Supporting information for

Recyclable, Self-healable, and Highly Malleable Poly(urethane-urea)s with Improved Thermal and Mechanical Performances

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2. Figure and Table Citations

1. Experimental procedures

Determination of equilibrium constants (K_{eq}) and dissociation rate (k_{-1}) of monoHUB

Determination of the K_{eq} of compound 2c: Since the K_{eq} of **2c** is fairly large, it is difficult to confirm the equilibrium concentrations of the amine, isocyanate, and urea species. The coexistence of these three species was confirmed only in a very dilute solution. To accurately obtain the binding constants, we used an ‘indirect’ way through an equilibrium reaction between different urea species using TBEA as the reference urea compound, whose equilibrium constant is reported to be 7.9×10^5 M^{-1} by Cheng[1]. To obtain K', compound **2c** (5.9 mg, 0.02 mmol) and compound **4b** (5.1 mg, 0.05 mmol) were dissolved in $CDCl_3$ (0.55 mL) and added into an NMR tube. ^1H NMR spectra were collected 72 h after mixing at 37 °C until equilibrium was reached (Scheme S7). The equilibrium constant of the reaction K' was calculated based on the ratio of the concentration of each species.

$$\boldsymbol{K_{eq,2c}} = [\boldsymbol{2c}]_{eq}/([\boldsymbol{1a}]_{eq} * [\boldsymbol{2b}]_{eq}) \tag{S1}$$

$$\boldsymbol{K'} = ([\boldsymbol{4c}]_{eq} * [\boldsymbol{2b}]_{eq})/([\boldsymbol{2c}]_{eq} * [\boldsymbol{4b}]_{eq}) \tag{S2}$$

$$\boldsymbol{K_{eq,4c}} = [\boldsymbol{4c}]_{eq}/([\boldsymbol{1a}]_{eq} * [\boldsymbol{4b}]_{eq}) \tag{S3}$$

By combining the two equations above, we would have:

$$\boldsymbol{K_{eq,4c}}/\boldsymbol{K'} = [\boldsymbol{2c}]_{eq}/([\boldsymbol{1a}]_{eq} * [\boldsymbol{2b}]_{eq}) = \boldsymbol{K_{eq,2c}} \tag{S4}$$

Determination of the k_{-1} of compound 2c: Model compound **2c** (5.9 mg, 0.02 mmol) was dissolved in 0.55 ml $CDCl_3$ and transferred to an NMR tube (Scheme S8). Then, excess butyl isocyanate (**4a**, 20 μL) was quickly added into the NMR tube and heated at 55 °C. ^1H NMR spectra were collected based on selected time intervals until about 30% of **2c** was consumed, and the resulting data were used to calculate the dissociation rate.

Determination of K_{eq} and k_{-1} of bisHUB

Determination of the K_{eq} of compound 3c: To obtain K'', compound **3c** (5.2 mg, 0.01 mmol) and compound **4b** (5.1 mg, 0.05 mmol) were dissolved in $CDCl_3$ (0.55 mL) and added into an NMR tube (Scheme S9). ^1H NMR spectra were collected after mixing at 37 °C for one week until equilibrium was reached. The equilibrium constant of the reaction K'' was calculated based on the ratio of the concentration of each species.

$$\boldsymbol{K'' = ([3b]_{eq} * [4c]^2{}_{eq})/([3c]_{eq} * [4b]^2{}_{eq})} \tag{S5}$$

$$\boldsymbol{K^2{}_{eq,4c}/K'' = [3c]_{eq}/(\,[1a]^2{}_{eq} * [3b]_{eq}) = K_{eq,3c}} \tag{S6}$$

Determination of k_{-1} of compound 3c: Model compound **3c** (5.2 mg, 0.01 mmol) was dissolved in 0.55 ml $CDCl_3$ and transferred to an NMR tube (Scheme S10). Then, excess butyl isocyanate (**4a**, 20 μL) was quickly added into the NMR tube and heatedat 55 °C. ^1H NMR spectra were collected at selected time intervals until about 30% of **3c** was consumed. The dissociation rates were calculated according to these data.

Dynamic exchanges of HUB-bearing polymers

^{1}H NMR spectra analyses: Apart from dissociation and amine exchange, a metathesis reaction is also the characteristic of a dynamic urea bond. To further investigate the HUB-based dynamic metathesis reaction, model compounds **6c** (111.67 mg) and **3c** (125.17 mg) in a 1:1 molar ratio (25×10^{-3} M) were dissolved in $CDCl_3$. The formation of **7c** was monitored by ^{1}H NMR spectroscopy after incubation at 37 ^{o}C for 48 h. The model compound **6c** was synthesized by mixing **4a** (99.13 mg, 1 mmol) and **3b** (124.2 mg, 0.5 mmol) in 10 mL $CDCl_3$. The mixture was stirred for 30 min at room temperature, and then the solvent was removed. Compound **6c** was obtained as a white powder and used without purification (Scheme S11).

GPC analyses[2]: m-Xylylenediisocyanate (**3a**, 188.18 mg, 1 mmol) and TBXA (**3b**, 248.41 mg, 1 mmol) were added into DCM (2.0 ml). The mixture was stirred at 37 ^{o}C for 2 h and was analyzed by GPC to verify whether poly(3a/3b) was synthesized. Then another equivalent of **3b** (248.41 mg, 1 mmol) was added, and the reaction was allowed to proceed for an additional 36 h. The solution was analyzed by GPC to determine whether poly(3a/3b) was depolymerized to form oligomers.

Ultimately, one equivalent of **3a** (188.18 mg, 1 mmol) was added into the solution to return the 3a: 3b ratio back to 1: 1. The solution was analyzed by GPC after four hours to confirm whether a higher M_W of poly(3a/3b) was re-formed.

Characterization

NMR spectra were performed on a Bruker DRX400 operating at Varian U400 (400 MHz), a UI500NB (500 MHz), or a UI600 (600MHz) spectrometer with TMS as an internal reference. If not stated otherwise, the test sample was 10 mg in 550 μl $CDCl_3$.

Gel permeation chromatography (GPC) experiments were performed on a system equipped with an isocratic pump (Model 1100, Agilent Technology, Santa Clara, CA, USA), a DAWN HELEOS multi-angle laser light scattering detector (MALLS detector, Wyatt Technology, Santa Barbara, CA, USA) and an OptilabrEX refractive index detector (Wyatt Technology, Santa Barbara, CA, USA). The detection wavelength of HELEOSwas set at 658 nm. Separations were performed using serially connected size exclusion columns (100 Å, 500 Å, 103 Å and 104 Å Phenogel columns, 5 μm, 300 × 7.8 mm, Phenomenex, Torrance, CA, USA) at 60 °C using DMF containing 0.1 M LiBr as the mobile phase.

Fourier transform infrared spectra (FTIR) were recorded on a Perkin Elmer 100 serial FTIR spectrophotometer by 32 scans from 4000 to 600 cm^{-1}, with a bandwidth set of 4 cm^{-1}, which is equipped with universal attenuated total reflectance (ATR), enabling the analysis of polymer samples in powder form.

Thermogravimetric analysis (TGA) was performed on TA instruments Q600 Simultaneous Thermal Analyzers. Samples were heated under a nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 600 ^{o}C. Since the materials are expected to withstand elevated temperatures for longer periods when being processed, isothermal TGA was conducted at 150°C for 2 h and at 180 °C for 2 h under a nitrogen atmosphere.

Differential scanning calorimetry (DSC) was performed on TA instruments Q2000 (Germany). The temperature procedure was heated from -60 to 180 °C with a ramping rate of 10 °C/min (first run) under a nitrogen atmosphere, cooling to -70 °C with a rate of −20 °C/min, and reheating to 150 °C with a rate of 10 °C/min. T_g was evaluated as the inflection point of the heat flow step at a scan rate of 10 ^{o}C/min in the second heating ramp.

The scratch-healing experiments were carried out using a Rockwell C indenter (tip radius 10 μm) mounted on a scratch test machine (Anton Paar, micro-scratch tester). In a progressive load mode, the test was conducted using three stages, including pre-scan, scratching and post-scan.

The transmittance of PUUs was tested using a Perkin Elma Lambda 25 UV-vis spectrometer with the wavelength from 500~800 nm. Accurate mass measurements were accomplished on Orbitrap MS (Q-Exactive, Thermo Scientific, San Jose, CA).

Dynamic mechanical analysis (DMA) was conducted on a DMA Q800 apparatus (TA Instruments, New Castle, DE, USA) under multi-frequency strain mode. Rectangular samples (ca. 1 mm (T) × 6 mm (W) × 30 mm (L) were tested at a frequency of 1 Hz, a strain of 0.1% and an oscillation amplitude of 10 μm. Heating ramp of 3 ^{o}C/min was applied from -70 °C to 150 °C under a nitrogen atmosphere.

Stress-relaxation experiment: Stress-relaxation analysis (SRA) was performed on a TA-Q800 DMA (TA instruments, New Castle, DE, USA) utilizing rectangle-shaped specimens (ca. 1 mm (T) × 6 mm (W) × 30 mm (L). The SRA experiments were performed in a strain control (10% strain) mode at a specified temperature. After equilibrating at this temperature for about five minutes, the stress decay was monitored. The relaxation modulus (ε) was normalized by initial value (ε_0). The characteristic relaxation time (τ^*) was defined as the time required for $\varepsilon/\varepsilon_0 = 1/e$ with exponential decay function: $\varepsilon(t) = \varepsilon_0 \exp(-t/\tau^*)$[3].

