were cooled at a rate of 10°C/min to °C and held at 30°C for 1 min, then scanned from 30°C to 125°C at a rate of 10°C/min.

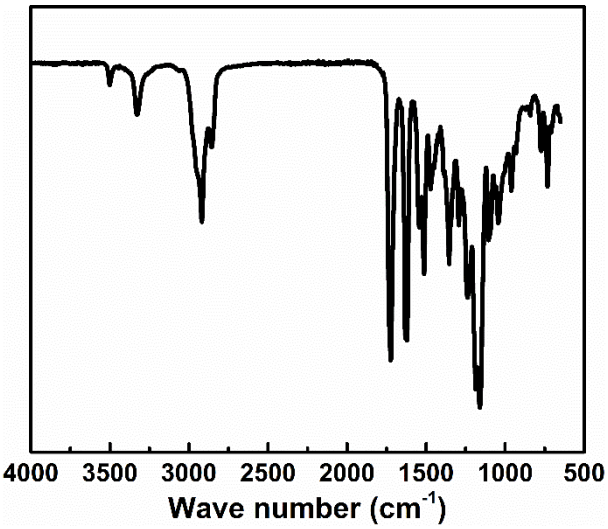

Figure S2 Infrared spectrum of PUU thermoset after 12 h of curing

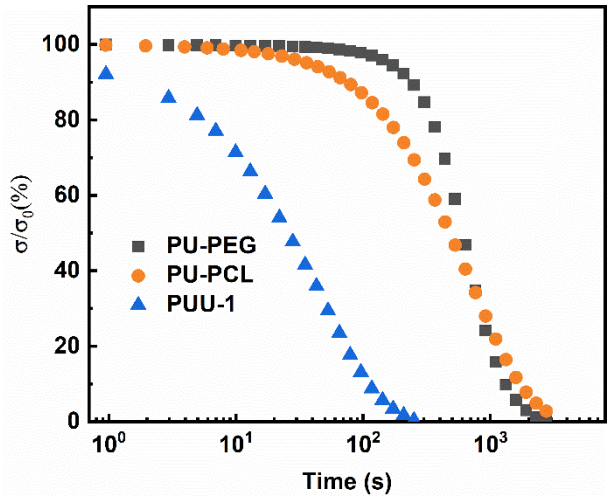

Figure S3 Stress relaxation of PU-PEG, PU-PCL and PUU-1 at 150°C. The τ* of PU-PEG and PU-PCL is 12.3min and 11.7min, respectively, and both the complete relaxation times (the time needed to reshape) are still more than 45min. However, the τ* of PUU-1 is 0.7min and it only needs 4.2min to fully relax, indicating the reconfigurability of PUU-1 is much faster than that of PU-PEG and PU-PCL even under high temperature.

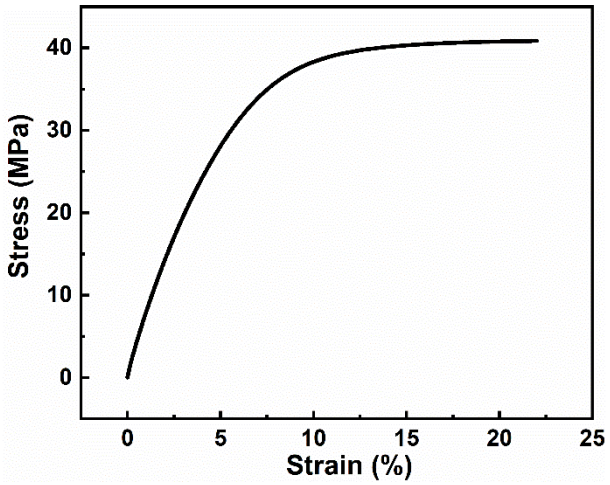

Figure S4 Representative stress-strain curve of PUU-1.

Table S1 Mechanical property of PUU-1

Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
0.76±0.06	40.5±1.3	20.9±3.1

References

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[2] C. Samuel, S. Barrau, J. M. Lefebvre, J. M. Raquez, P. Dubois, *Macromolecules.* **2014**, *47*, 6791.