

Supporting Information

Healable Reconfigurable Reprocessable Thermoset Shape Memory Polymer with Highly Tunable Topological Rearrangement Kinetics

Zizheng Fang[‡], Ning Zheng[‡], Qian Zhao, Tao Xie**

State Key Laboratory of Chemical Engineering, College of Chemical and Biological
Engineering, Zhejiang University, 38 Zheda Road, Hangzhou, 310027, P. R. China

*E-mail: qianzhao@zju.edu.cn.

*E-mail: taoxie@zju.edu.cn.

Experimental descriptions:

Materials. Poly(ethylene glycol)diol (PEG) ($M_n=2,000$) was purchased from Sigma-Aldrich and dehydrated in a vacuum drying oven prior to use. Hexamethylene diisocyanate (HDI), glycerin (GLY), and ditin butyl dilaurate (DBTDL) were all purchased from Aladdin. *N,N'*-di-tert-butylethylenediamine (TBEA) was purchased from TCI. Unless otherwise noted, all chemical reagents were used as received.

Synthesis of shape memory poly(urea-urethane) networks. PEG was dissolved in butyl acetate at room temperature and a glycerin solution (20 wt% in *N,N'*-dimethylformamide, DMF) was added. A stoichiometric amount of HDI and TBEA was introduced (note: significant heat generated). The mixture was then poured into an aluminum pan together with DBTDL (1 wt% in butyl acetate). After cured at 60 °C for 4 h, the sample was vacuum-dried at 60 °C overnight and demolded.

Dynamic mechanical analysis. Dynamic mechanical analysis (DMA) was conducted using DMA Q800 (TA instruments). The stress relaxation curves were performed in a “stress relaxation” mode with an iso-strain value set at 50%. Shape memory and combined shape memory/plasticity cycles were performed in a “strain rate” mode. The shape fixity ratio (R_f) and the shape recovery ratio (R_r) for the shape memory characterization and the shape retention ratio (R_{ret}) for the solid-state plasticity were calculated using equations defined in our previous publication.²⁰⁻²²

Melting temperature testing. Differential scanning calorimetry (DSC) were conducted using DSC Q200 (TA instruments) with a heating and cooling rate of 10 °C

min⁻¹. Dynamic mechanical analyses (DMA Q800, TA instruments) were performed at a heating rate of 3 °C min⁻¹ in a “multi-frequency, strain” mode at 1 Hz, 0.2% strain.

Gel contents testing. All samples were solvent extracted for 24 h in butyl acetate and the solvent was refreshed once during the tests. A minimum of three specimens were tested for each sample.

Uniaxial tensile testing. Tensile measurements were performed using a Zwick/Roell BW91272 tester (Germany) with a uniaxial extension rate of 100 mm min⁻¹. A minimum of three specimens were tested for each sample.

The crosslinking density (V_e) was calculated by equation (1):

$$E(T) = 3RTV_e \quad (1)$$

where E is the rubber modulus, R is the universal gas constant, and T is the absolute temperature.

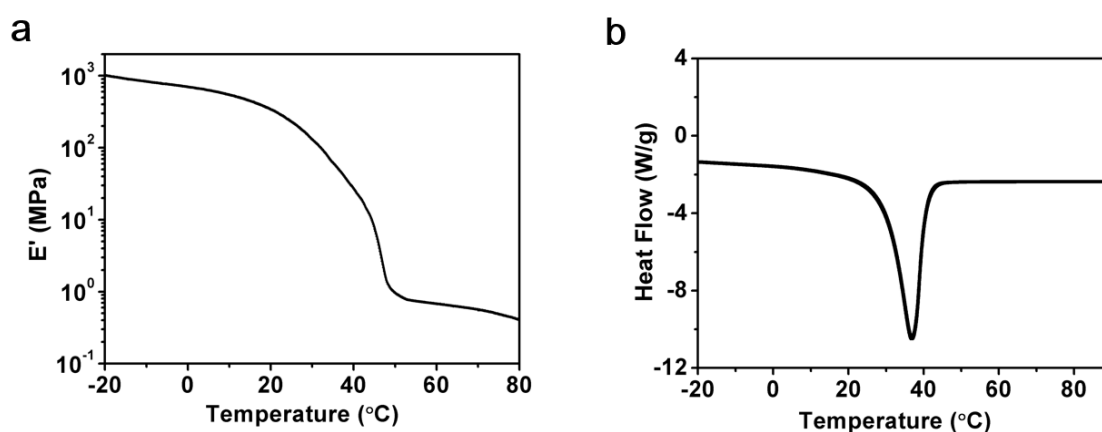


Figure S1. Thermo-mechanical characterization of PUU3. (a) DMA curve. (b) DSC curve.

