

SUPPORTING INFORMATION

Thermoresponsive Self-Healable and Recyclable Polymer Networks Based on Dynamic Quinone Methide-Thiol Chemistry

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Experimental

Materials

Benzyl mercaptan, 2-mercaptoethanol, polytetramethylene ether glycol (PTMEG) ($M_n = 850$), hexamethylene diisocyanate (HDI), dibutyltin dilaurate (DBTDL), triethanolamine, terephthalic acid bis(2-hydroxyethyl) ester, trimethylamine (TEA), petroleum ether (PE), ethyl acetate (EA), N,N-dimethylformamide (DMF) were purchased as reagent grade from Alfa Aesar, Aldrich, Acros, J&K Chemical, or Beijing Chemical Reagent Co. and used as received unless otherwise noted. Polytetramethylene ether glycol (PTMEG) ($M_n = 850$) 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 Diol-1 were synthesized according to literature.¹

Characterization

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at room temperature.

Attenuated total reflectance infrared spectroscopy (ATR-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.

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.

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 200 °C. T_g values were

calculated from the maximum value of $\tan \delta$.

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 five 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 (~ 1.7 g), and then placed into a rectangular mould (*ca.* 40 mm L \times 40 mm W) under a hot press (150 °C, 10 MPa, vacuum) for 40 min. The mould was cooled to room temperature by cold water in ~ 15 min and the reprocessed samples were demolded. The same procedure was repeated for another two cycles.

Stress-relaxation experiments were performed on a TA instruments DMA Q800 using rectangular samples (*ca.* 8 mm L \times 4.5 mm W \times 0.7 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 37% ($1/e$).

Creep-recovery experiments were performed on a TA instruments DMA Q800 using rectangular samples (*ca.* 8 mm L \times 4.5 mm W \times 0.7 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.

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 50 °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: $GF = W_1/W_0$, $SR = W_2/W_0$.

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

The same preparation process was used to synthesize adducts **1** and **1'**. *p*QM (700 mg, 1.99 mmol) and TEA (497 μ L, 3.58 mmol) were dissolved in 9.8 mL DMF, in which 2-mercaptoethanol (174.4 μ L, 2.38 mmol) or benzyl mercaptan (279.3 μ L, 2.38 mmol) was added. The reactions were performed at ambient condition for 1 min. The resultant crude adduct **1** was dissolved in DCM (20 mL) and extracted with H₂O (3 \times 20 mL). The organic phase was collected and dried by MgSO₄. The solvent was removed in vacuum and the crude product was purified by a silica column with PE/EA (v/v = 4/1) as the eluent to afford pure adduct **1** (838 mg, 98%). The resultant crude adduct **1'** was purified by a silica column with PE/DCM (v/v = 4/1) as the eluent to remove TEA catalyst, unreacted benzyl mercaptan, and DMF solvent to afford pure adduct **1'** (938 mg, 99%). For adduct **1**: ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 8.00 (d, $J = 8.3$ Hz, 2H), 7.54 (d, $J = 8.2$ Hz, 2H), 7.18 (s, 2H), 5.19 (s, 1H), 5.17 (s, 1H), 3.90 (s, 3H), 3.70-3.59 (m, 2H), 2.67-2.52 (m, 2H), 2.02 (s, 1H), 1.40 (s, 18H). ¹³C-NMR (101 MHz, CDCl₃), δ (ppm): 166.84, 153.16, 147.16, 136.13, 130.66, 129.94, 129.01, 128.35, 124.78, 60.45, 53.86, 52.09, 35.48, 34.43, 30.26. HRMS (ESI) m/z calculated for C₂₅H₃₃O₄S [M - H⁺] 429.2105, found 429.2108. For adduct **1'**: ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.99 (d, $J = 8.3$ Hz, 2H), 7.47 (d, $J = 8.3$ Hz, 2H), 7.31-7.15 (m, 5H), 7.13 (s, 2H), 5.17 (s, 1H), 4.91 (s, 1H), 3.87 (s, 3H), 3.52 (s, 2H), 1.39 (s, 18H). ¹³C-NMR (101 MHz, CDCl₃), δ (ppm): 166.93, 153.09, 147.21, 137.93,

136.05, 130.66, 129.91, 129.09, 128.90, 128.59, 128.47, 127.08, 125.11, 53.54, 52.09, 36.78, 34.47, 30.35. HRMS (ESI) m/z calculated for $C_{30}H_{35}O_3S$ [M - H⁺] 475.2312, found 475.2313.

