Electronic Supplementary Information

Self-reinforced and self-healing dynamic covalent polymeric

networks with shifting chemical structures

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Experimental Section

1. Material and methods

N-(tert-Butyl)-*N*-ethylamine (TBEA, 98%+), butylamine (BA, 99%+), and 2-isocyanatoethyl methacrylate (IEMA, >98%, stabilized with butylated hydroxytoluene) were purchased from TCI America. Trimethylolpropane tris(3-mercaptopropionate) (TMPTMP, >95%) and 2-(tert-butylamino)ethyl methacrylate (TBEMA, 97%) were purchased from Sigma-Aldrich. 1-Butanethiol (BT, 99%+), hexyl isocyanate (HI, 99%), and 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%) were purchased from Acros Organics. Chloroform (99.8%) was purchased from Thermo Scientific. All these chemicals were used as received without further purification.

^{1}H NMR spectra were recorded at 500 MHz on a Varian INOVA-500 spectrometer at 25 °C in CDCl$_3$, using tetramethylsilane as an internal standard. FT-IR spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer at room temperature (r.t.). For FT-IR analysis of polymer samples, their bulk sections (after the removal of their surface layers) were analyzed. Differential scanning calorimetry (DSC) analysis was performed using a TA Instruments DSC Q2000 under a nitrogen atmosphere, with a heating rate of 10 °C/min in the temperature range from -60 °C to 60 °C. For DSC analysis of polymer samples, their bulk sections were analyzed. Glass transition temperature (T$_g$) was measured from the third heating cycle of each measurement. Tensile testing was performed at r.t. by using Instron Tensile Tester Model 3343, with a 50 N load cell and a stretching rate of 10 mm/min.

2. Synthesis of 1-(tert-butyl)-1-ethyl-3-hexylurea (TBEHU)

In a typical reaction (**Scheme S1**), hexyl isocyanate (254 mg, 2.0 mmol) and CHCl$_3$ (1.5 mL) were added into a Schlenk flask under a nitrogen atmosphere. TBEA (202 mg, 2.0 mmol) was dissolved in CHCl$_3$ (1.0 mL), and the solution was slowly added to the flask. The reaction mixture was stirred in an ice bath for 10 min, and then at r.t. for 12 h. Most of the solvent was removed by using a rotary evaporator. The remaining solvent was completely removed under vacuum to give the target compound as a colorless oil in 97% yield. The chemical structure of the final product was verified by ^{1}H NMR and FT-IR analysis (**Fig. S1** and **S7**).

3. Synthesis of *S*-butyl hexylcarbamothioate (SBHCAT)

In a typical reaction (**Scheme S2**), hexyl isocyanate (254 mg, 2.0 mmol) and CHCl$_3$ (1.5 mL) were weighted and added into a Schlenk flask under a nitrogen atmosphere. BT (200 mg, 2.2 mmol) was dissolved in CHCl$_3$ (1.0 mL), and the solution was slowly added to the flask. The reaction mixture was stirred at 40 °C for 12 h. Then, most of the solvent and excessive BT were removed by using a rotary evaporator. Further evaporation under vacuum gave the target compound as a colorless oil in 95% yield. The chemical structure of the final product was verified by ^{1}H NMR and FT-IR analysis (**Fig. S2** and **S7**).

4. Synthesis of *N*-butyl-*N′*-hexylurea (BHU)

In a typical reaction (**Scheme S3**), BA (146 mg, 2.0 mmol) and CHCl$_3$ (1.5 mL) were added into a Schlenk flask under a nitrogen atmosphere. Hexyl isocyanate (254

mg, 2.0 mmol) was dissolved in $CHCl_3$ (1.0 mL), and the solution was slowly added to the flask. The reaction mixture was stirred in an ice bath for 10 min, and then at r.t. for 12 h. Most of the solvent was removed by using a rotary evaporator. The remaining solvent was completely removed under vacuum to give the target compound as a white solid in 97% yield. The chemical structure of the final product was verified by ^{1}H NMR analysis (**Fig. S5**).

5. Model study for the conversion of hindered urea to thiourethane

Three parallel reactions were conducted at 60 °C (using an oil bath) without UV irradiation, r.t. without UV irradiation, and r.t. with UV irradiation (λ_{max} = 365 nm), respectively. For each reaction, TBEHU (228 mg, 1.0 mmol) and BT (90 mg, 1.0 mmol) were added to a flask under a nitrogen atmosphere; 1 wt% of DMPA relative to the total weight of TBEHU and BT was also added in the trial for UV irradiation. Then the reaction mixtures were stirred at a specific temperature, with or without UV irradiation. At time intervals, ~20 mg of reaction mixture was taken out every time for ^{1}H NMR analysis to determine reaction extent.

6. Model study for the conversion of unhindered urea to thiolurethane

Two parallel reactions were conducted at 60 °C (using an oil bath) and r.t., respectively. For each reaction, BHU (200 mg, 1.0 mmol), BT (90 mg, 1.0 mmol), and $CDCl_3$ (0.1 mL) were added to a flask under a nitrogen atmosphere, and then the reaction mixture was stirred at a specific temperature. At time intervals, ~25 mg of the

reaction mixture was taken out every time for ^{1}H NMR analysis to determine the reaction extent.

7. Synthesis of 2-(1-(tert-butyl)-3-(2-(methacryloyloxy)ethyl)ureido)ethyl methacrylate (TBMEM)

In a typical reaction (**Scheme S4**), IEMA (4.65 g, 30 mmol) and $CHCl_3$ (9.0 mL) were added into a Schlenk flask under a nitrogen atmosphere. TBEMA (5.55 g, 30 mmol) was dissolved into $CHCl_3$ (9.0 mL) and the solution was injected into the flask slowly by using a syringe pump. The reaction mixture was stirred in an ice bath for 30 mins, and then at r.t. for 12 h. Most of the solvent was removed using a rotary evaporator. Further evaporation under vacuum gave the target compound as a viscous colorless oil in 95% yield. The chemical structure of the final product was verified by ^{1}H NMR analysis (**Fig. S8**).

8. Preparation of dynamic crosslinked polymeric networks (DCPNs)

In a typical reaction for the preparation of a DCPN sample, a mixture of TMPTMP and TBMEM ($[TMPTMP]_0$:$[TBMEM]_0$ = 2:3), as well as DMPA ($[0.1$ wt% relative to the total weight of TMPTMP and TBMEM), was vortexed for 2 min. Then it was cast into a mold, followed by photocuring for 20 min using a UVP CX-2000 UV crosslinker (λ_{max} = 365 nm; intensity = 0.4 J/cm^2). The sample was flipped over at 10 min to ensure the consistency of UV curing conditions for both top and bottom sides.

9. Quantification of thiol groups in DCPNs

The remaining percentages of thiol groups in DCPNs were estimated by FT-IR analysis based on measuring the intensities of S-H stretching adsorption at 2570 cm^{-1} (as heights of adsorption peaks, H_{S-H}) of DCPNs relative to the reaction mixture (before UV irradiation), using ester C=O stretching adsorption at ~1733 cm^{-1} (as heights of adsorption peaks, $H_{C=O}$) as a constant reference before and after the reaction (because ester groups were not involved in reactions, the total carbonyl groups from ester groups were constant).

$$\text{Remaining thiol (\%)} = \frac{H_{S-H}/H_{C=O} \text{ for DCPN}}{H_{S-H}/H_{C=O} \text{ for reaction mixture}} \times 100\%$$

10. Study of time-dependent self-reinforcement effects of DCPNs

Freshly prepared dog-bone-shaped samples without cutting/heating history were incubated at 60 ℃ for 0.5, 1.5, 3, 6, and 12 h. Then, the stress-strain curves of these samples were obtained and compared.