Uniaxial tensile measurements were performed on an INSTRON 3367 Long travel Elastomeric Extensometer controlled by Bluehill Lite software at a crosshead speed of 20 mm/min, using a rectangular film with an effective gauge dimension: 30mm (L) × 6 mm (W) × 1 mm (T). Tensile strength measurements were carried out according to the UNE-EN-ISO 527 standard. Each result was the average from at least three samples.

Swelling experiment[4]: The swelling experiment was performed as follows. The PUU sample (ca. 25 mm (L) × 10 mm (W) × 1 mm (T)) was immersed in the typical chemical solvents (~ 10 ml) at room temperature. After 72 h, the swelling ratio (SR) was calculated according to the formula (S7). After that, the insoluble materials were dried in a vacuum drying oven until the weight reached a constant, and the gel fraction (GF) was obtained according to the formula (S8).

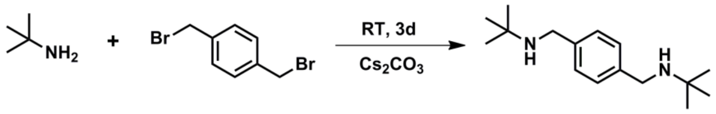
$$\mathbf{SR} = \frac{(\boldsymbol{m_1} - \boldsymbol{m_0})}{\boldsymbol{m_0}} \tag{S7}$$

$$\mathbf{GF} = \frac{\boldsymbol{m_2}}{\boldsymbol{m_0}} \tag{S8}$$

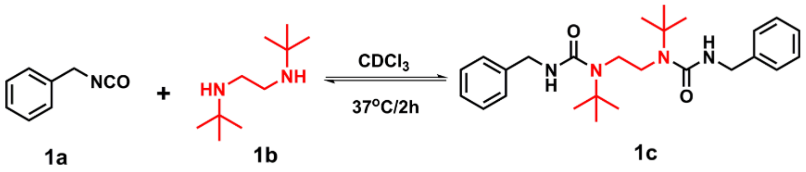
Where, m_0 is the original weight of the sample, m_1 is the mass of the sample after swelling, and m_2 is the mass of the sample after drying. To further prove the crosslinking structure of PUUs, solubility test of PUU-a was carried out at 60 ^{o}C with $CHCl_3$ as the solvent. The calculation of SR and GF was the same as the swelling experiment at room temperature.

Reprocessing experiments: The PUU networks were cut into pieces (~ 2.0 g), and then placed into a rectangular mold (ca. 30 mm (L) × 6 mm (W) × 1 mm (T)) using a hot press at 80 °C under the load of 3 MPa for required periods of time. The mold was cooled naturally to room temperature by cold water in ~ 10 min. Finally, the transparent square specimens were obtained after demolding. The structure and mechanical properties of the multiple reprocessed specimens were evaluated to verify the recyclability.

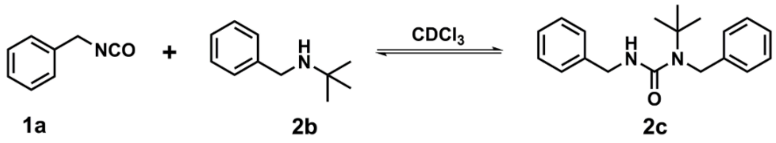
Self-healing experiments: Self-healing performance was characterized by tensile tests, which were performed on rectangle-shaped specimens (ca. 30 mm (L) × 6 mm (W) × 1 mm (T)) at a crosshead speed of 20 mm/min using a universal testing machine (INSTRON 3367). The PUU film was cut into two parts by an art knife, then the scratched parts were put together, and treated at a certain temperature for different times. Having been cooled to room temperature, the optical microscope was used to monitor the scratch at different time intervals during the heating process, then the self-healing performance was characterized by tensile tests.



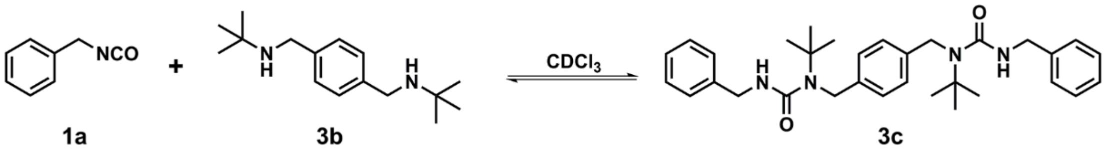
Scheme S1. Synthesis of TBXA.



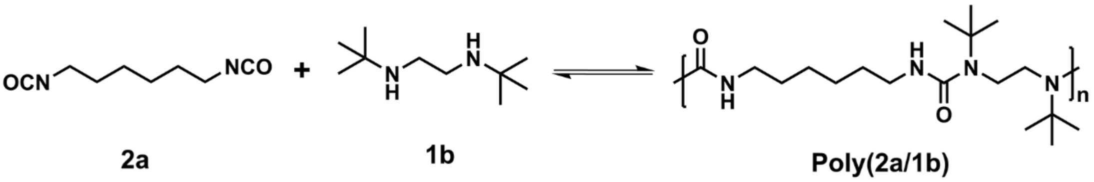
Scheme S2. Synthesis of compound **1c**.



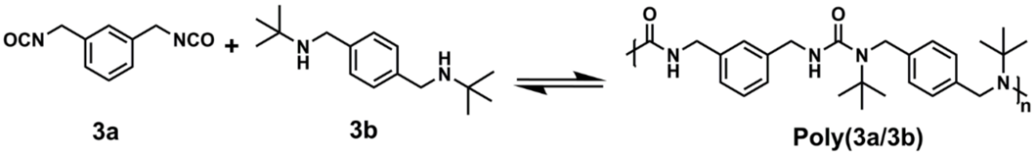
Scheme S3. Synthesis of compound **2c**.



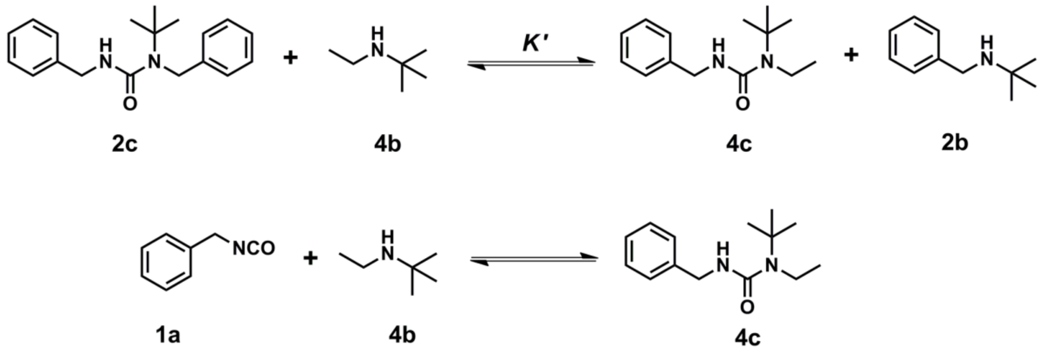
Scheme S4. Synthesis of compound **3c**.



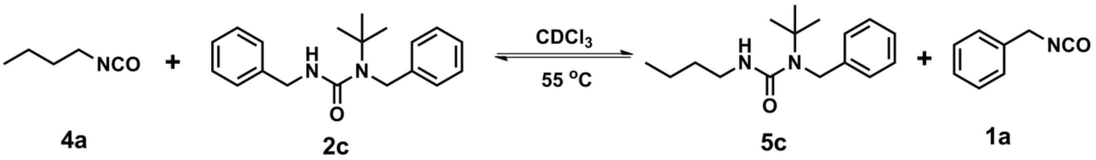
Scheme S5. Poly(2a/1b), HUB-bearing dynamic polymers, prepared via the polyaddition of **2a** and **1b**.



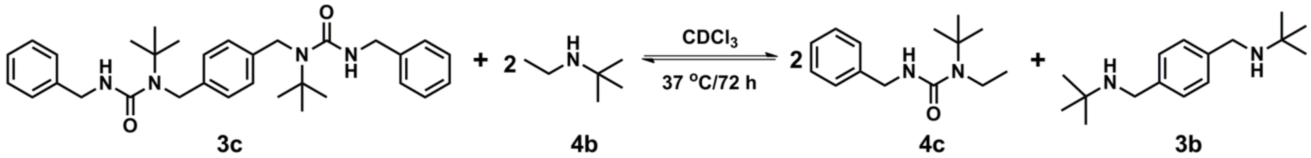
Scheme S6. Poly(3a/3b), HUB-bearing dynamic polymers, prepared via the polyaddition of **3a** and **3b**.