Kinetic Studies on Dynamic Exchange Reaction

The same process was used to carry out the dynamic exchange reactions. In the nitrogen atmosphere, adduct **1** (215 mg, 0.5 mmol) and benzyl mercaptan (59 μ L, 0.5 mmol) were dissolved in 3.33 mL DMF. For the reverse reaction, adduct **1'** (290 mg, 0.6 mmol) and 2-mercaptoethanol (42.2 μ L, 0.6 mmol) were dissolved in 4 mL DMF. After mixing, the solution was transferred to a 5 mL small vial, capped and then heated in an oil bath at 120 °C. At designed reaction time, 0.15 mL of solution was taken out for ¹H-NMR characterization.

Preparation of Dynamic Covalent Polyurethane Network P1

Diol-**1** (5.47 g, 0.0119 mol), PTMEG (20.23 g, 0.0238 mol), HDI (8 g, 0.0476 mol), and triethanolamine (1.18 g, 0.00794 mol) were dissolved in dry DMF (53 mL) followed by the addition of DBTDL (60 mg, 0.0952 mmol).^{2,3} 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 24 h in a vacuum oven at 50 °C. After immersing the resultant polymer network in ethyl acetate for 72 h, a transparent cross-linked polyurethane bulk material could be obtained under vacuum at 50 °C to remove solvents.

Preparation of Covalent Polyurethane Control Network P2

Terephthalic acid bis(2-hydroxyethyl) ester (3.03 g, 0.0119 mol), PTMEG (20.23 g, 0.0238 mol), HDI (8 g, 0.0476 mol), and triethanolamine (1.18 g, 0.00794 mol) were dissolved in dry DMF (49 mL)

followed by the addition of DBTDL (60 mg, 0.0952 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 24 h in a vacuum oven at 50 °C. After immersing the resultant polymer network in ethyl acetate for 72 h, a transparent cross-linked polyurethane bulk material could be obtained under vacuum at 50 °C 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 seconds to reattach. Materials were placed in a preheated oven at designed temperature for different time periods. The healed specimens were subjected to tensile tests.

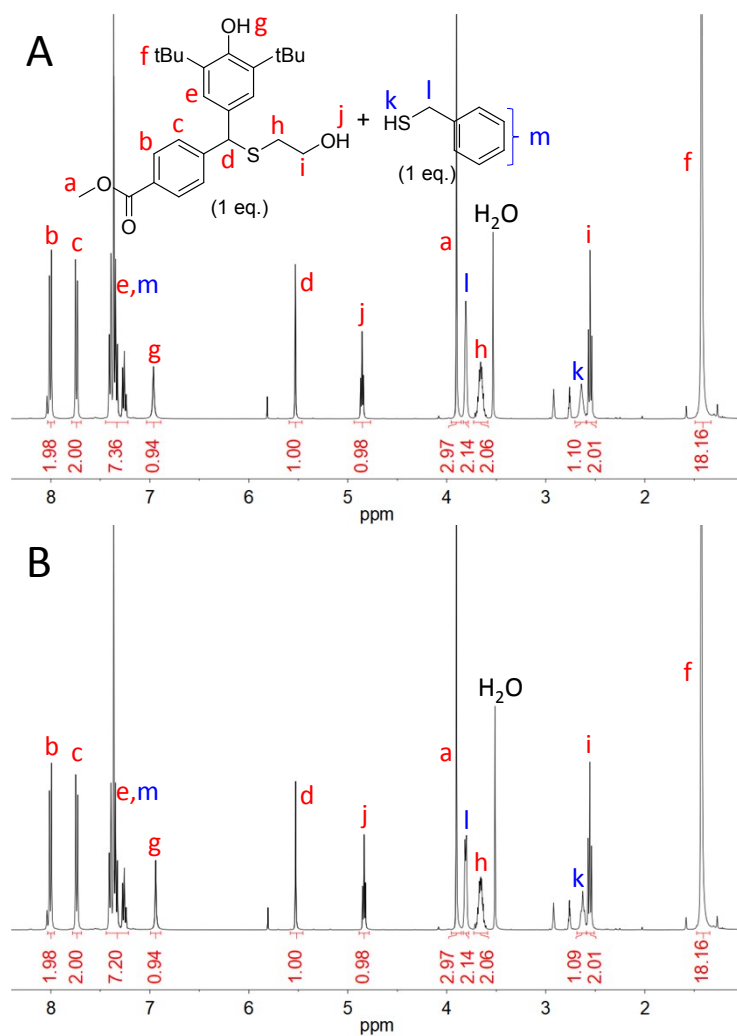


Figure S1. ¹H-NMR spectra of the dynamic exchange reaction of adduct **1** (1 equiv) and benzyl mercaptan (1 equiv) at ambient temperature in deuterated DMF solution with reaction time of 0 min (A) and 24 h (B).