11. Self-healing of dog-bone-shaped DCPN samples

To examine the self-healing ability of the pristine DCPNs, freshly prepared dog-bone-shaped samples were cut in the middle by a sharp surgery knife, and then the resulting two pieces from each sample were gently pressed against each other for 1 min and subsequently the self-healing process was allowed under the given conditions (i.e., at 60 ℃ for 12 h or 37 ℃ for 12 d, under air). Freshly prepared samples without cutting/heating history, as well as samples incubated at 60 ℃ for 12 h or 37 ℃ for 12 d without cut, were prepared and used as controls. To examine the self-healing

performance of DCPNs with heating history, a dog-bone-shaped sample was first

incubated at 60 °C for 12 h, followed by a cut in the middle and self-healing at 60 °C
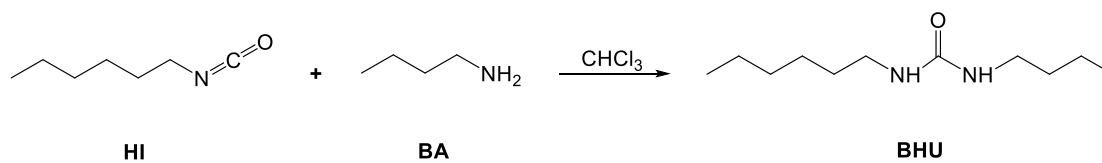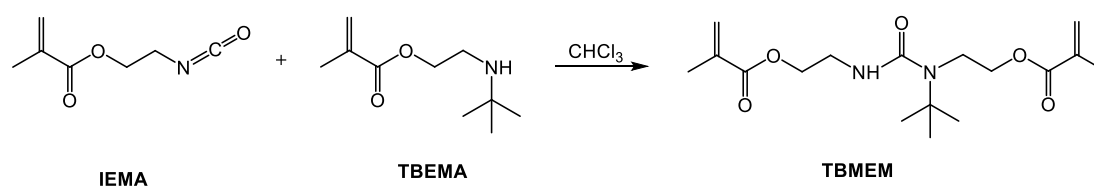
for another 12 h.

Supplementary Schemes
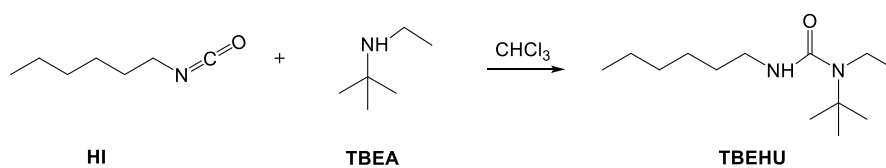
Scheme S1. Synthesis of TBEHU
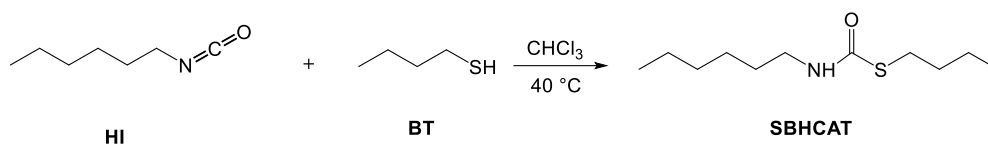
Scheme S2. Synthesis of SBHCAT

Scheme S3. Synthesis of BHU

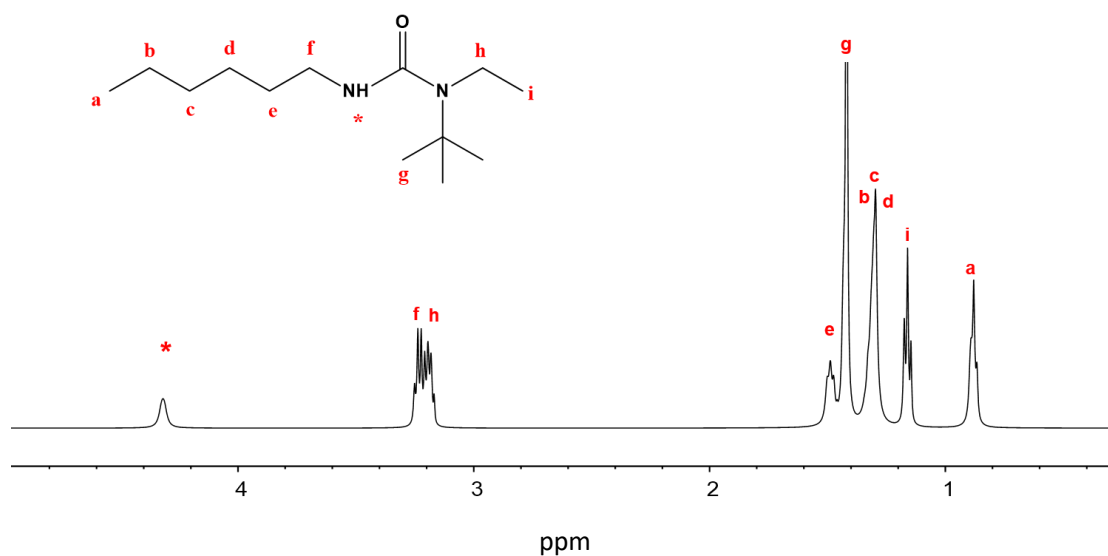**Scheme S4.** Synthesis of TBMEM

Supplementary Figures

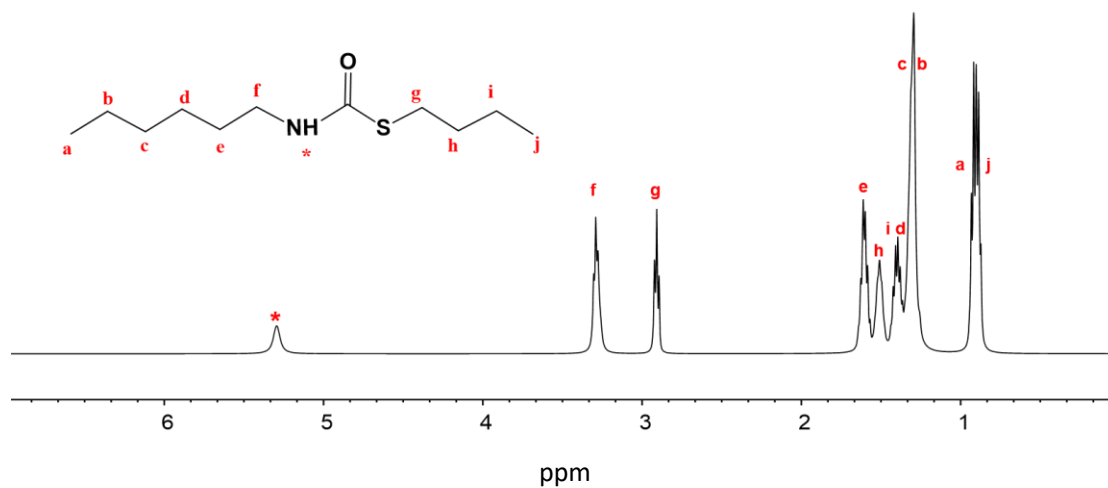**Fig. S1.** ^{1}H NMR (500 MHz) spectrum of TBEHU in CDCl$_3$.
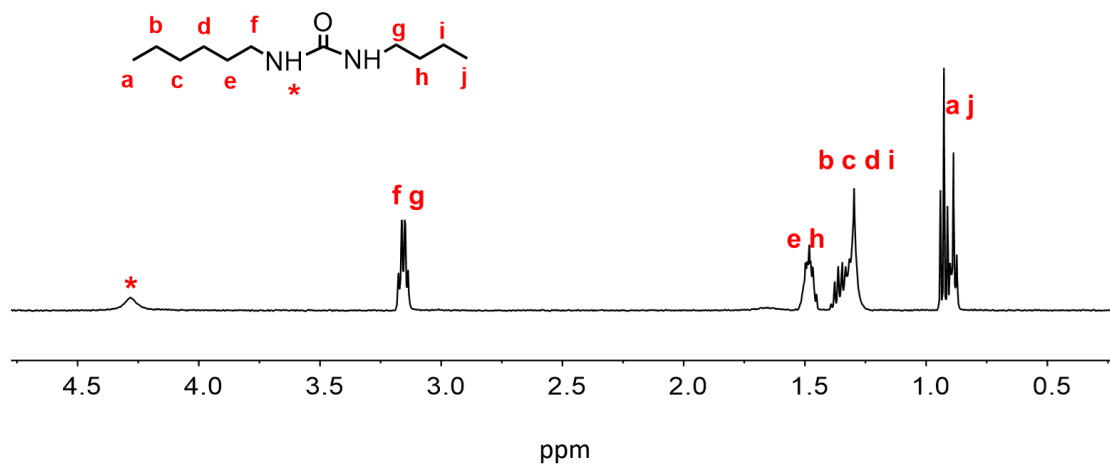