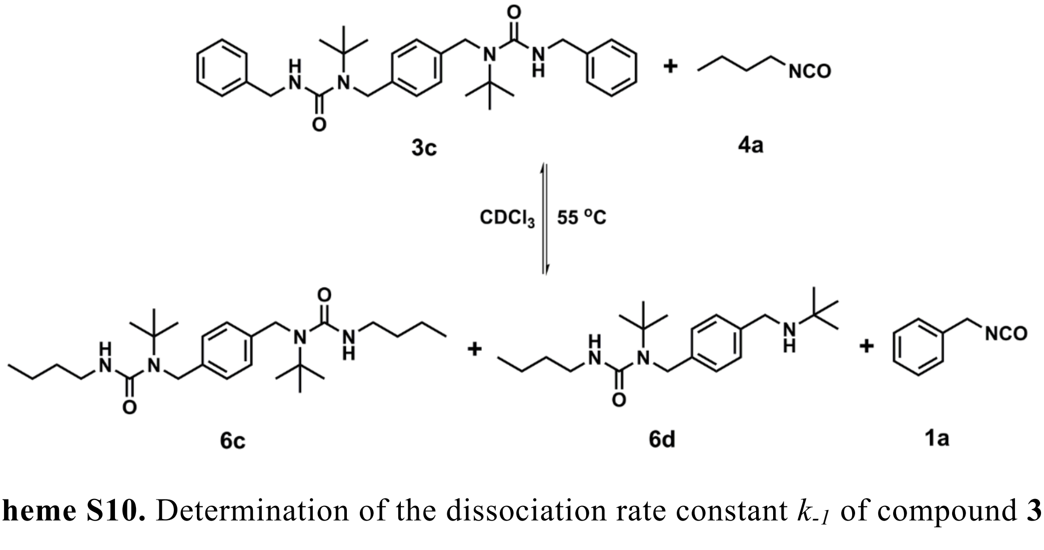
Scheme S7. Determinationof the K_{eq} of compound **2c**.



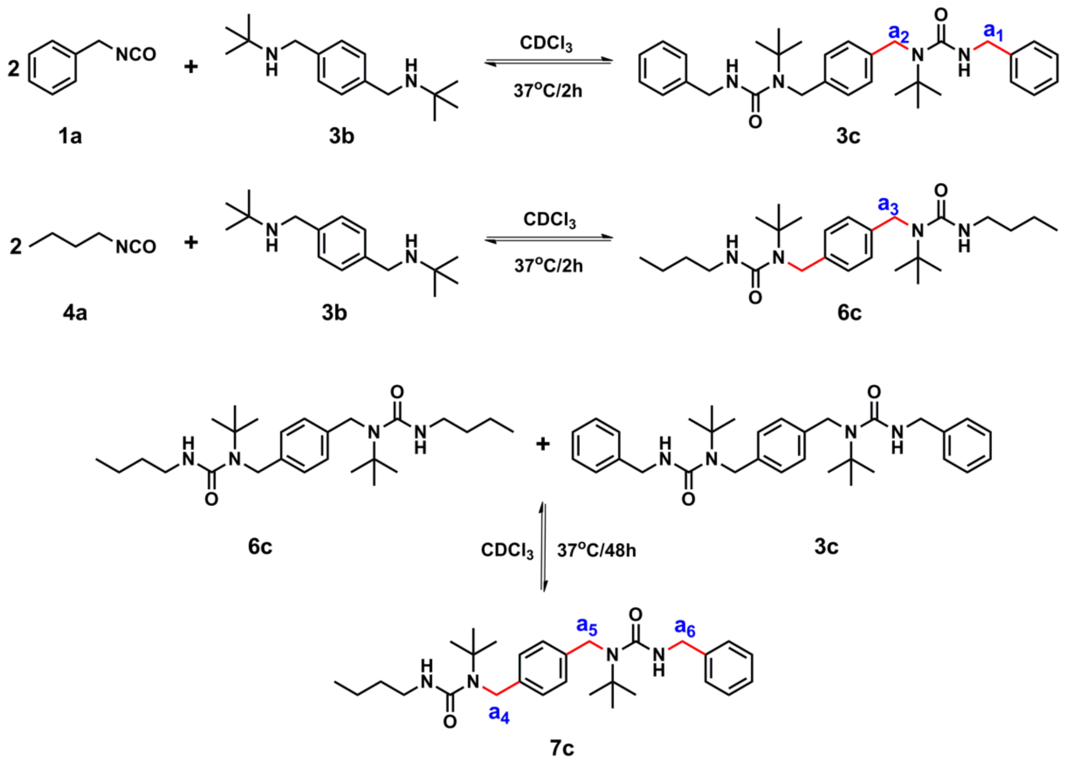
Scheme S8. Determination of the dissociation rate constant k_{-1} of compound **2c**.



Scheme S9. Determination of the equilibrium constant K_{eq} of compound **3c**.



Scheme S10. Determination of the dissociation rate constant k_{-1} of compound **3c**.



Scheme S11. Chemical structures of three model compounds (**3c**, **6c** and **7c**), and the reversible exchange reaction between **6c** and **3c**.

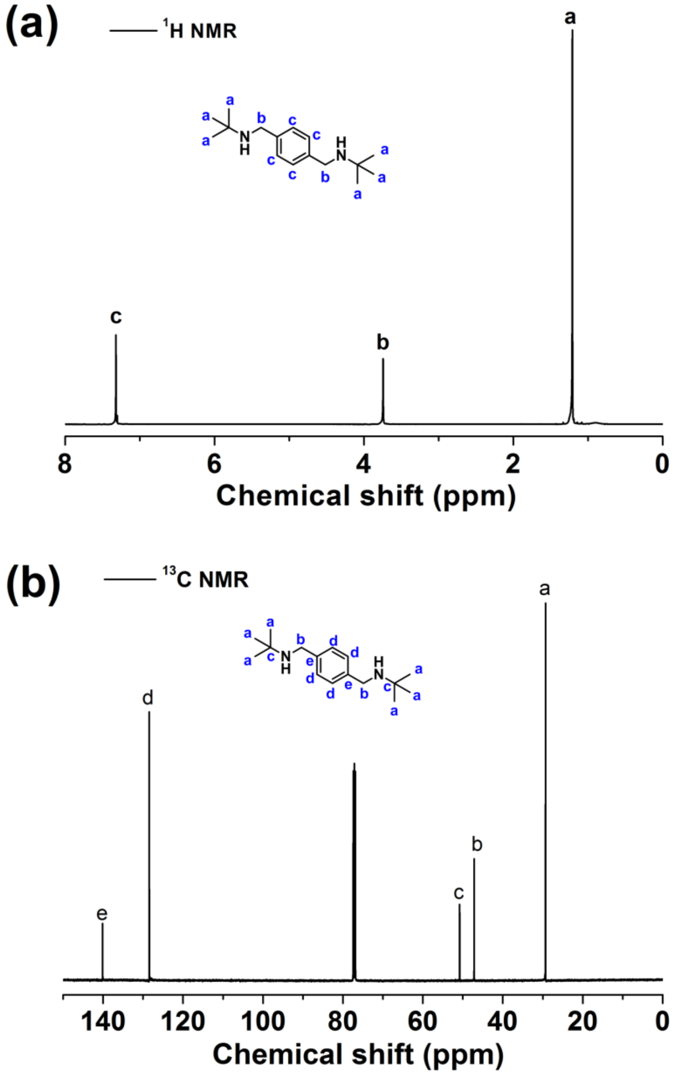


Figure S1. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of TBXA.

^{1}H NMR (500 MHz, CDCl3):δ 7.28 (s, 4H), 3.70 (s, 4H), 1.17 (s, 18H). ^{13}C NMR (125 MHz, CDCl3): δ 140.1, 128.4, 50.8, 47.2, 29.3.

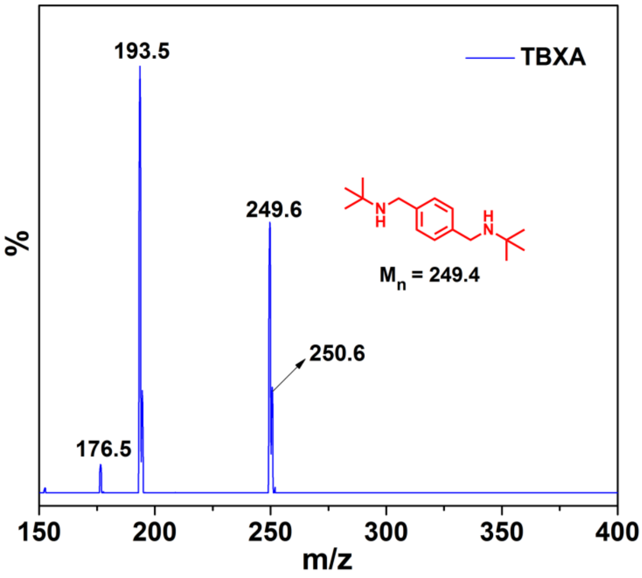


Figure S2. MS-ESI spectrum of TBXA.

MS-ESI: C16H29N2 [M•H]+, calculated: 249.4, found: 249.6.

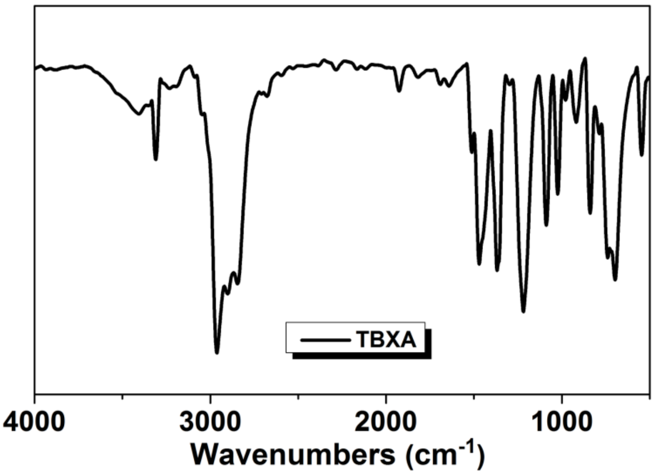


Figure S3. FTIR spectrum of TBXA.

FTIR (cm^{-1}): 3309, 2962, 2842, 1643, 1512, 1460, 1367, 1278, 838.

