

SUPPORTING INFORMATION

Catalyst-free room-temperature self-healing polymer networks based on dynamic covalent quinone methide-secondary amine chemistry

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Experimental

Materials

Hexamethylene diisocyanate (HDI), 2-(methylamino)ethanol, 2-benzylaminoethanol, polytetramethylene ether glycol (PTMEG) ($M_n = 850$), dibutyltin dilaurate (DBTDL), triethanolamine, bis(2-hydroxyethyl) terephthalate (Diol-2), triethylamine (TEA), dichloromethane (DCM), ethyl acetate (EA), *N,N*-dimethylformamide (DMF) were purchased as reagent grade from Alfa Aesar, Acros, Aldrich, J&K Chemical, or Beijing Chemical Reagent Co. and used as received unless otherwise noted. PTMEG was vacuum dried at 120 °C for 2 h before use. DMF dry solvent was refluxed over calcium hydride. 2,6-di-*t*-butyl-7-phenyl-*p*-quinone methide (*p*QM) and compound **a** were synthesized according to literature.^{1,2}

Characterization

¹H NMR was recorded on a Bruker Avance 400 spectrometer at room temperature.

Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris 1 TGA under air atmosphere with heating rate of 10 °C/min from 25 to 700 °C.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FT-IR) was performed on a Bruker Tensor27 IR spectrophotometer at room temperature. The scanning region was 4000-600 cm⁻¹, and the scanning times and resolution were 32 and 2 cm⁻¹, respectively.

Dynamic mechanical analysis (DMA) was performed on a TA instruments DMA Q800 in a tension film mode. Rectangular samples (*ca.* 8 mm L × 4.5 mm W × 0.7 mm T) were tested at a frequency of 1 Hz and a strain of 0.05%. Heating ramps of 3 °C/min were applied from -70 to 75 °C. T_g values were calculated from the maximum value of $\tan \delta$.

The gel fraction (GF) and swelling ratio (SR) of samples were determined at room temperature by soaking the sample in ethyl acetate for three days with the ethyl acetate refreshed each day. After that, the insoluble polymer was dried under vacuum at 40 °C to the constant weight (W_1). The original weight of the sample was expressed as W_0 . The weight of the swollen sample immediately taken out of ethyl acetate was signed as W_2 . Therefore, the gel fraction (GF) and the swelling ratio (SR) were calculated according to the formulas: $GF = W_1/W_0$, $SR = W_2/W_0$.

Tensile tests were performed on an Instron 3365 instrument with a 50 mm/min strain rate at approximately 25 °C, equipped with a 5 kN load cell, using dumbbell shape specimens with an effective gauge dimensions: length of 25 mm, width of 3 mm and thickness of approximately 0.8 mm. The average of the results of three individual tensile tests was recorded for each sample.

Recycling experiments were performed in a vacuum mould pressing machine (FM450, China). The original specimen was cut into small pieces (~ 1.8 g), and then placed into a rectangular mould (*ca.* 40 mm L × 40 mm W) under a hot press (60 °C, 10 MPa) for 12 h. The mould was cooled to room temperature by cold water in ~ 10 min and the reprocessed samples were demolded. The same procedure was repeated for another two cycles.

Creep-recovery experiments were performed on a TA instruments DMA Q800 using rectangular samples (*ca.* 8 mm L × 5.0 mm W × 0.8 mm T). In creep-recovery tests, the samples were equilibrated for 5 minutes at specified temperature, then pulled in a constant stress 0.1 MPa and held for 30 min. After that, the stress was released and the sample would recover for another 30 min at a specified temperature.

Stress-relaxation experiments were performed on a TA instruments DMA Q800 using rectangular samples (*ca.* 8 mm L × 5.0 mm W × 0.8 mm T). In stress relaxation tests, the samples were performed in a strain control (10% strain) mode at a specified temperature. After equilibrating at this temperature for about 5 minutes, the change of

relaxation modulus (G) with time in this process was recorded. The relaxation modulus (G) was normalized by initial value (G_0). The characteristic relaxation times (τ) were defined as the time at normalized relaxation modulus of $1/e$.