Fig. S2. ^{1}H NMR (500 MHz) spectrum of SBHACT in CDCl$_3$.
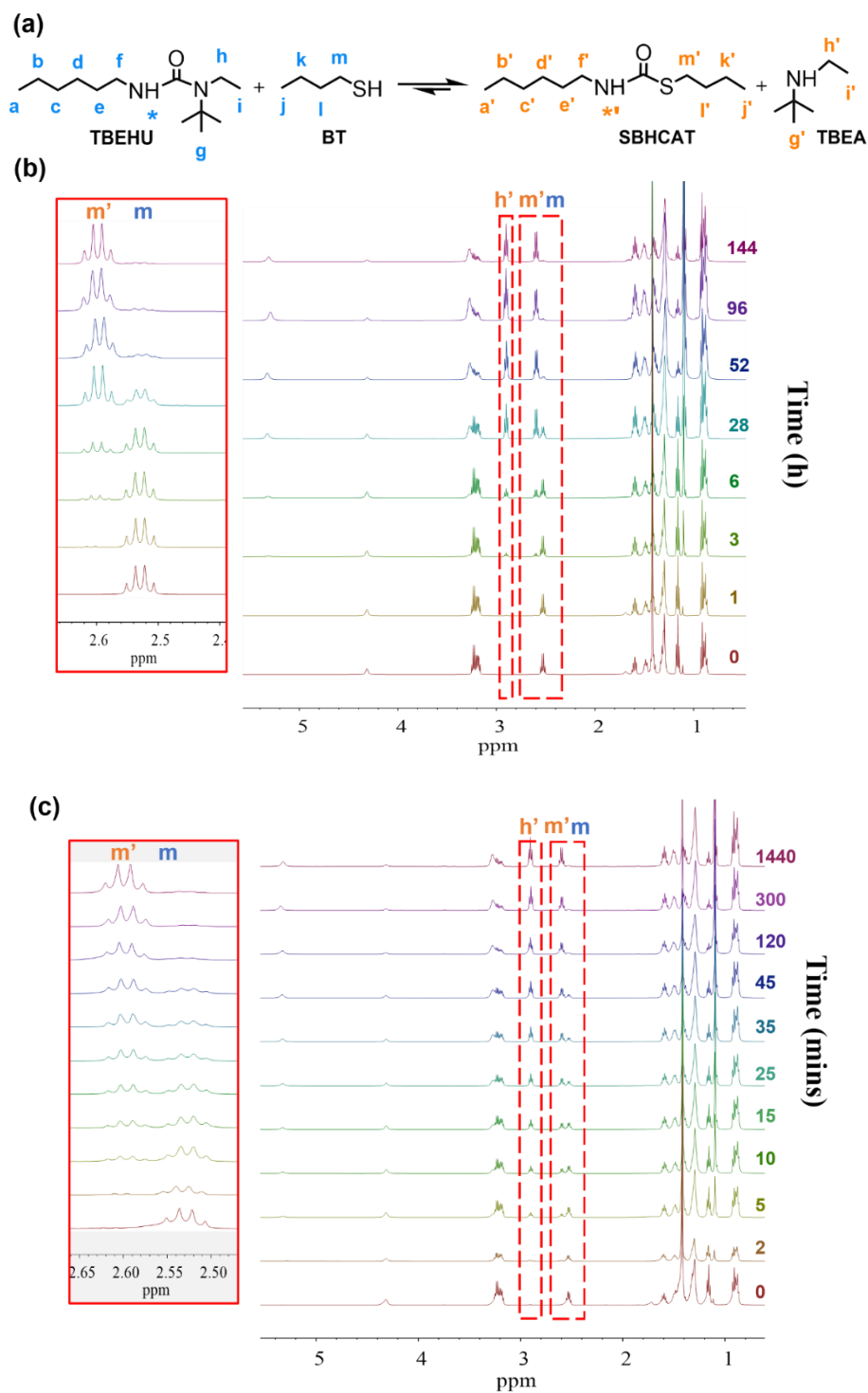
Fig. S3. (a) Schematic illustration of a small-molecule model reaction of TBEHU with BT for the conversion of hindered urea to thiourethane; (b) ^{1}H NMR monitoring of the reaction undergoing at r.t.; and (c) ^{1}H NMR monitoring of the reaction undergoing at 60 °C.
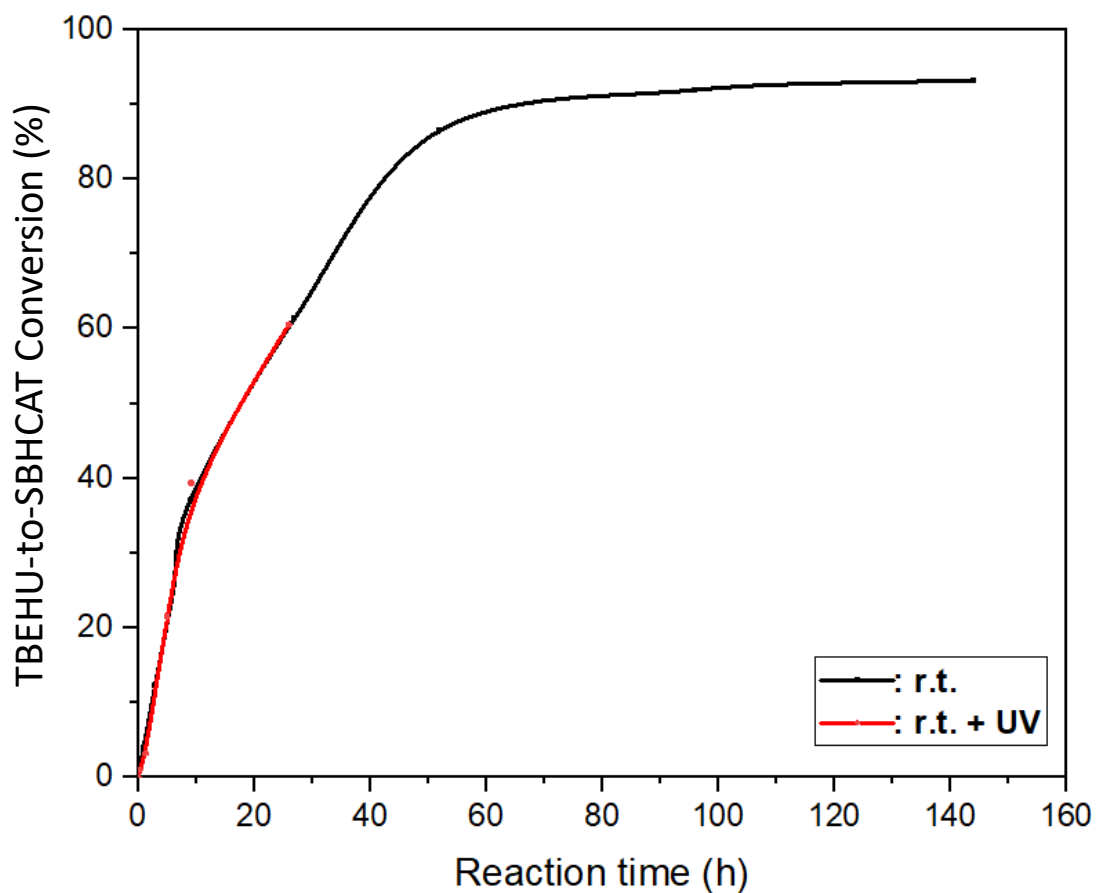
Fig. S4. Kinetics (shown as time-dependent conversion from TBEHU to SBHCAT) of the reaction of TBEHU and BT to form SBHCAT and TBEA. Black line: reaction at r.t. without the presence of DPMA (no UV irradiation); red line: reaction at r.t. with the presence of DMPA (1 wt% relative to the total weight of TBEHU and BT) under UV irradiation (λ_{max} = 365 nm).