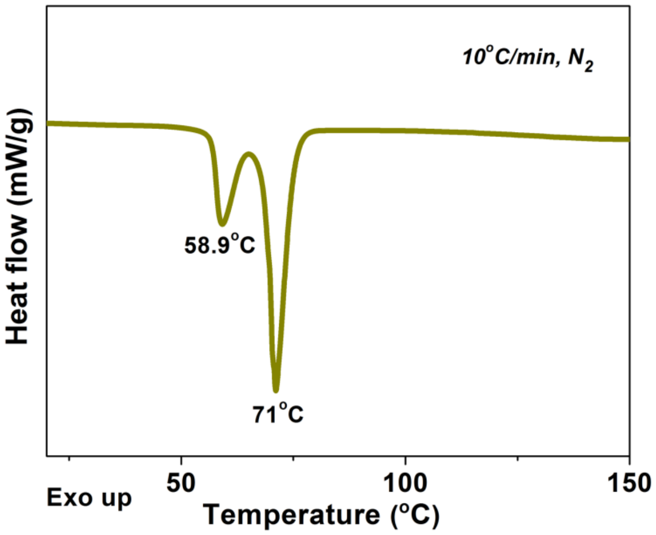


Figure S4. DSC curve of TBXA with different stoichiometric ratios under a nitrogen atmosphere from room temperature to 300 °C at a heating rate of 10 ^{o}C/min.

Melting point (T_m): 58.9 ^{o}C, 71 ^{o}C.

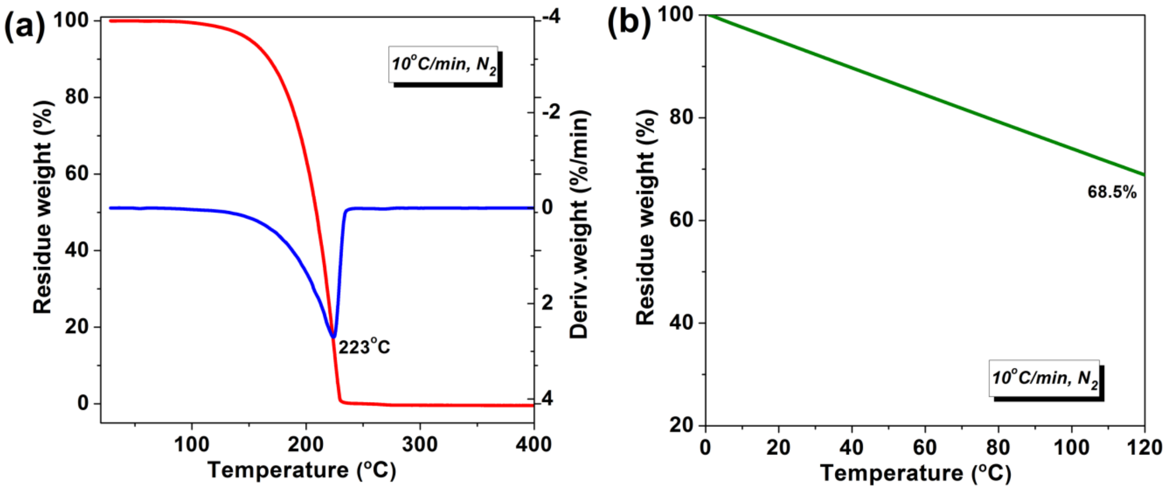


Figure S5. (a) TGA and DTG curves of TBXA under a nitrogen atmosphere from room temperature to 400 °C at a heating rate of 10 ^{o}C/min; (b) The isothermal TGA curve of TBXA at 100 ^{o}C for 120 min under a nitrogen atmosphere.

Thermal decomposition temperature (T_d) of TBXA is 223 ^{o}C; The residue weight of TBXA is 68.5% after incubating at 100 ^{o}C for 120 min.

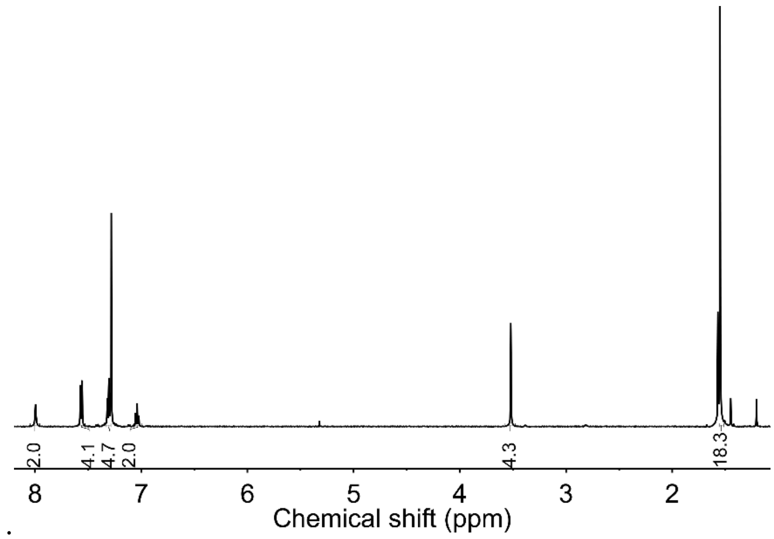


Figure S6. ^{1}H NMR spectrum of model compound **1c**.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (s, 2H), 7.54 (dd, *J* = 7.9, 1.3 Hz, 4H), 7.28 (t, 4H), 7.02 (m, 2H), 3.50 (s, 4H), 1.54 (s, 18H).

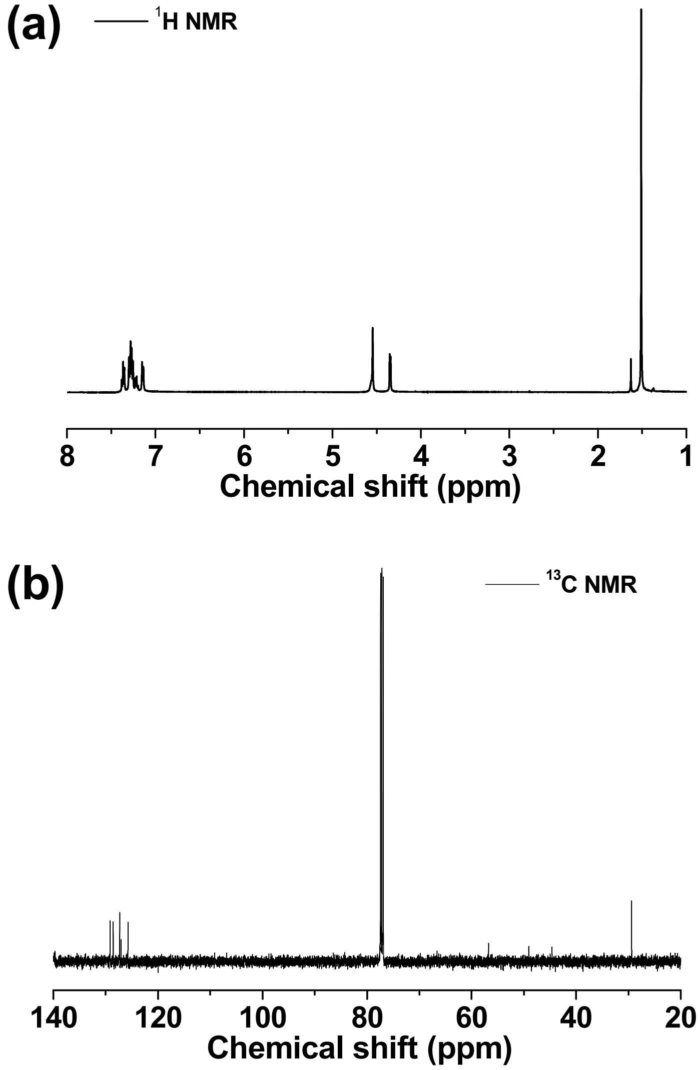


Figure S7. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of **2c**.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11~7.36 (m, 10H), 4.53 (b, 1H), 4.52 (s, 2H), 4.33 (d, 2H), 1.50 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 129.2, 128.6, 127.3, 127.0, 125.8, 77.4, 77.2, 76.9, 56.76, 49.1, 44.62, 29.4.