Synthesis of Adducts **1** and **1'**

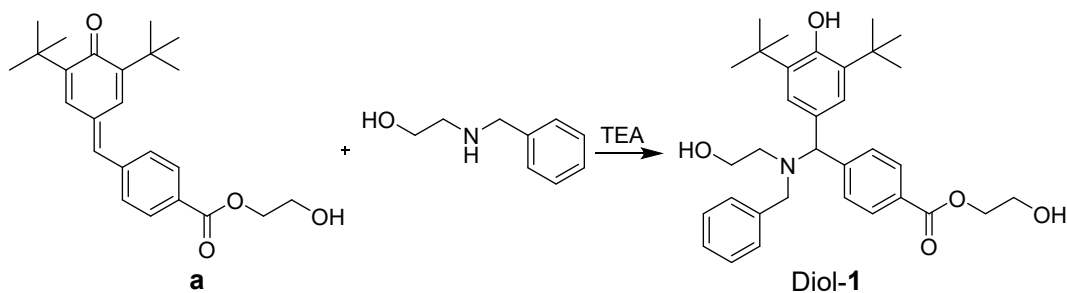
The same preparation process was used to synthesize adducts **1** and **1'**. *p*QM (600 mg, 1.7 mmol) and TEA (310 mg, 3.06 mmol) were dissolved in 4.3 mL DMF, in which 2-benzylaminoethanol (309 mg, 2.04 mmol) or 2-(methylamino)ethanol (153 mg, 2.04 mmol) was added. The reactions were performed at ambient condition for 5 min. The resultant crude adduct **1** was dissolved in DCM (70 mL) and extracted with H₂O (5 × 70 mL). The organic phase was collected and dried by MgSO₄. The solvent was concentrating to give the adduct **1** (823 mg, 96%). The resultant crude adduct **1'** was dissolved in DCM (70 mL) and extracted with H₂O (5 × 70 mL). The organic phase was collected and dried by MgSO₄. The solvent was concentrating to give the adduct **1'** (691 mg, 95%). For adduct **1**: ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.01 (d, 2H), 7.49 (d, 2H), 7.37-7.22 (m, 5H), 7.10 (s, 2H), 4.90 (s, 1H), 3.91 (s, 3H), 3.65 (s, 2H), 3.58-3.50 (m, 2H), 2.74-2.66 (m, 2H), 1.40 (s, 18H). For adduct **1'**: ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.97 (d, 2H), 7.48 (d, 2H), 7.11 (s, 2H), 4.45 (s, 1H), 3.89 (s, 3H), 3.69-3.55 (m, 2H), 2.65-2.52 (m, 2H), 2.17 (s, 3H), 1.40 (s, 18H).

Kinetic Studies on Dynamic Exchange Reaction

Adduct **1** (50.4 mg, 0.1 mmol) was dissolved in 0.3 mL DMF-d₇, 2-(methylamino)ethanol (7.5 mg, 0.1 mmol) was dissolved in 0.2 mL DMF-d₇. After the locking and shimming processes by a blank sample of pure DMF-d₇, the above adduct **1** DMF-d₇ solution (0.3 mL) and 2-(methylamino)ethanol DMF-d₇ solution (0.2 mL) were mixed in one NMR test tube and characterized by Bruker Avance 400 spectrometer right away. The reaction process was then

monitored by successive ^1H NMR characterization with a designed reaction time interval. The same process was used to carry out the reverse dynamic exchange reactions only by changing the reactants to adduct **1'** and 2-benzylaminoethanol.

Synthesis of Diol-1



Diol-1: Compound **a** (900 mg, 2.35 mmol) and TEA (429 mg, 4.24 mmol) were dissolved in DMF (5.9 mL) followed by the addition of 2-benzylaminoethanol (427 mg, 2.82 mmol). The reactions were performed at ambient condition for 5 min. The resultant crude adduct Diol-1 was dissolved in DCM (100 mL) and extracted with H₂O (5 × 100 mL). The organic phase was collected and dried by MgSO₄. The solvent was concentrating to give the colorless-to-pale yellow liquid Diol-1 (1.2 g, 95%). ^1H NMR (400 MHz, CDCl₃), δ (ppm): 8.00 (d, 2H), 7.48 (d, 2H), 7.39-7.21 (m, 5H), 7.11 (s, 2H), 4.90 (s, 1H), 4.49-4.42 (m, 2H), 4.01-3.91 (m, 2H), 3.65 (s, 2H), 3.59-3.49 (m, 2H), 2.75-2.61 (m, 2H), 1.40 (s, 18H).