Fig. S5. ^{1}H NMR (500 MHz) spectrum of BHU in CDCl$_3$.
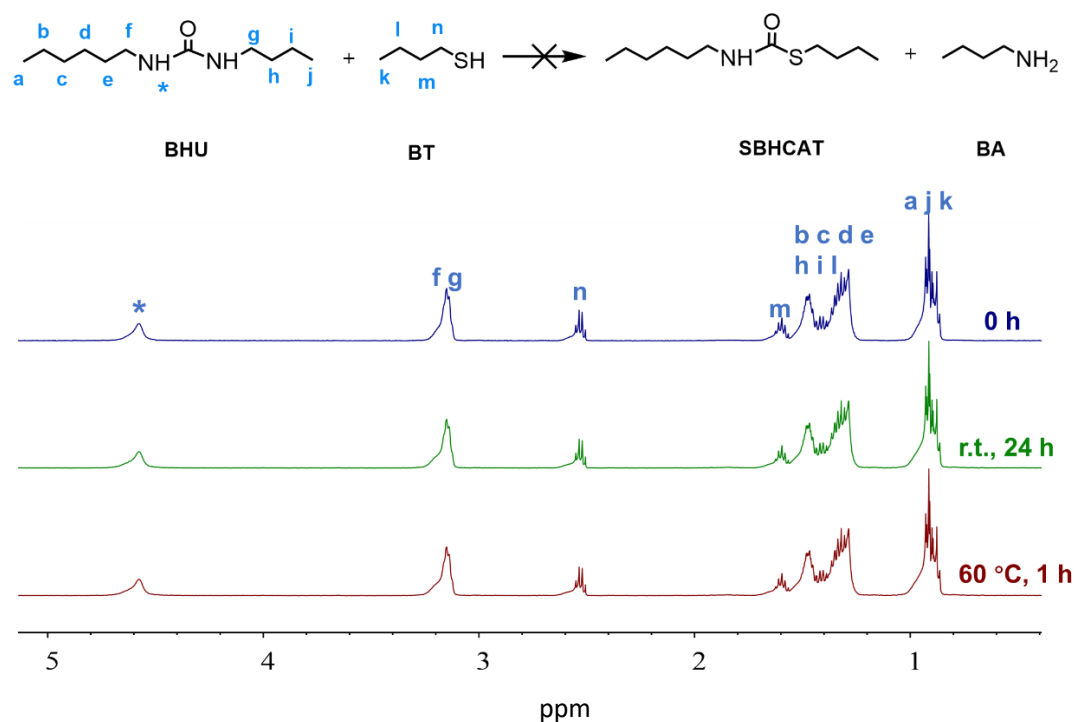
Fig. S6. Schematic illustration of a small-molecule model reaction of BHU (unhindered urea) with BT (top); ^{1}H NMR monitoring of the reaction, showing no occurrence of reaction at r.t. for 24 h or 60 °C for 1 h (bottom).
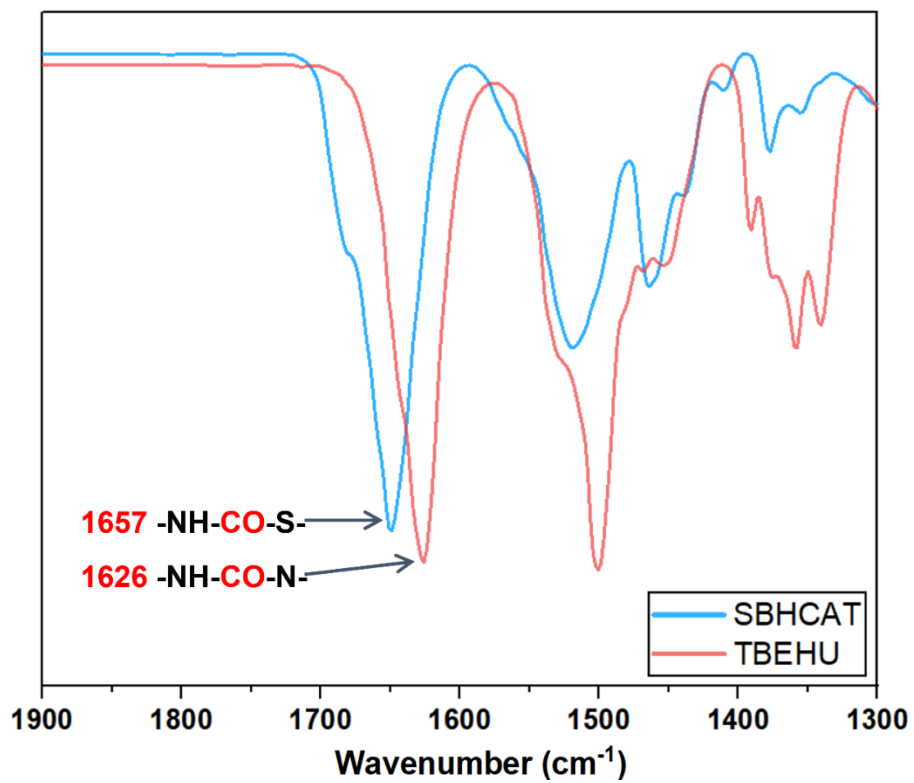
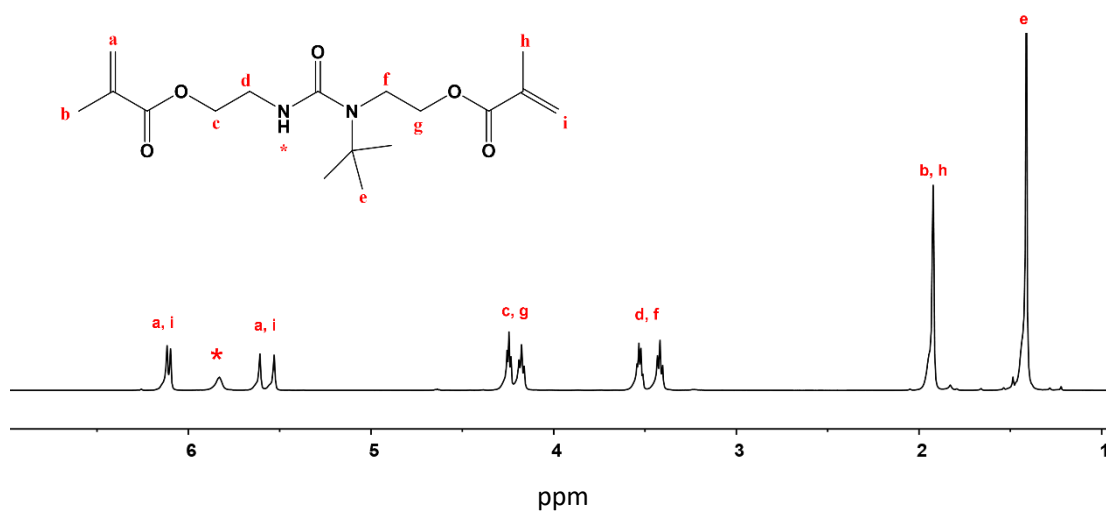**Fig. S7.** FT-IR results of TBEHU (blue line) and SBHCAT (red line).

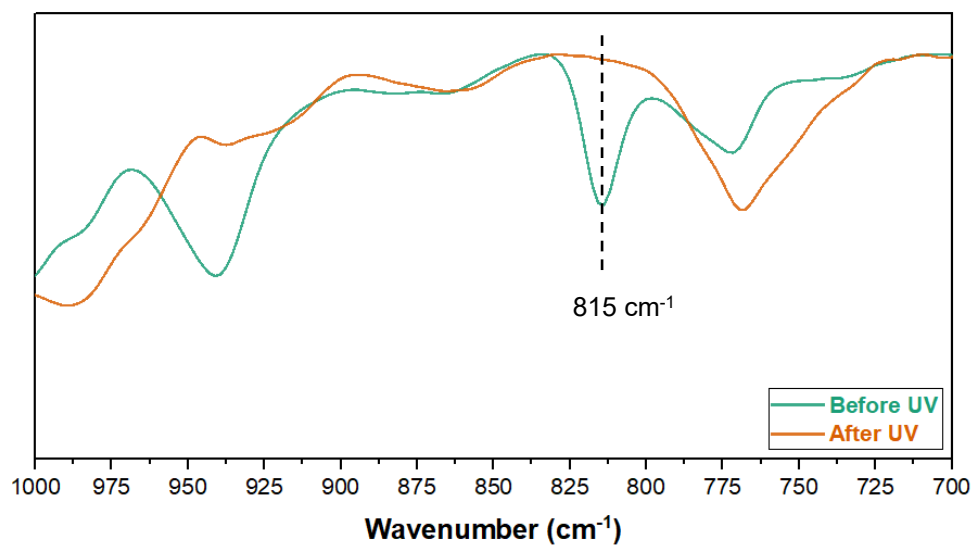
Fig. S8. ^{1}H NMR (500 MHz) spectrum of TBMEM in CDCl$_3$.