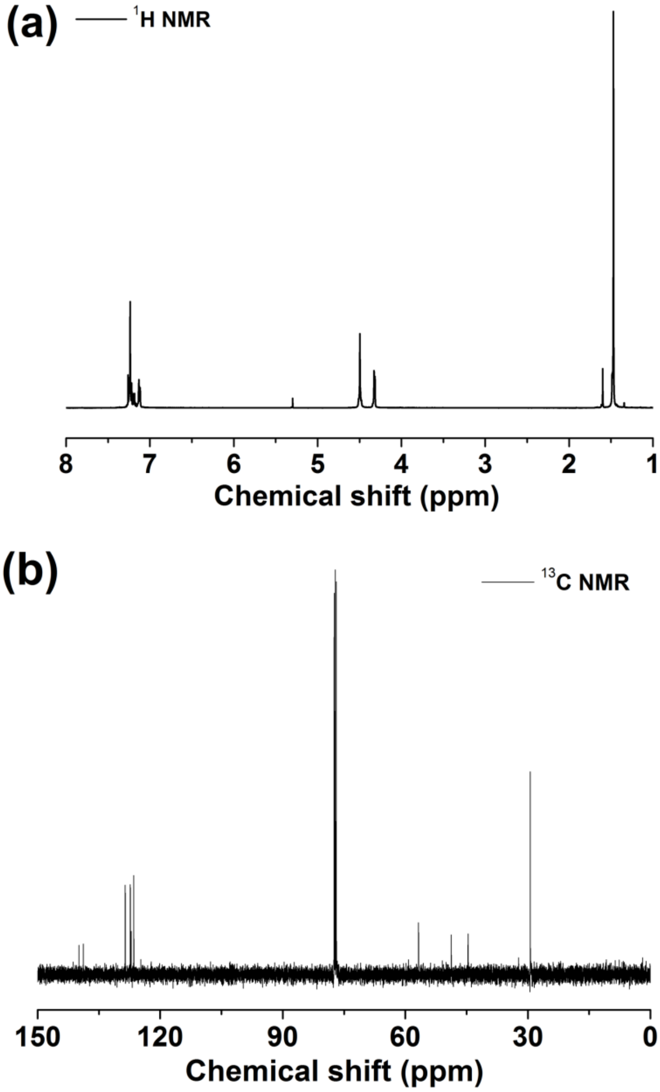


Figure S8. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of **3c**.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.27-7.10 (m, 10H), 4.54-4.45 (m, 6H), 4.32 (d, *J* = 5.5 Hz, 4H), 1.47 (s, 18H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 159.4, 139.9, 138.8, 128.6, 127.3, 127.1, 126.5, 77.4, 77.2, 76.9, 56.8, 48.8, 44.6, 29.4.

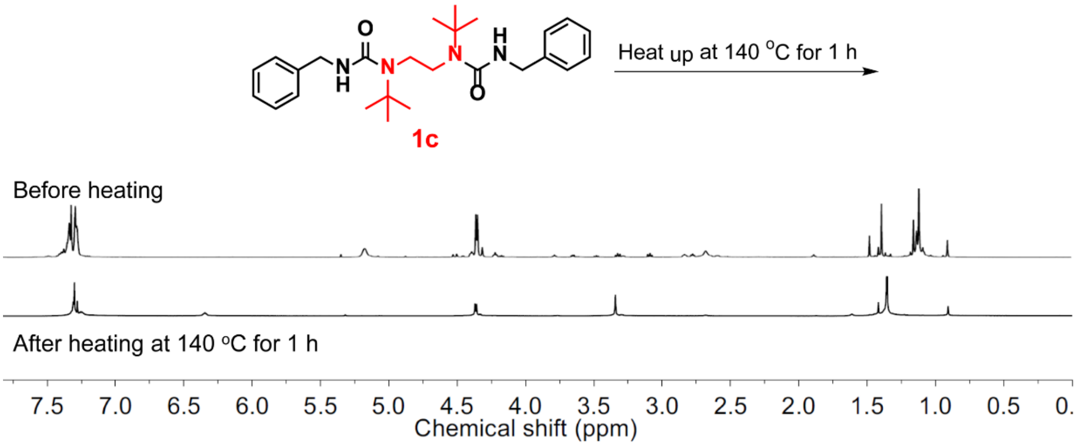


Figure S9. ^{1}H NMR spectra of model compound **1c** before and after heat-treatment at 140 °C for 1 h.

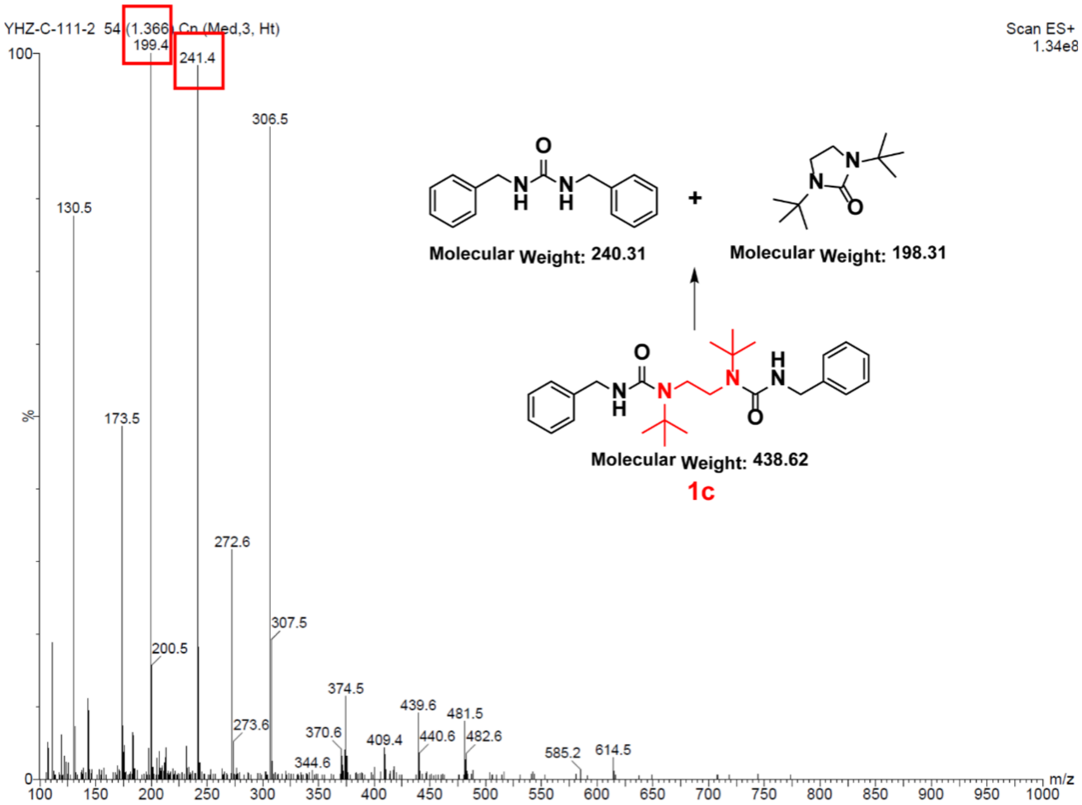


Figure S10. ESI-Mass spectrum of model compound **1c** after heat-treatment at 140 °C for 1 h. Marked peaks correspond to the degraded urea compound and the five-membered cyclic byproduct.

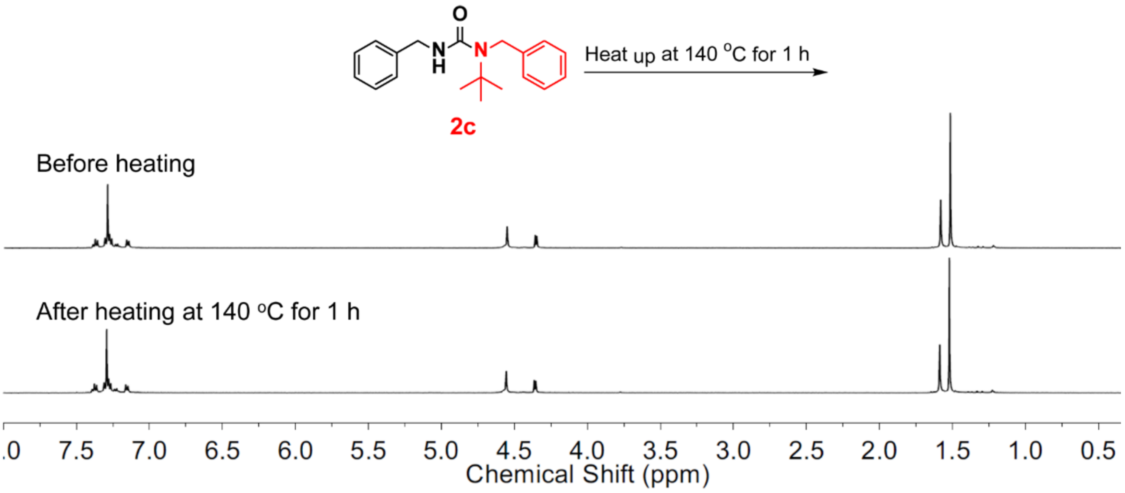


Figure S11. ^{1}H NMR spectra of model compound **2c** before and after heat-treatment at 140 °C for 1h.

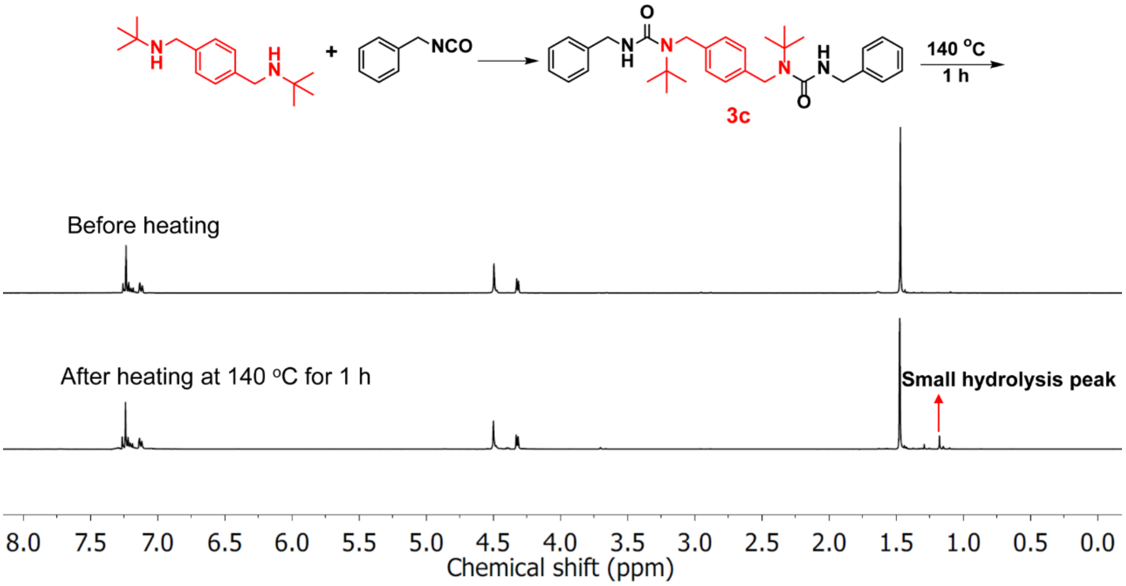


Figure S12. ^{1}H NMR spectra of model compound **3c** before and after heat-treatment at 140 °C for 1h.