Preparation of Dynamic Covalent Polyurethane Network P1

Diol-1 (5 g, 0.00937 mol), HDI (6.31 g, 0.0375 mol), PTMEG (15.93 g, 0.0187 mol), and triethanolamine (0.93 g, 0.00625 mol) were dissolved in dry DMF (41 mL) followed by the addition of DBTDL (59 mg, 0.094 mmol). After stirring the reaction solution for 5 min, the reaction mixture was transferred to pre-formed molds and cured for another 24 h at room temperature. The material was removed from the molds and allowed to dry for 48 h in a vacuum oven at 40 °C. After

immersing the resultant polymer network in ethyl acetate for 72 h with the ethyl acetate refreshed each day, a transparent cross-linked polyurethane bulk material could be obtained under vacuum at 40 °C for 48 h to remove solvents.

Preparation of Covalent Polyurethane Control Network P2

Diol-2 (5 g, 0.02 mol), HDI (13.23 g, 0.0787 mol), PTMEG (33.43 g, 0.0393 mol), and triethanolamine (1.95 g, 0.0131 mol) were dissolved in dry DMF (82 mL) followed by the addition of DBTDL (124 mg, 0.2 mmol). After stirring the reaction solution for 5 min, the reaction mixture was transferred to pre-formed molds and cured for another 24 h at room temperature. The material was removed from the molds and allowed to dry for 48 h in a vacuum oven at 40 °C. After immersing the resultant polymer network in ethyl acetate for 72 h with the ethyl acetate refreshed each day, a transparent cross-linked polyurethane bulk material could be obtained under vacuum at 40 °C for 48 h to remove solvents.

Self-Healing of Dynamic Covalent Polyurethane Network P1

Dynamic covalent polyurethane network **P1** was cut into half with a razor blade. The samples were placed in contact by applying gentle pressure with fingers for several minutes to reattach. Materials were then placed at 25 °C or 60 °C for self-healing with different time periods. The self-healed specimens were subjected to tensile tests.