Fig. S9. FT-IR spectra of the initial thiol–methacrylate reaction mixture (before UV irradiation) and the resulting freshly prepared DCPN sample (after UV irradiation).
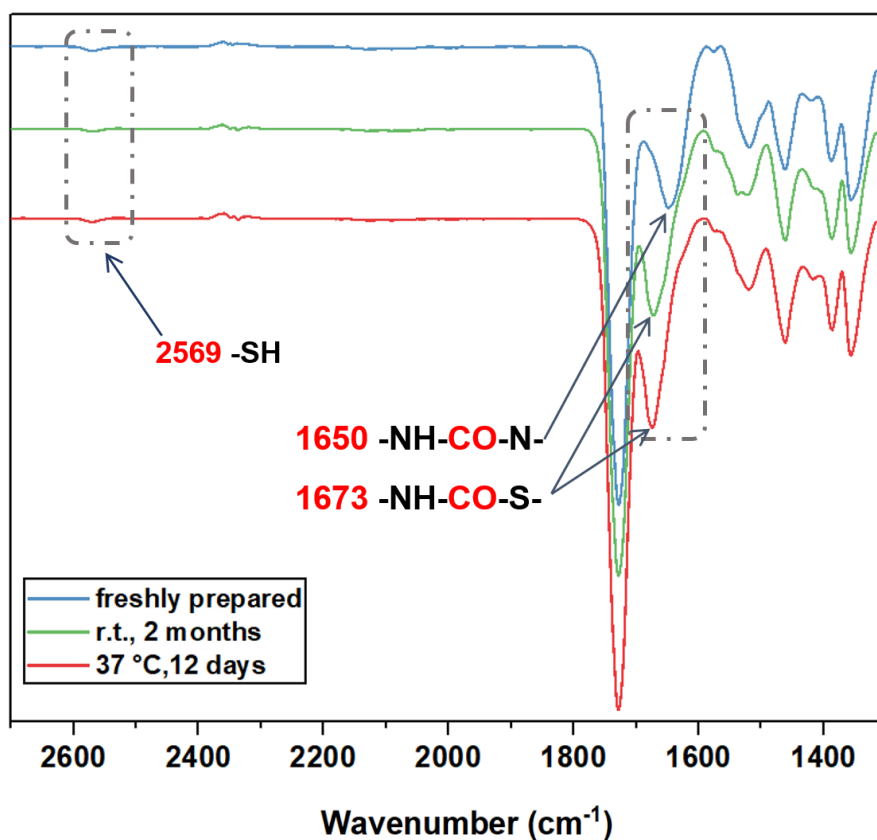

Fig. S10. FT-IR monitoring of the occurrences of dynamic bond shifting at r.t. for 2 months and at 37 °C for 12 days (a freshly prepared sample as control).
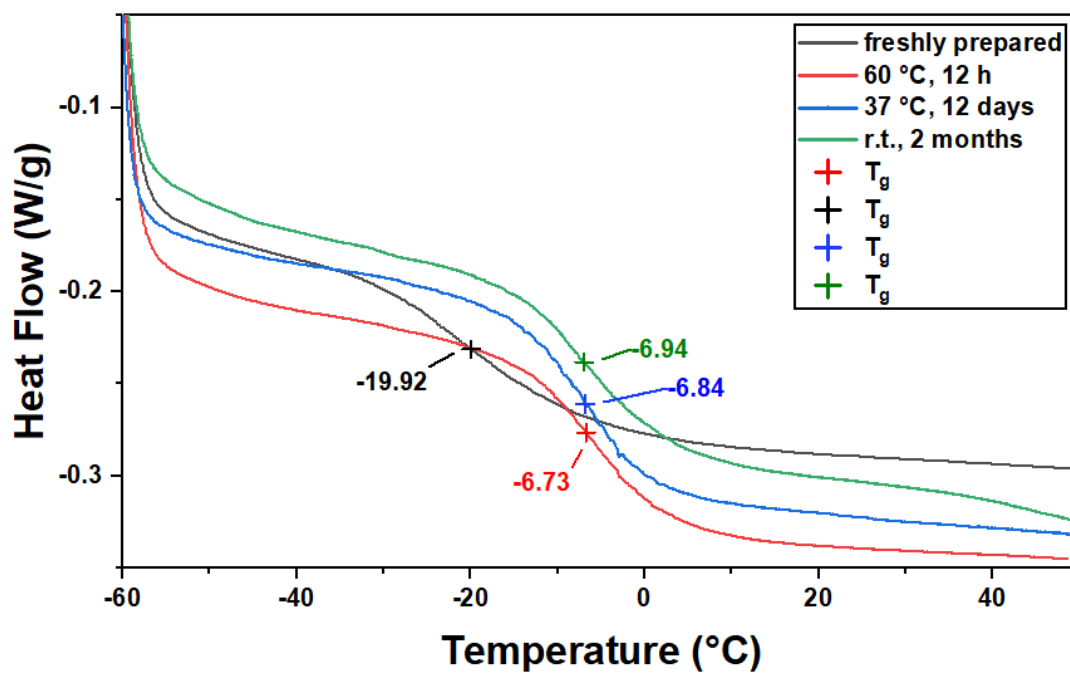
Fig. S11. DSC analysis of DCPNs, including a freshly prepared sample (T_g = -19.92 °C), a sample incubated at 60 °C for 12 h (T_g = -6.73 °C), a sample incubated at 37 °C for 12 days (T_g = -6.84 °C), and a sample incubated at r.t. for two months (T_g = -6.94 °C).
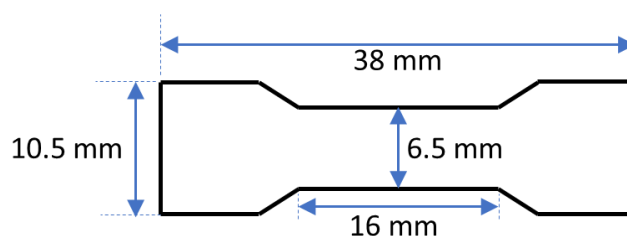

Fig. S12. The dimensions of the dog-bond-shaped sample (thickness: 4 mm).
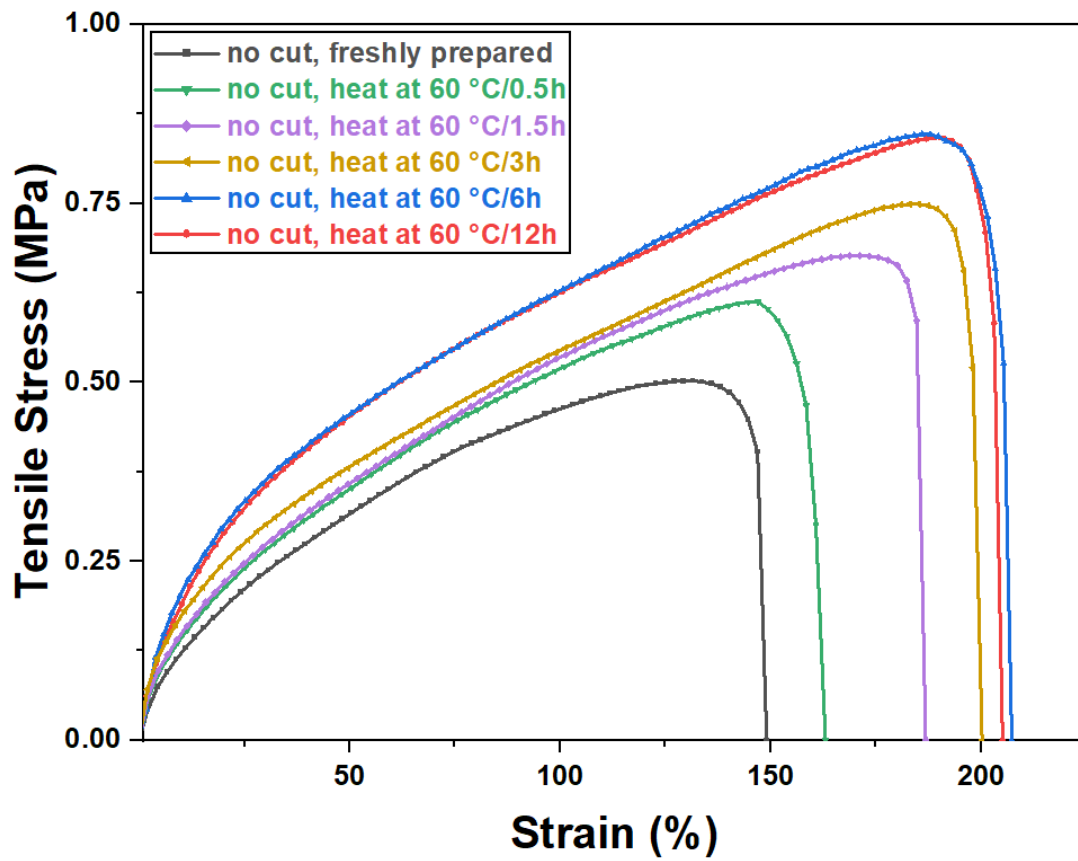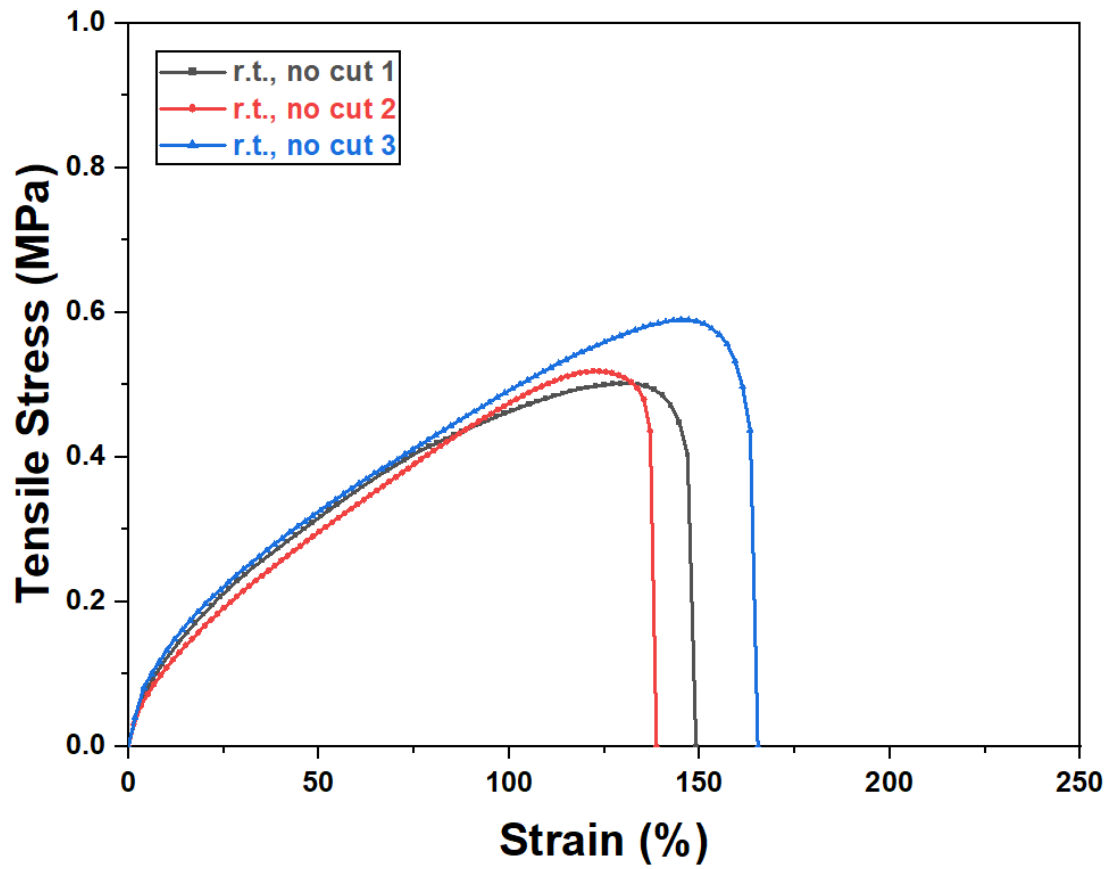
Fig. S13. Stress-strain curve comparison of freshly prepared dog-bone-shaped samples