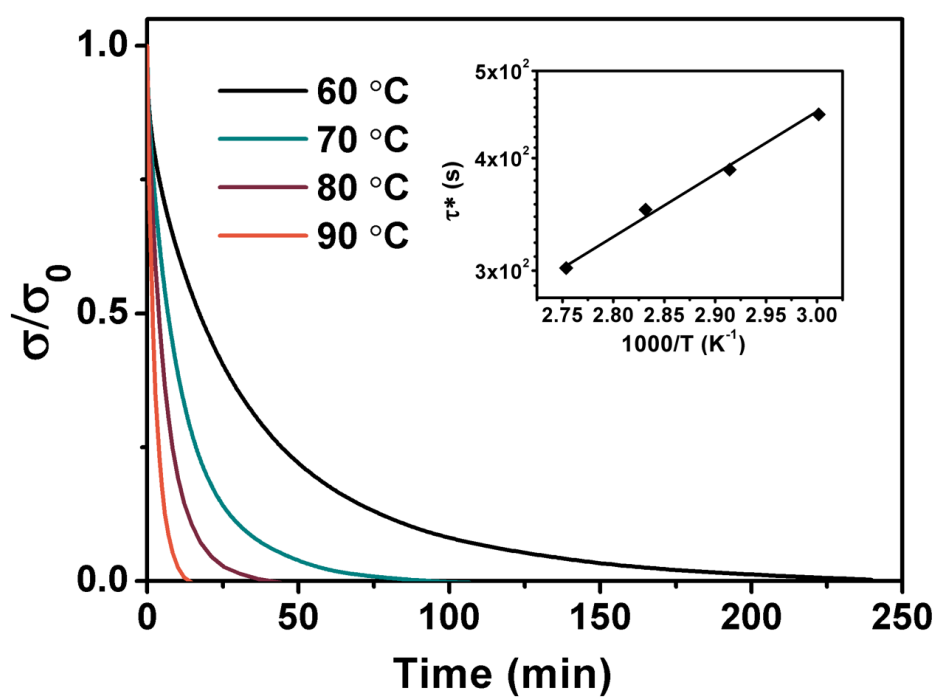


Figure S2. The stress relaxation curves of **PUU3** with different temperatures and the corresponding Arrhenius fitting curve (inset).

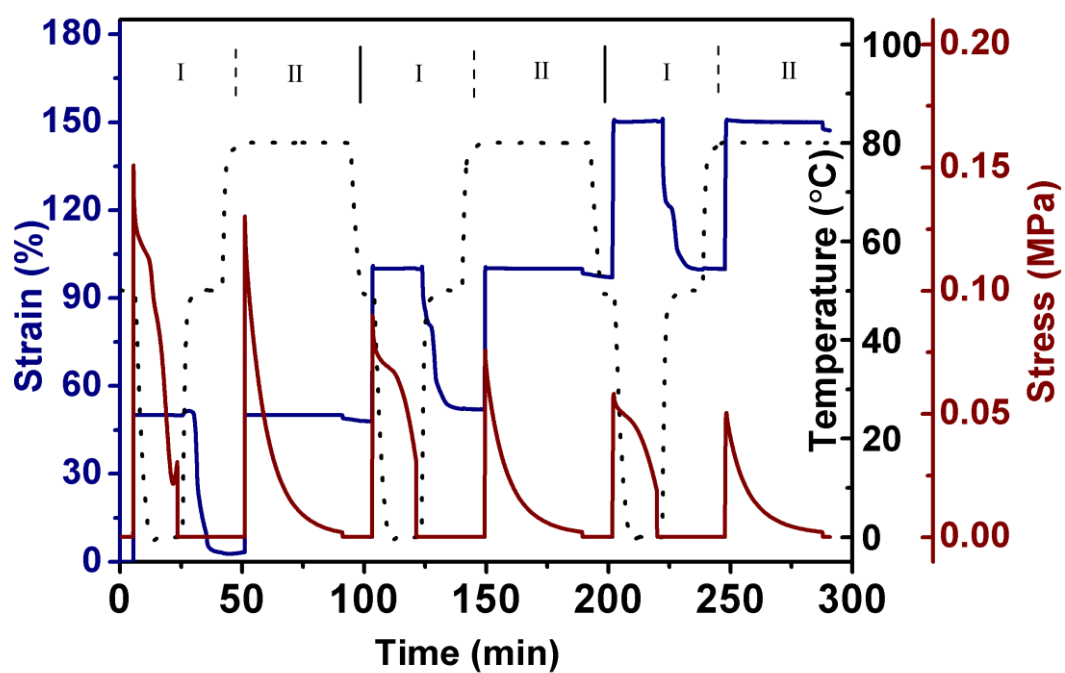


Figure S3. Multiple shape memory and plasticity cycles of **PUU3**. (label “I”: shape memory cycle; label “II”: plasticity cycle)