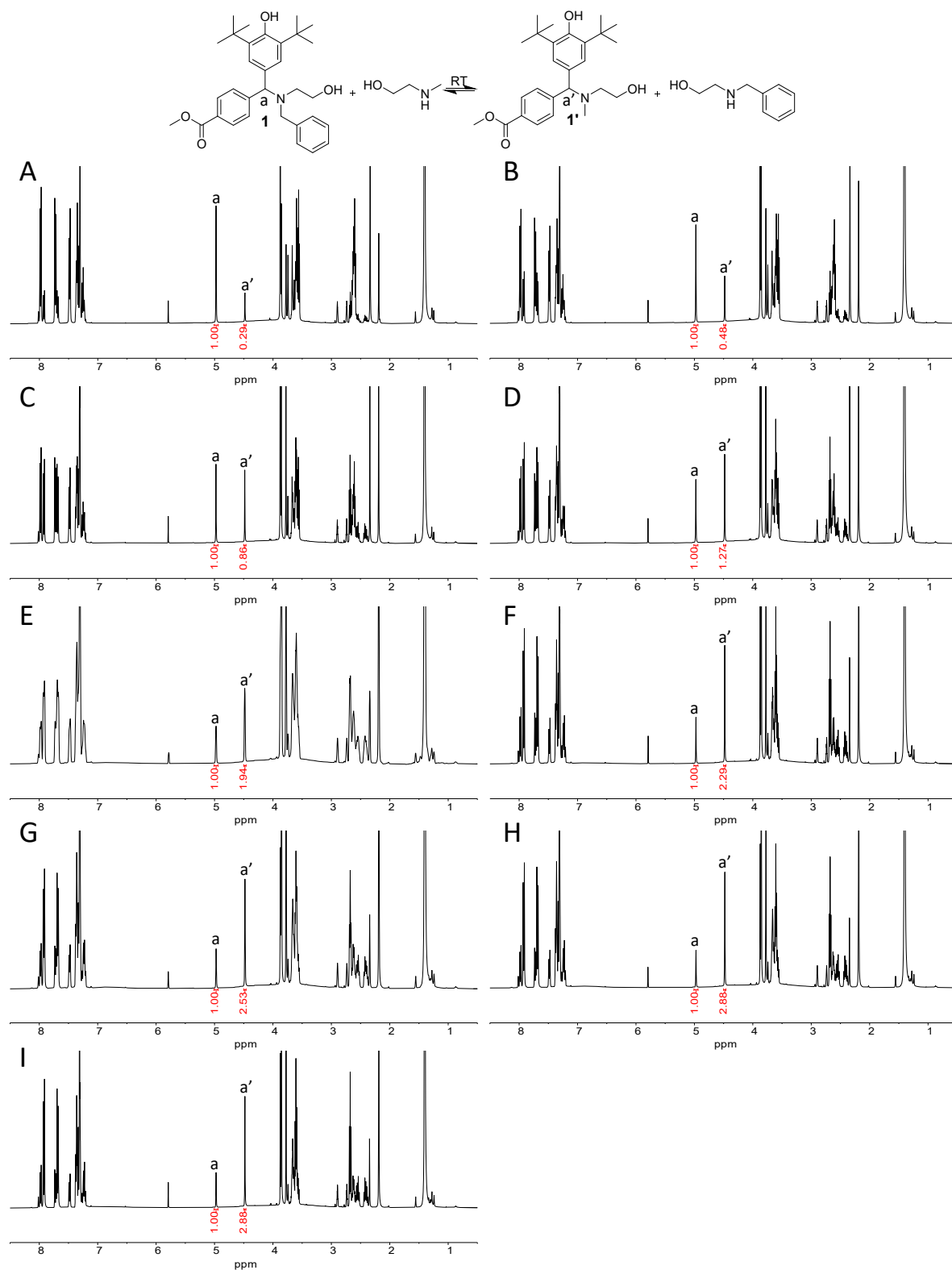


Figure S1. ¹H NMR spectra of the dynamic exchange reaction of adduct **1** (1 equiv.) and 2-(methylamino)ethanol (1 equiv.) in DMF-d₇ solution with reaction time of 30 min (A), 1.5 h (B), 3 h (C), 6 h (D), 9 h (E), 12 h (F), 18 h (G), 24 h (H) and 30 h (I). The equilibrium content of adduct **1'** was calculated by $\text{Area}(a')/(\text{Area}(a)+\text{Area}(a'))$. The equilibrium content of adduct **1** was calculated by $1-(\text{Area}(a')/(\text{Area}(a)+\text{Area}(a')))$.