and the dog-bone-shaped samples incubated at 60 °C for 0.5, 1.5, 3, 6, and 12 h.
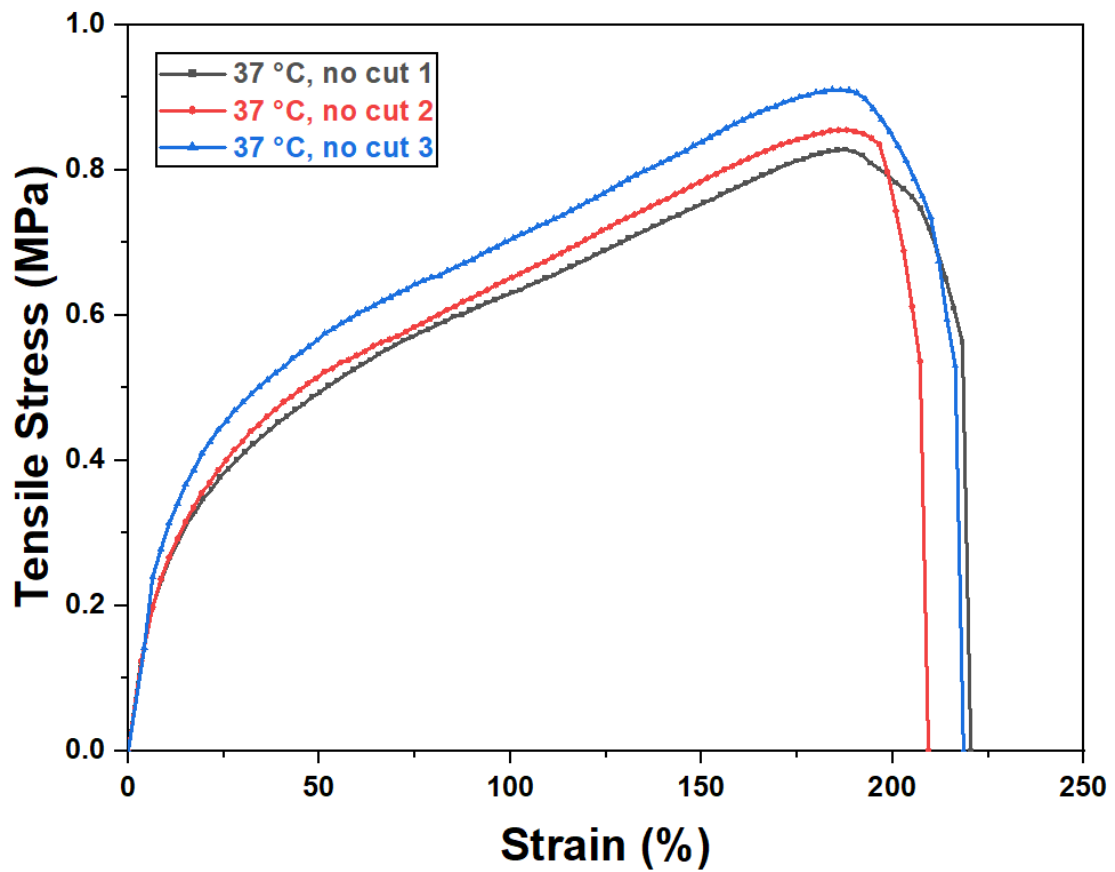
Freshly prepared sample at room temperature (no cut)			
Sample #	Young's Modulus (MPa)	Toughness (MJ·m^{-3})	Ultimate strength (MPa)	Ultimate strain (%)
1	2.14	0.53	0.50	149
2	2.16	0.48	0.52	138
3	2.30	0.65	0.59	163
Avg	2.20±0.1	0.55±0.07	0.54±0.05	150±13