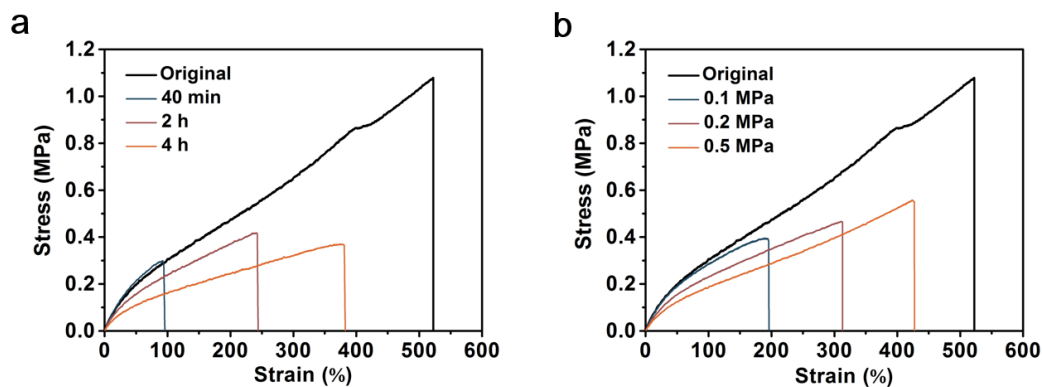


Figure S4. Representative stress-strain curves of **PUU3**. (a) The self-healed samples. (b) The reprocessed samples. Note that the ϵ_{\max} values reported in the main text represents average values from at least three repeat tests. While the ϵ_{\max} has recovered well, the recovered rubbery modulus in both (a) and (b) reached only 60%. The significant reduction in rubbery modulus is most likely due to the unfavorable hydrolysis of the hindered urea bonds (see reference 19 in the main text) and the hygroscopic PEG in the networks. Although modulus is less relevant for the purpose of the current study, it can nevertheless be improved if less hygroscopic monomers are used in the network.

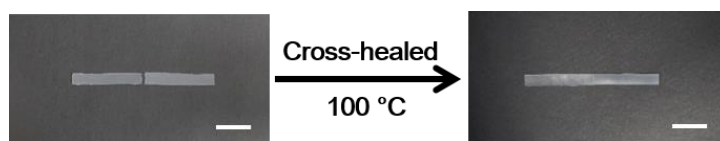


Figure S5. Two thin films with different rearrangement kinetics were cross-healed together. Scale bars, 15 mm. (left: **PUU3**, right: **PUU1**)

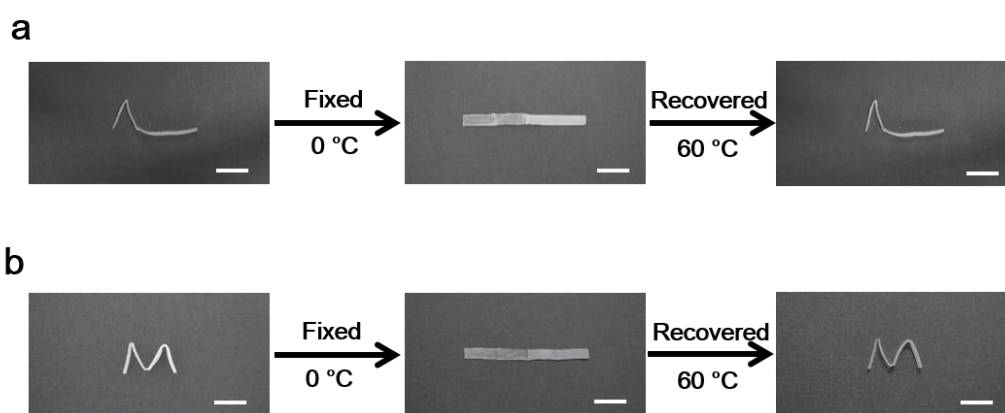


Figure S6. Demonstration of the shape memory behavior of poly(urea-urethane) with different permanent shapes obtained by plasticity at different temperatures. The sample in Figure S4 was folded into an “M” shape and underwent plastic deformation at different temperatures. (a) Annealing at 80 °C resulted in selective plasticity of the **PUU3** segment while the **PUU1** segment remained unchanged. (b) Annealing at 100 °C led to permanent shape change in both segments, thus the permanent shape became “M”. Scale bars, 15 mm.