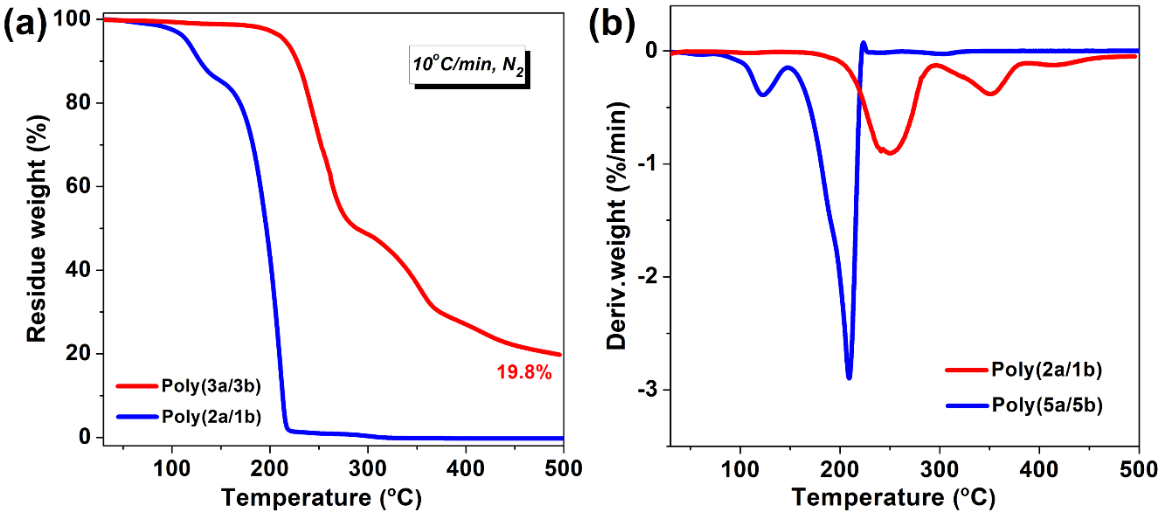


Figure S13. TGA (a) and DTG (b) curves of Poly(2a/1b) and Poly(3a/3b) under a nitrogen atmosphere from room temperature to 500 °C at a heating rate of 10 °C/min.

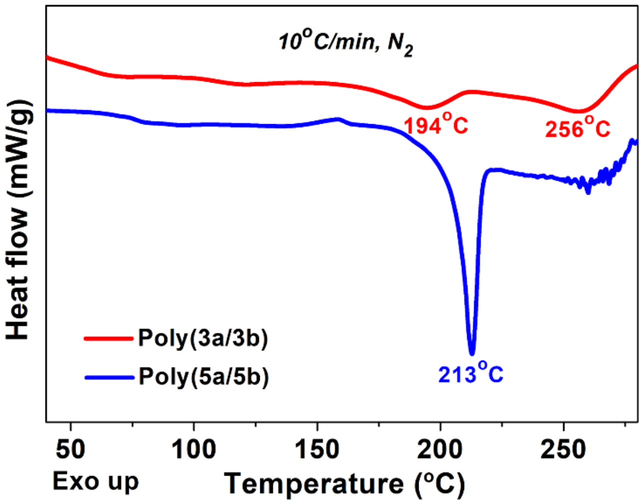


Figure S14. DSC curves of Poly(2a/1b) and Poly(3a/3b) under a nitrogen atmosphere from room temperature to 300 °C at a heating rate of 10 °C/min.

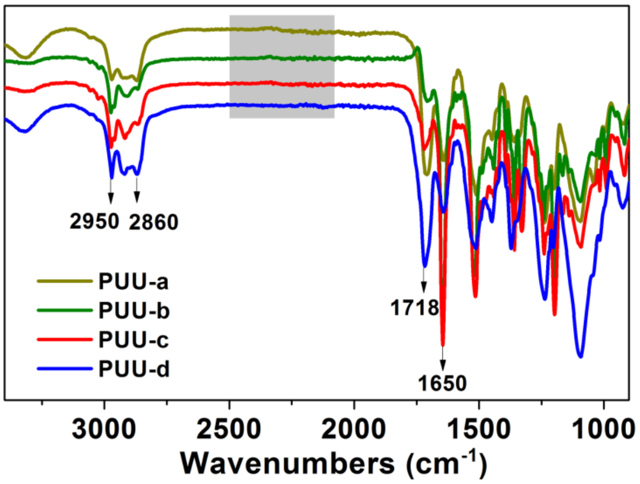


Figure S15. FTIR spectra of PUUs with different stoichiometric ratios.

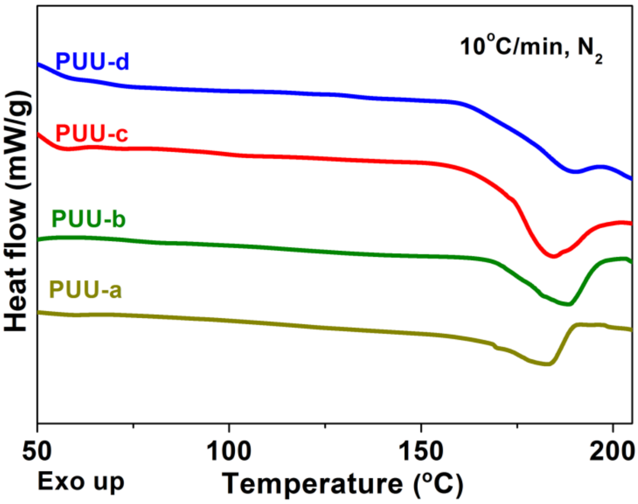


Figure S16. DSC curves of PUUs with different stoichiometric ratios under a nitrogen atmosphere from room temperature to 300 °C at a heating rate of 10 °C/min.

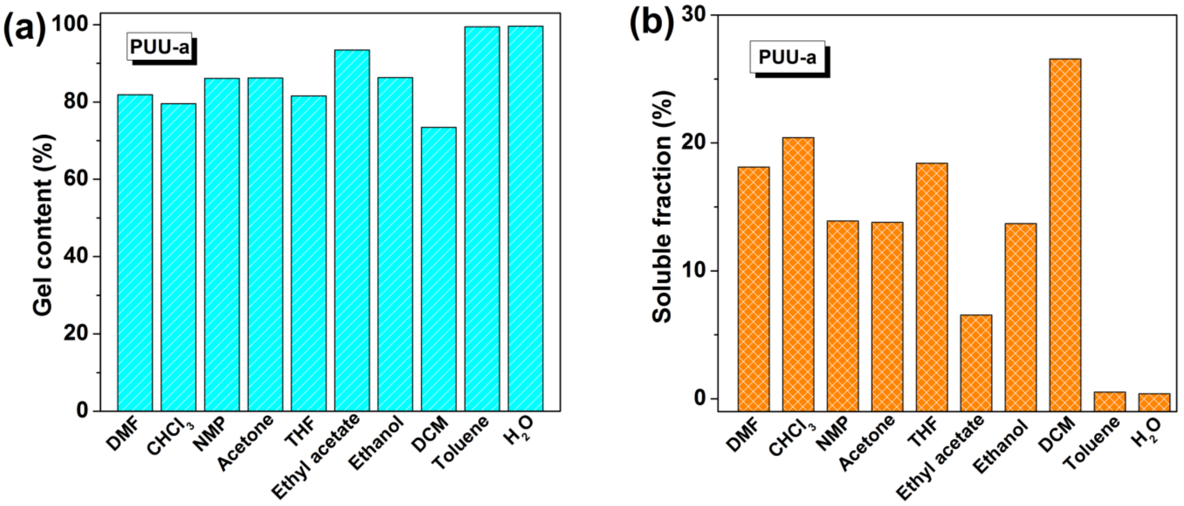


Figure S17. Gel content (a) and swelling ratios (b) of PUU-a in different solvents for 48 h at room temperature.

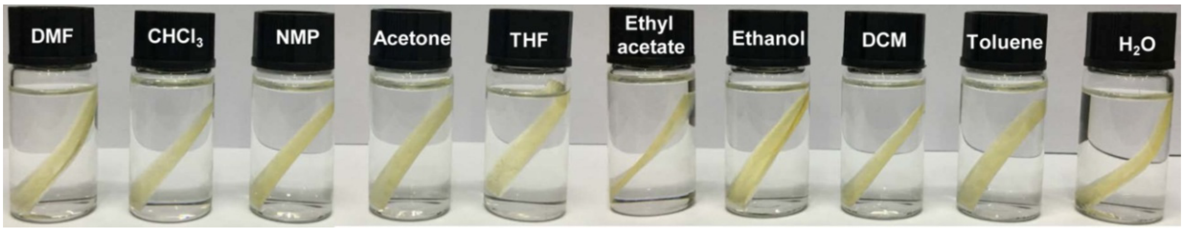


Figure S18. Swelling experiment of the PUU-a. The PUU-a sample (ca. 25 mm (L) × 10 mm (W) × 1 mm (T)) was immersed in H_2O and the typical chemical solvents (~ 10 ml) at room temperature. After 72 h, the SR was calculated according to the formula.