Fig. S14. Stress-strain curves and data of mechanical properties for freshly prepared dog-bone-shaped samples (no cut).
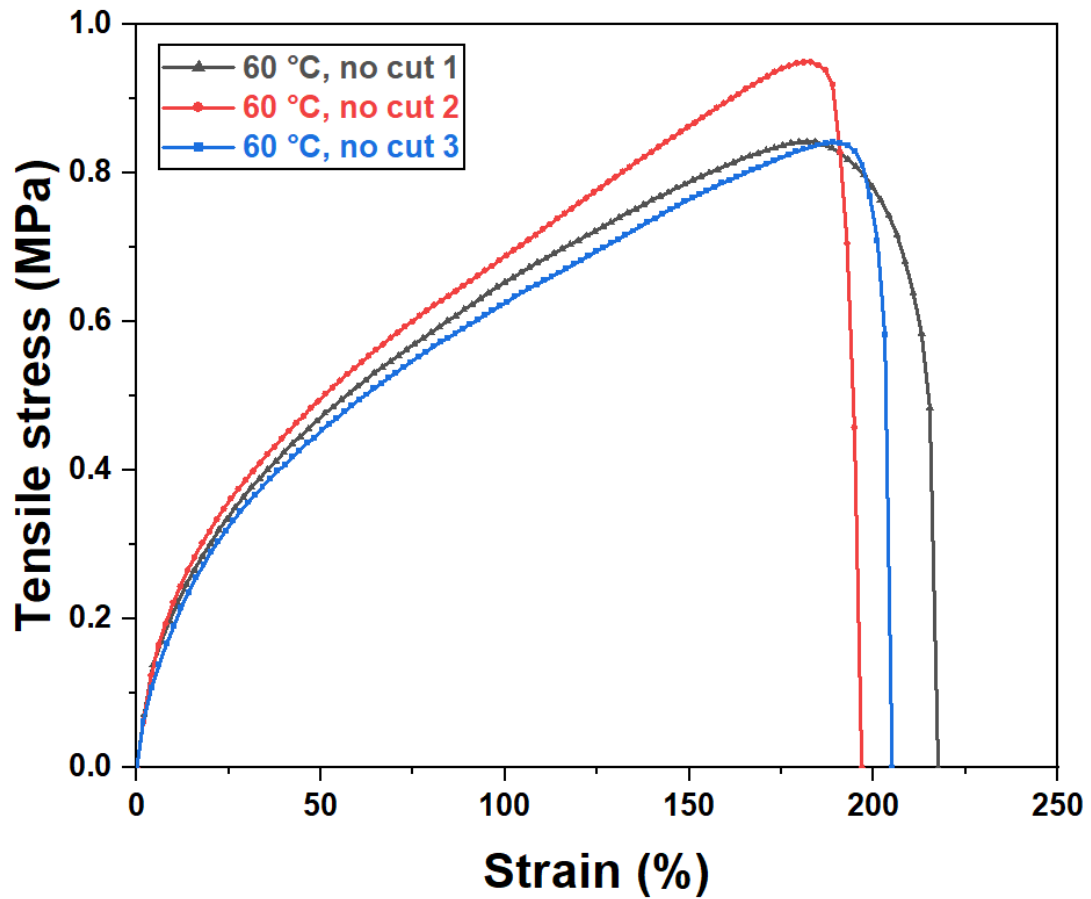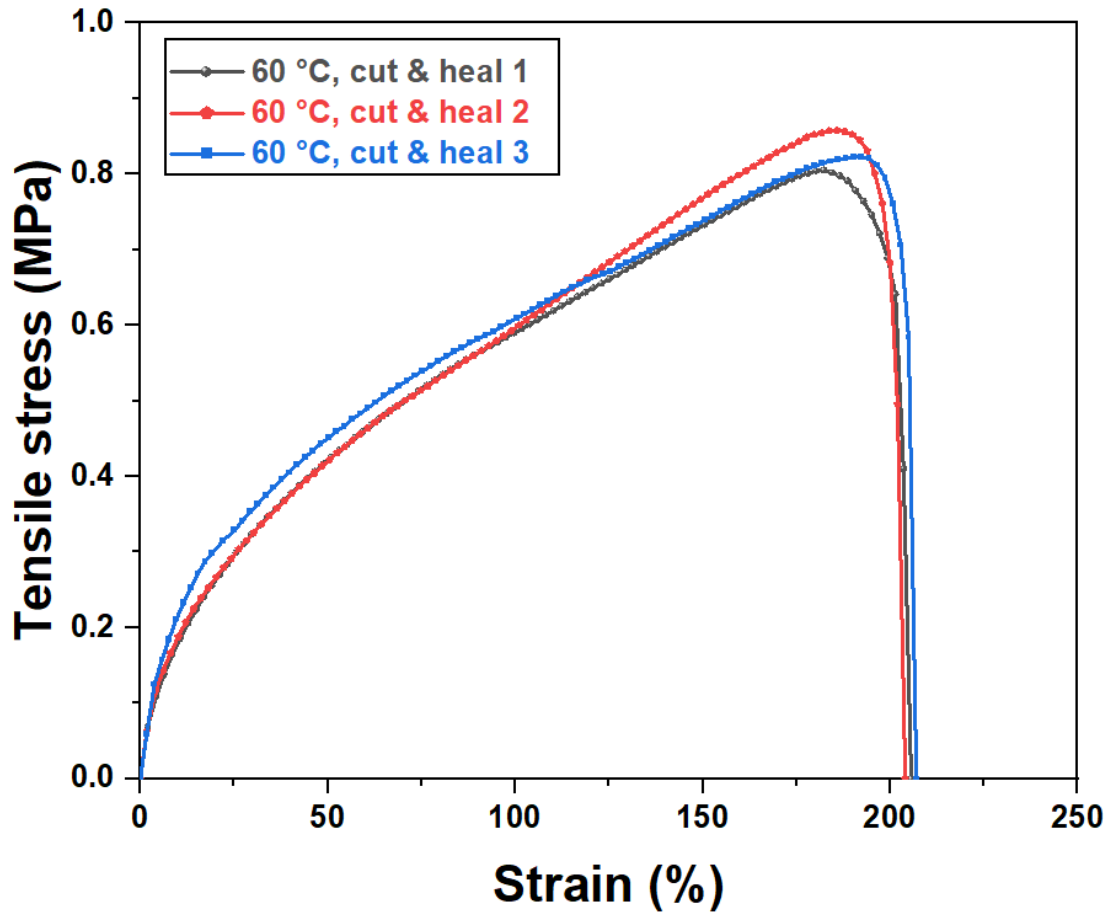
Incubation at 60 ℃ for 12h (no cut)				
Sample #	Young's Modulus (MPa)	Toughness (MJ·m⁻³)	Ultimate strength (MPa)	Ultimate strain (%)
1	3.56	1.31	0.84	215
2	3.48	1.25	0.94	194
3	3.53	1.19	0.84	203
Avg	3.52±0.04	1.25±0.06	0.87±0.07	204±11

Fig. S15. Stress-strain curves and data of mechanical properties for dog-bone-shaped samples incubated at 60 °C for 12 h (no cut).

Incubation at 37 ℃ for 12days (no cut)				
Sample #	Young's Modulus (MPa)	Toughness (MJ·m^{-3})	Ultimate strength (MPa)	Ultimate strain (%)
1	3.69	1.33	0.82	218
2	3.54	1.34	0.87	216
3	3.35	1.44	0.91	218
Avg	3.53±0.15	1.31±0.07	0.86±0.05	212±5

Fig. S16. Stress-strain curves and data of mechanical properties for dog-bone-shaped samples incubated at 37 ℃ for 12 days (no cut)

Cut then healed at 60 ℃ for 12 h			
Sample #	Young's Modulus (MPa)	Toughness (MJ·m⁻³)	Ultimate strength (MPa)	Ultimate strain (%)
1	3.56	1.13	0.81	203
2	3.59	1.15	0.86	201
3	3.34	1.18	0.82	204
Avg	3.50±0.09	1.15±0.03	0.83±0,03	203±2

Fig. S17. Stress-strain curves and data of mechanical properties for dog-bone-shaped samples that were cut and then self-healed by incubation at 60 ℃ for 12 h.
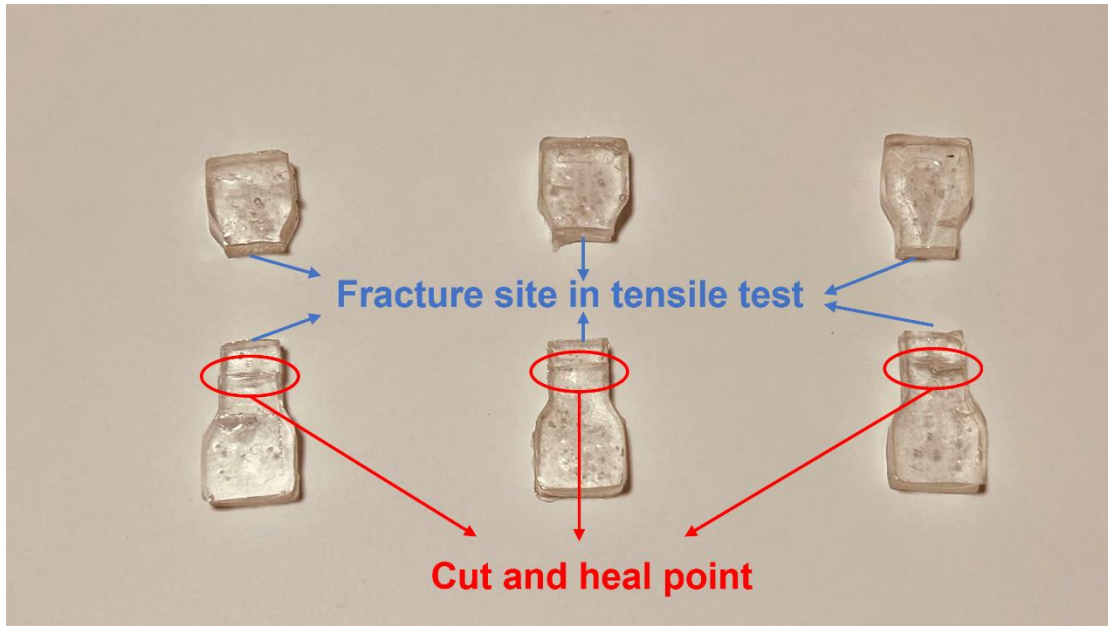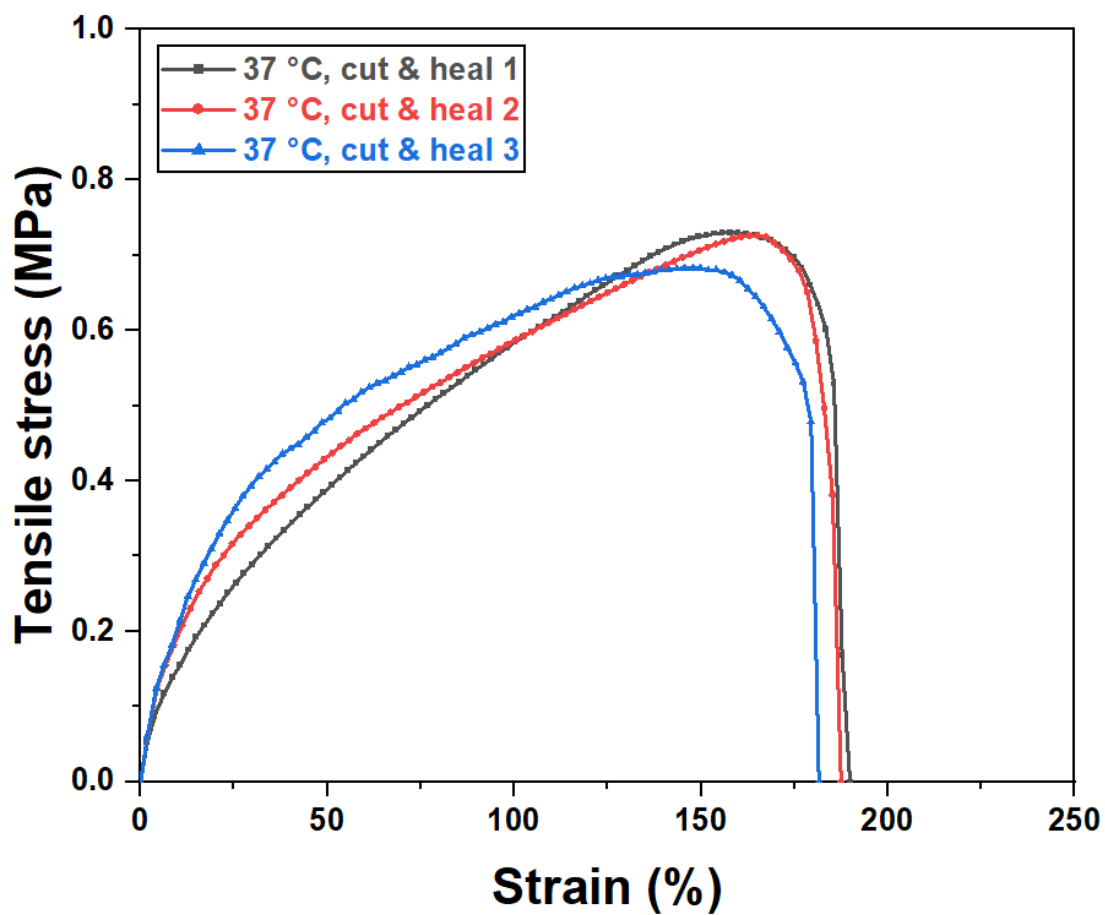
Fig. S18. Fracture sites of dog-bone-shaped samples that were cut and then self-healed by incubation at 60 ℃ for 12 h.