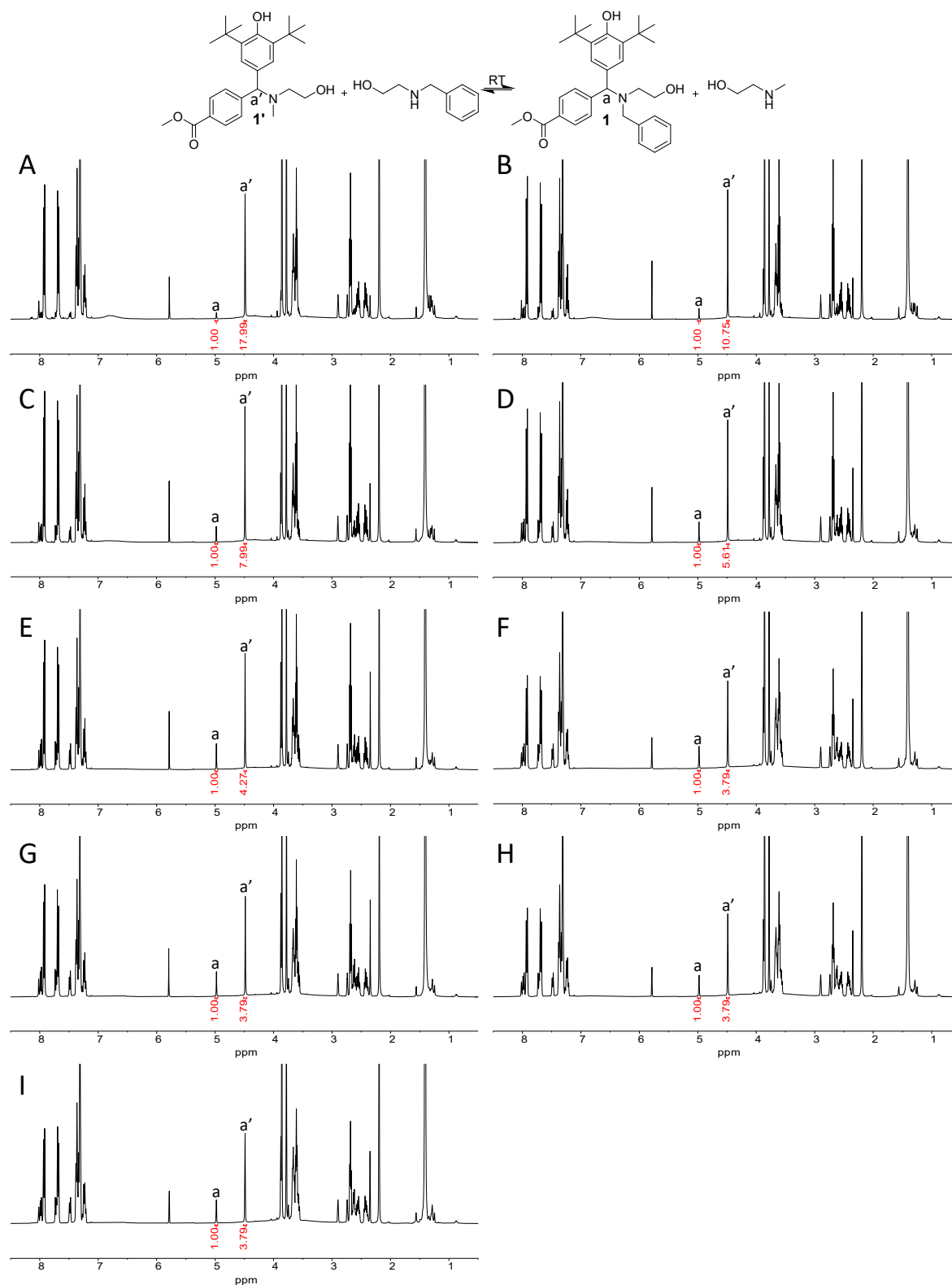
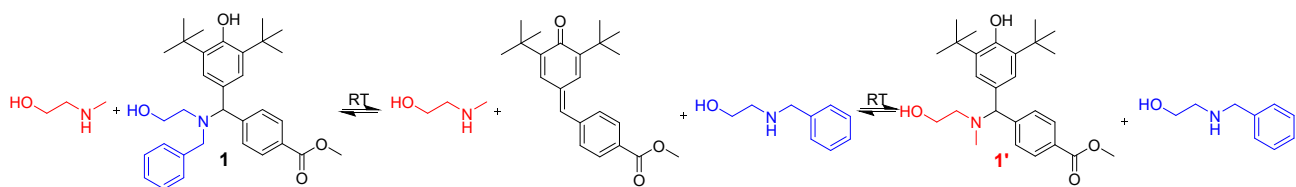


Figure S2. ^1H NMR spectra of the dynamic exchange reaction of adduct **1'** (1 equiv.) and 2-benzylaminoethanol (1 equiv.) in DMF-d_7 solution with reaction time of 30 min (A), 1.5 h (B), 3 h (C), 6 h (D), 9 h (E), 12 h (F), 18 h (G), 24 h (H), and 30 h (I). The equilibrium content of adduct **1** was calculated by $\text{Area(a)}/(\text{Area(a)}+\text{Area(a')})$. The equilibrium content of adduct **1'** was calculated by $1-(\text{Area(a)}/(\text{Area(a)}+\text{Area(a'))})$.



Scheme S1. Proposed mechanism of dynamic covalent *p*QM-2° amine addition reaction at 25 °C.