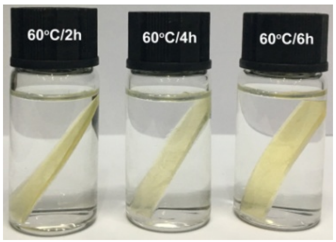


Figure S19. The swelling experiment of PUU-a (ca. 25 mm (L) × 10 mm (W) × 1 mm (T)) in $CHCl_3$ at 60 ^{o}C for different times.

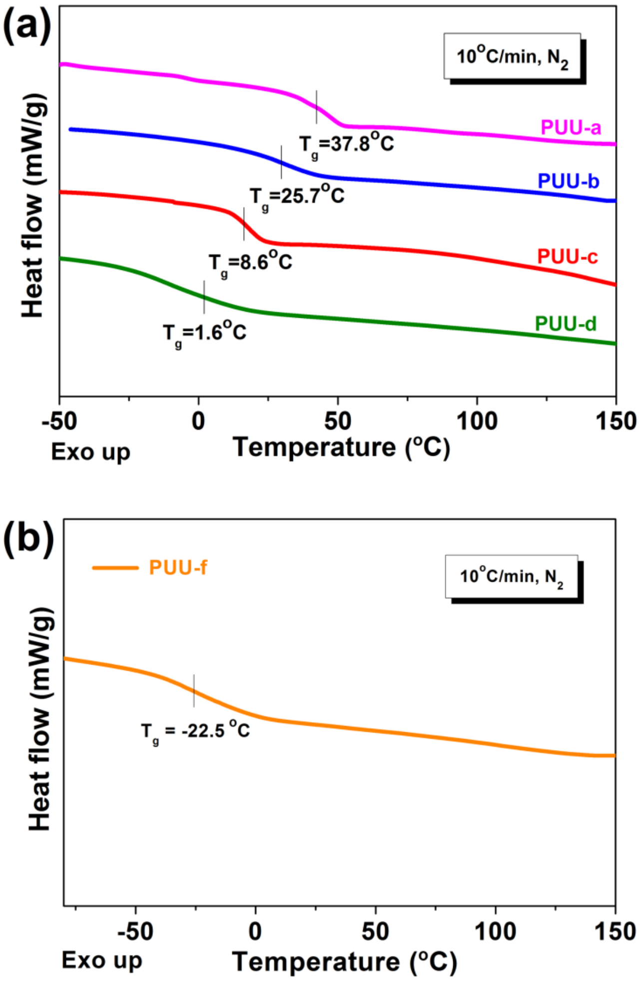


Figure S20. T_gs of PUUs with different stoichiometric ratios obtained from DSC curves under a nitrogen atmosphere from room temperature to 300 °C at a heating rate of 10 ^{o}C/min: (a) PUU-a, PUU-b, PUU-c, and PUU-d; (b) PUU-f.

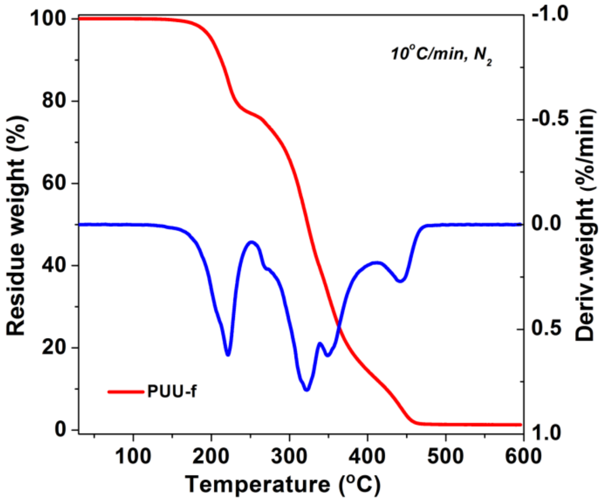


Figure S21. TGA and DTG curves of the PUU-f under a nitrogen atmosphere from room temperature to 600 °C at a heating rate of 10 °C/min.

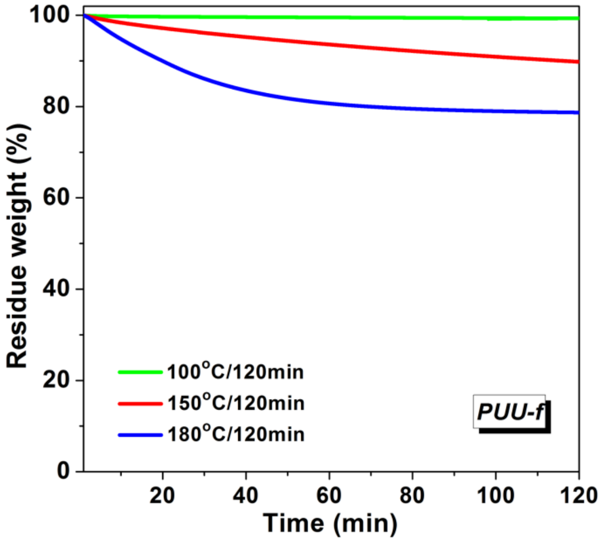


Figure S22. Isothermal TGA curves of PUU-f at 100 °C, 150 °C and 180 °C for 120 min under a nitrogen atmosphere.

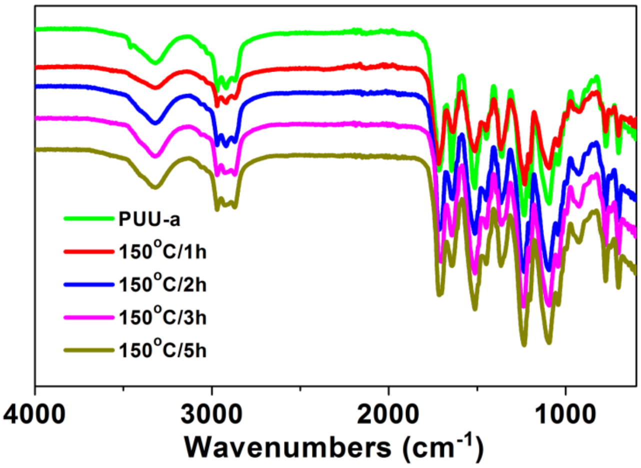


Figure S23. FTIR spectra of PUU-a after heat treatment at 150 °C for different hours.

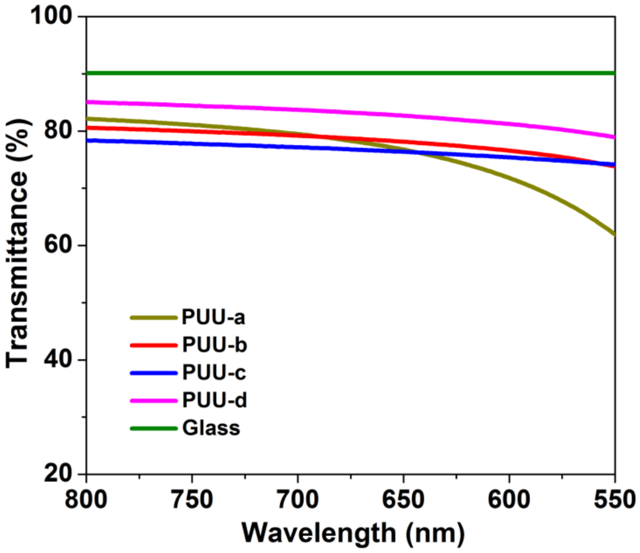


Figure S24. The visible spectra of glass and PUUs with different stoichiometric ratios.

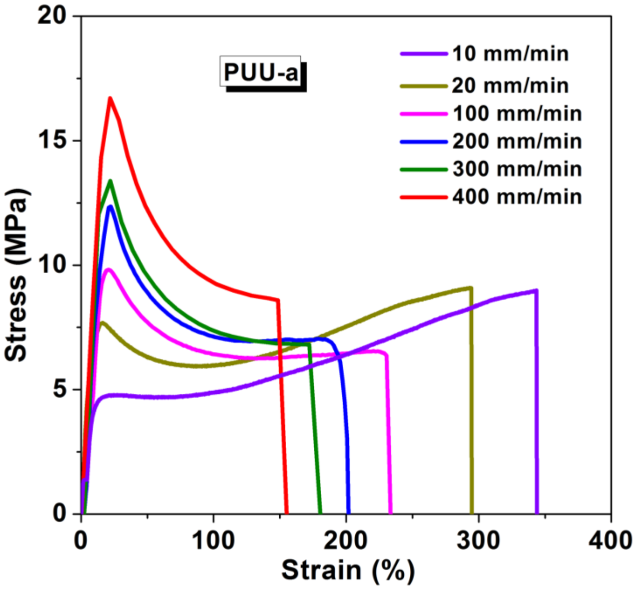


Figure S25. Stress-strain curves of PUU-a with different stretching speeds.