Cut then healed at 37 ℃ for 12 days				
Sample #	Young's Modulus (MPa)	Toughness (MJ·m⁻³)	Ultimate strength (MPa)	Ultimate strain (%)
1	2.85	0.95	0.73	186
2	3.13	0.96	0.73	185
3	3.27	0.96	0.69	179
Avg	3.13±0.23	0.96±0.01	0.73±0.03	185±5

Fig. S19. Stress-strain curves and data of mechanical properties for dog-bone-shaped samples that were cut and then self-healed by incubation at 37 ℃ for 12 days.
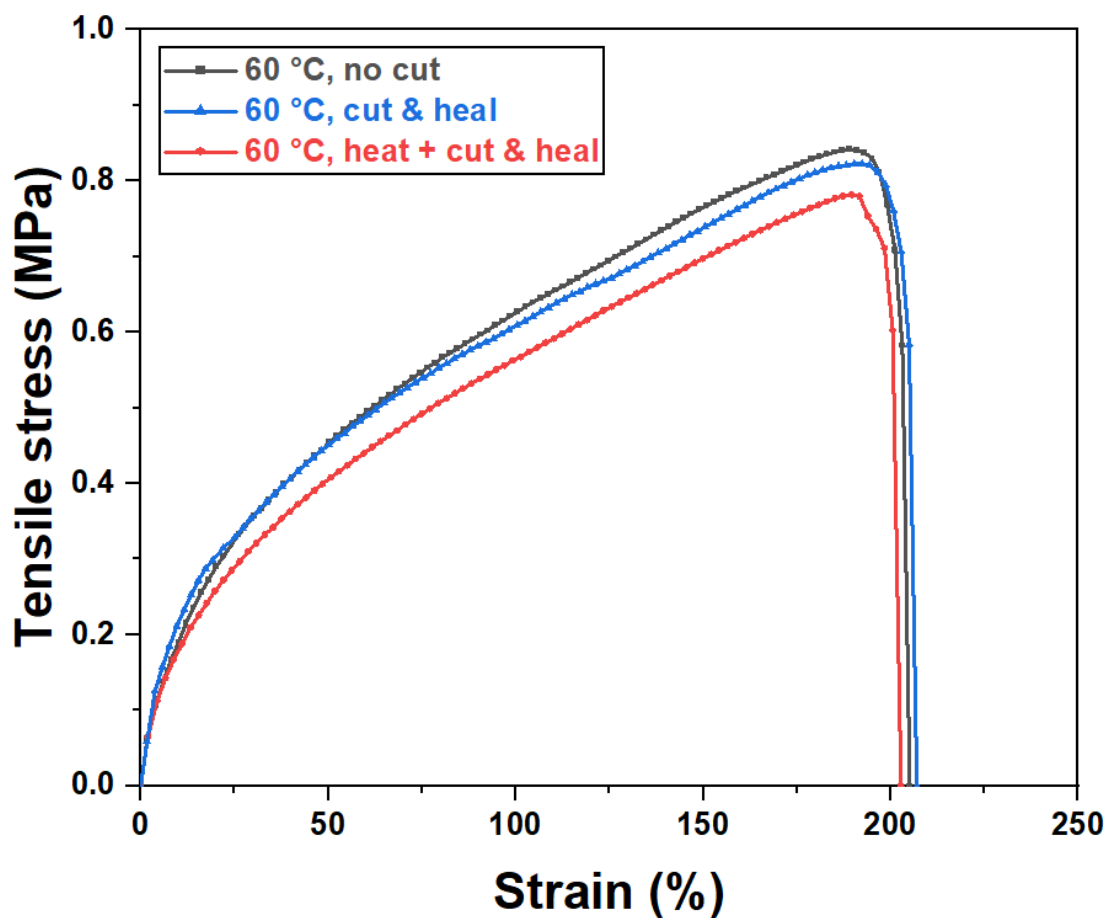
Fig. S20. Stress-strain curve for a dog-bone-shaped sample incubated at 60 °C for 12 h first, then cut and self-healed at 60 °C for 12 h (red line), as compared with a sample just incubated at 60 °C for 12 h without cut (black line) and a sample self-healed at 60 °C for 12 h after a cut at r.t. (blue line).
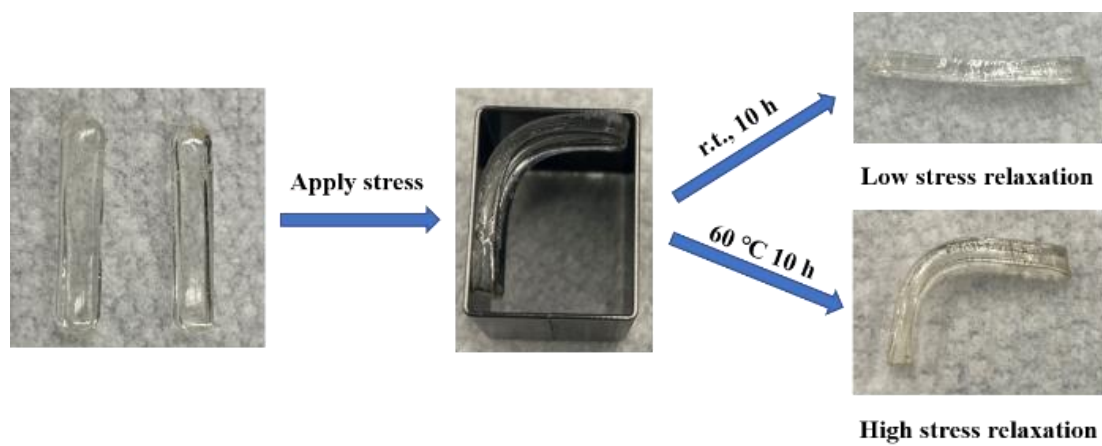
Fig. S21. Stress relaxation for bar-shaped DCPN samples at r.t. and 60 °C.