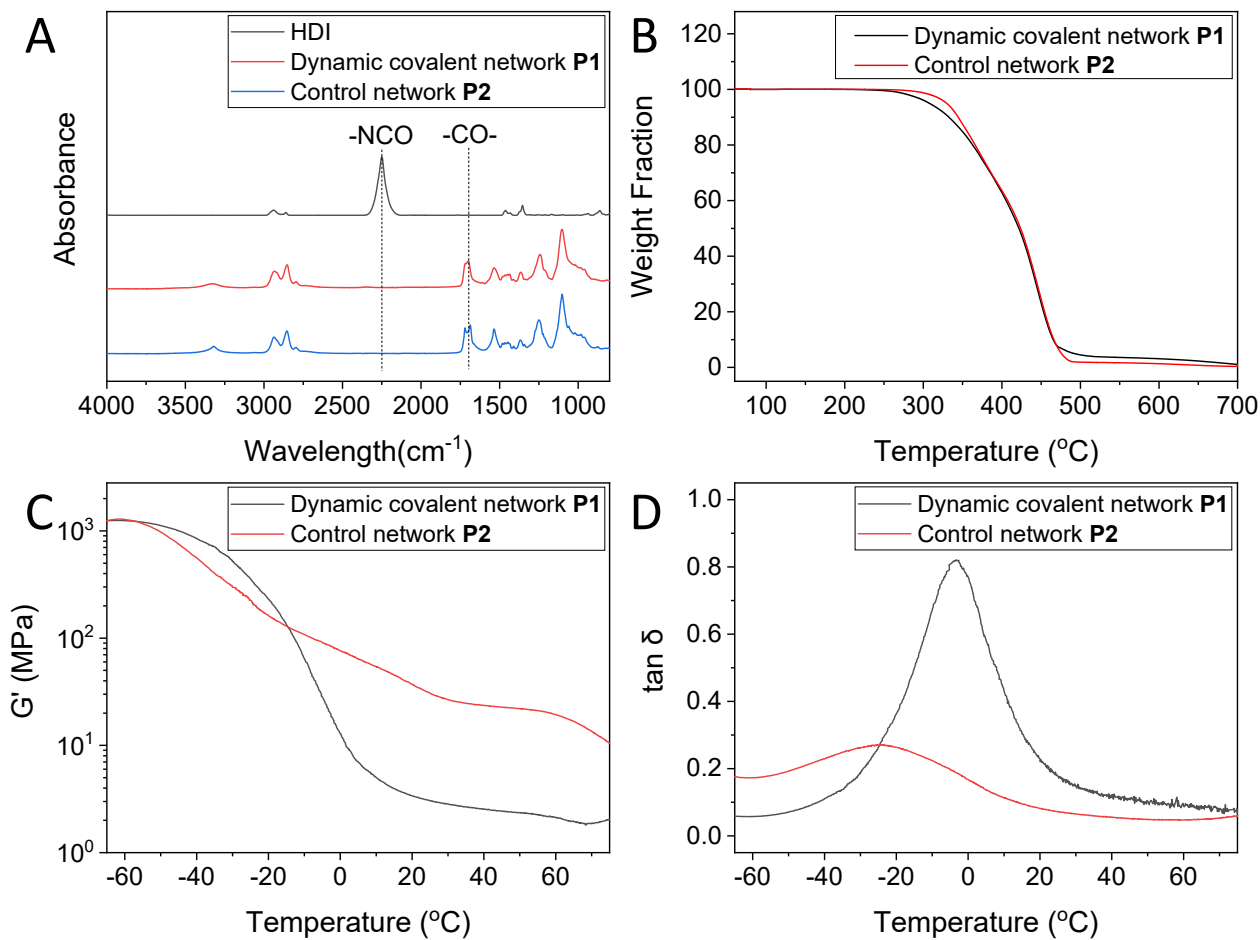


Figure S3. ATR-FT-IR spectra (A), TGA (B), temperature dependence of storage modulus (G') (C), and temperature dependence of loss factor ($\tan \delta$) (D) of the dynamic covalent polyurethane network **P1** and the control covalent polyurethane network **P2**.

Table S1. Mechanical properties of original and healed polyurethane networks.