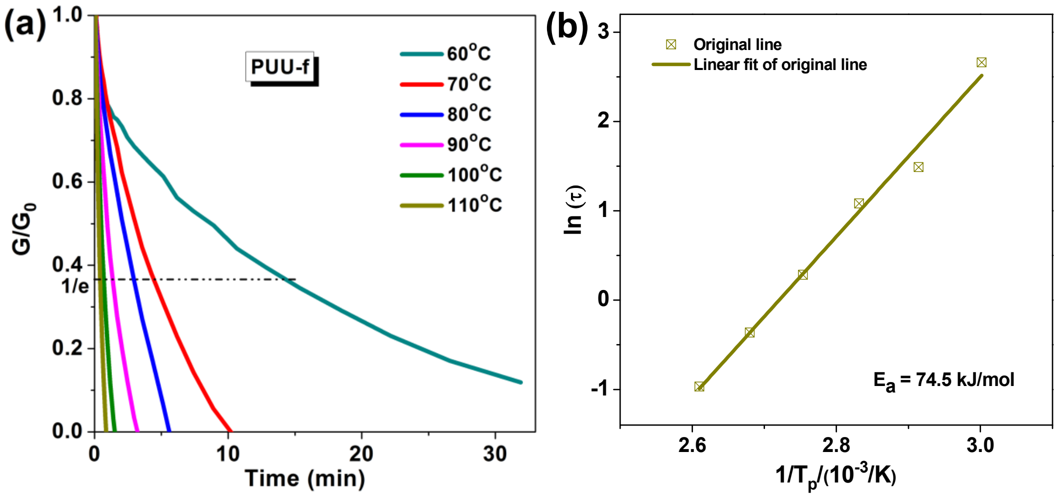


Figure S26. (a) Stress relaxation curves of PUU-f; (b) A plot of the linear regression of the logarithm of relaxation time ln *τ* vs. reciprocal of temperature 1/T.

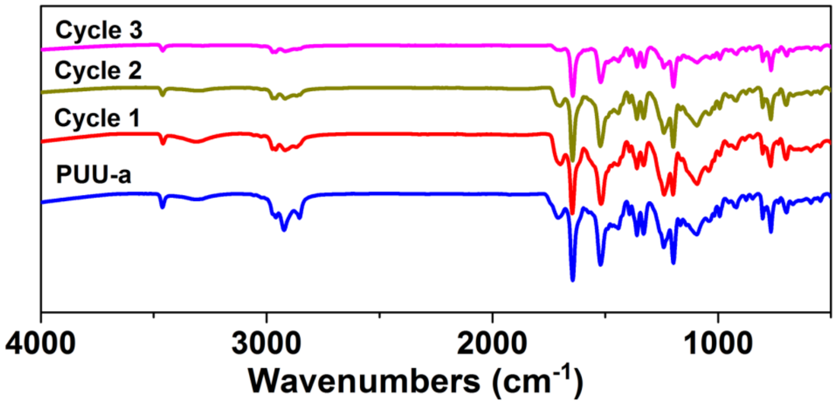


Figure S27. FTIR spectra of the virgin and multiple recycled PUU-a samples by utilizing solid phase recycling method.

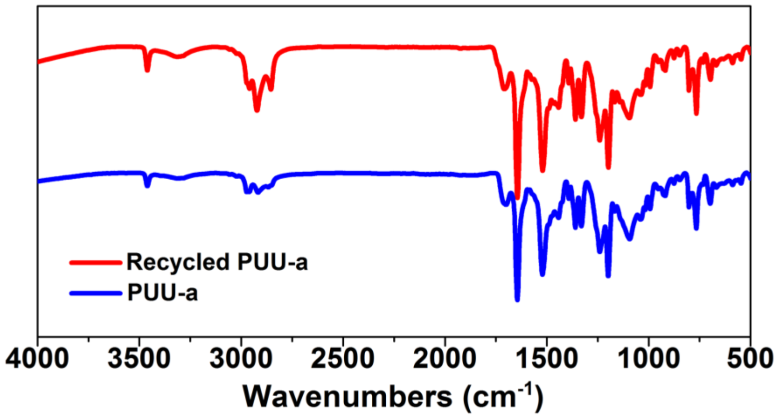


Figure S28. FTIR spectra of the pristine and recycled PUU-a.

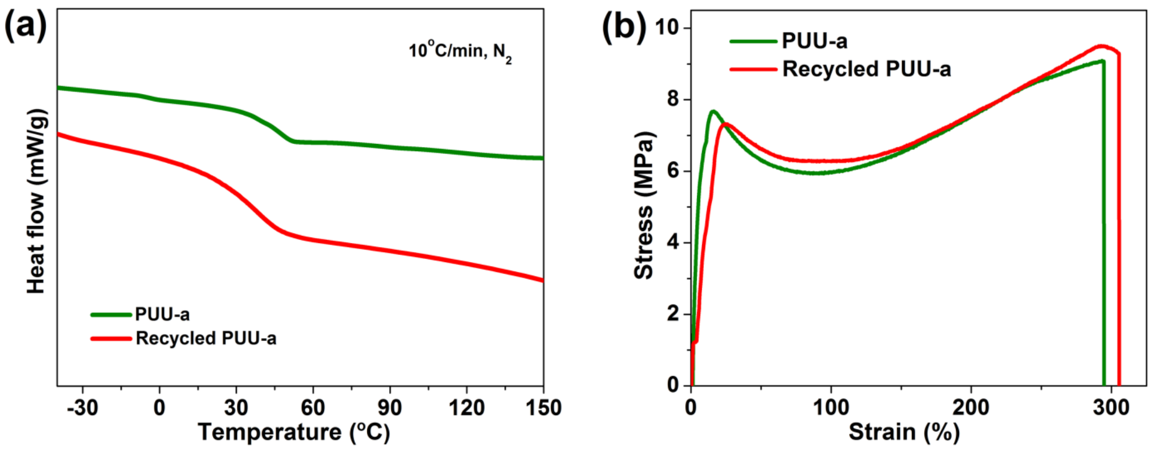


Figure S29. (a) T_g of the pristine and recycled PUU-a obtained from the DSC curves under a nitrogen atmosphere at a heating rate of 10 °C/min; (b) stress-strain curves of the pristine and recycled PUU-a.

Table S1. The components of PUUs.

Samples		TEA	XDI	TBXA	TEG	PPG	4-phenylenedimethanamine
PUU-a	Molar ratio	1	6	2	2	0.5	/
PUU-b		1	6	2	1.5	1	/
PUU-c		1	6	2	1	1.5	/
PUU-d		0.75	6	2	1.4	1.4	/
PUU-e		1	6	/	2	0.5	2

Table S2. Thermal characteristics of the Poly(2a/1b) and Poly(3a/3b) obtained from TGA and DTG curves.

Samples	$T_{5\%}^{a}$ (°C)	$T_{10\%}^{b}$ (°C)	$T_{d,max}^{c}$ (°C)	$R_{500\,°C}^{d}$ (%)
Poly(3a/3b)	215	228	249, 351	19.8
Poly(2a/1b)	115	128	120, 208	0

[a] Thermal decomposition temperature at 5% weight loss.

[b] Thermal decomposition temperature at 10% weight loss.

[c] The maximum rate of the weight loss.

[d] Residue weight at 500 °C.

Table S3. Thermal characteristics of the PUU-a and PUU-f obtained from isothermal TGA and DTG curves .

Samples	Residue weight (%)		
	100 ^{o}C/120 min	150 ^{o}C/120 min	180 ^{o}C/120 min
PUU-a	99.22	95.93	83.57
PUU-f	99.20	89.79	78.70

Table S4. Mechanical properties of PUU-a with different stretching speeds from stress-strain curves.

Tension Rate (mm/min)	**Young's modulus (MPa)**	**Breaking stress (MPa)**	**Elongation at break (%)**
10	87.95	7.76	343.8
20	132.7	9.04	292.8
100	190.2	10.86	233.9
200	234.0	14.01	202.3
300	296.1	15.90	180.6
400	315.4	18.94	155.1

Table S5. Mechanical properties of PUU-a after multiple recycling processes from stress-strain curves by utilizing solid phase recycling method.

Samples	**Young's modulus (MPa)**	**Breaking stress (MPa)**	**Elongation at break (%)**
PUU-a	132.7	9.04	292.8
Cycle 1	118.9	8.75	315.3
Cycle 2	102.4	8.51	326.1
Cycle 3	97.5	8.14	388.7

Table S6. Mechanical properties of the pristine and recycled PUU-a from stress-strain curves.

Samples	**Young's modulus (MPa)**	**Breaking stress (MPa)**	**Elongation at break (%)**
PUU-a	132.7	9.04	292.8
Recycled PUU-a	135.2	9.21	305.5

Table S7. Mechanical properties of original and healed PUU-c with different healing temperature and healing times from stress-strain curves.

Samples	**Young's modulus (MPa)**	**Breaking stress (MPa)**	**Elongation at break (%)**
PUU-c	1.52	2.31	529.5
25 ^{o}C/48 h	1.36	1.74	400.2
40 ^{o}C/12 h	1.40	2.25	505.4
60 ^{o}C/2 h	1.43	2.19	460.3
80 ^{o}C/0.5 h	7.86	2.16	350.0

Table S8. Mechanical properties of original and healed PUU-c with different healingtimes at 40 ^{o}C from stress-strain curves.

Samples	**Young'smodulus (MPa)**	**Breaking stress (MPa)**	**Elongation at break (%)**
PUU-c	1.52	2.31	529.5
40 ^{o}C/2 h	0.24	0.62	351.6
40 ^{o}C/6 h	0.82	1.03	448.5
40 ^{o}C/8 h	1.21	2.04	487.2
40 ^{o}C/12 h	1.40	2.25	505.4

3. REFERENCES

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