Sample	Original		Condition	Healed		Recovery	
	Stress of break ^a (MPa)	Strain of break ^a (%)		Stress of break ^a (MPa)	Strain of break ^a (%)	Stress ^b (%)	Strain ^c (%)
P1	8.91 ± 0.19	2178 ± 17	25 °C, 6 h	1.64 ± 0.02	971 ± 13	18	45
			25 °C, 12 h	2.50 ± 0.19	1304 ± 35	28	60
			25 °C, 24 h	7.21 ± 0.15	1849 ± 43	81	85
			25 °C, 48 h	7.27 ± 0.21	1862 ± 9	82	85
			60 °C, 6 h	3.35 ± 0.16	1477 ± 7	38	68
			60 °C, 12 h	7.73 ± 0.16	1955 ± 14	87	90
			60 °C, 24 h	7.53 ± 0.09	1922 ± 11	85	88
			60 °C, 48 h	7.52 ± 0.11	1959 ± 26	84	90
P2	19.93 ± 0.60	2887 ± 45	25 °C, 48 h	2.12 ± 0.08	85 ± 7	11	3

^a Average values and standard deviations measured with three individual tensile tests. ^b Average stress recovery was calculated by the ratio of average stress of break between the healed and the original samples. ^c Average strain recovery was calculated by the ratio of average strain of break between the healed and the original samples.

Table S2. Mechanical properties of original and recycled dynamic covalent polyurethane network**P1.**

Sample	Stress of break ^a (MPa)	Strain of break ^a (%)	Storage modulus (MPa)	T _g (°C)
Original (P1)	8.91 ± 0.19	2178 ± 17	1252	-3
Recycle 1	7.87 ± 0.30	1902 ± 18	1314	-4
Recycle 2	7.67 ± 0.14	1779 ± 44	1277	-4
Recycle 3	7.33 ± 0.11	1732 ± 42	1248	-4

^a Average values and standard deviations measured with three individual tensile tests.

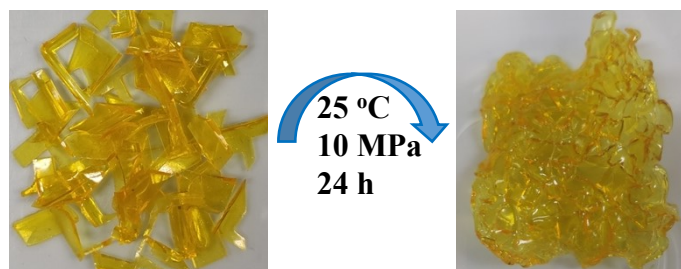


Figure S4. Reprocessing of the dynamic covalent polyurethane network **P1** by a pressing process at 25 °C and 10 MPa for 24h.

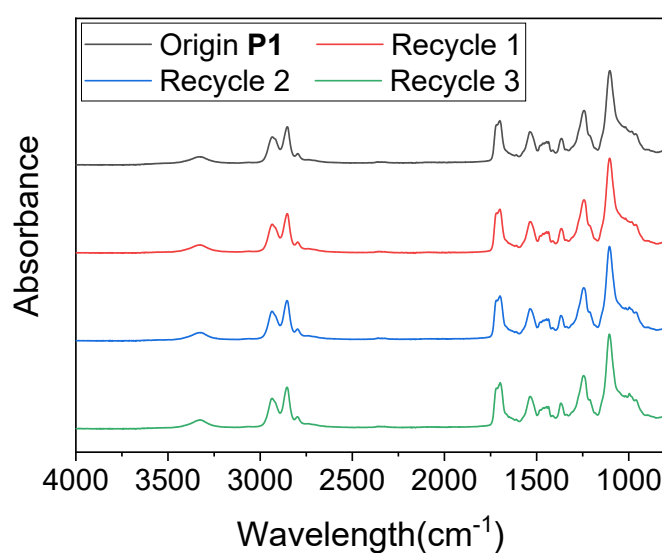


Figure S5. ATR-FT-IR spectra of the original and the recycled **P1**.

References

1. L. Xiang, X. F. Liu, Y. X. He and K. Zhang, *Macromolecules*, 2020, **53**, 5434-5444.
2. L. Xiang, X. F. Liu, H. Zhang, N. Zhao and K. Zhang, *Polym. Chem.*, 2020, **11**, 6157-6162.