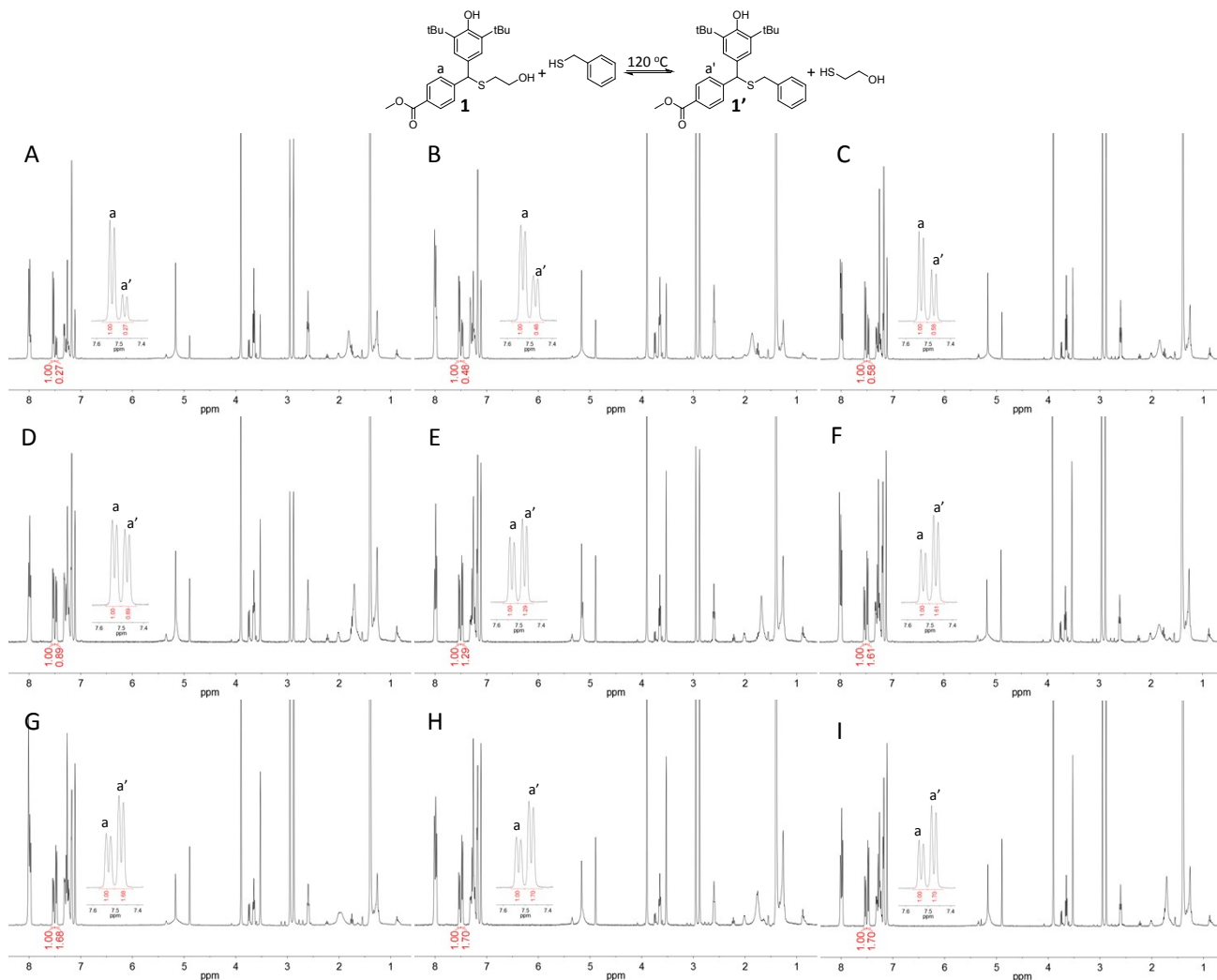


Figure S2. $^1\text{H-NMR}$ spectra (in CDCl_3) of the dynamic exchange reaction of adduct **1** (1 equiv) and benzyl mercaptan (1 equiv) at $120\text{ }^\circ\text{C}$ in DMF solution with reaction time of 2 min (A), 5 min (B), 10 min (C), 30 h (D), 1 h (E), 2 h (F), 3 h (G), 4 h (H), and 5 h (I). The equilibrium content of adduct **1'** = $A_{a'}/(A_a + A_{a'})$.

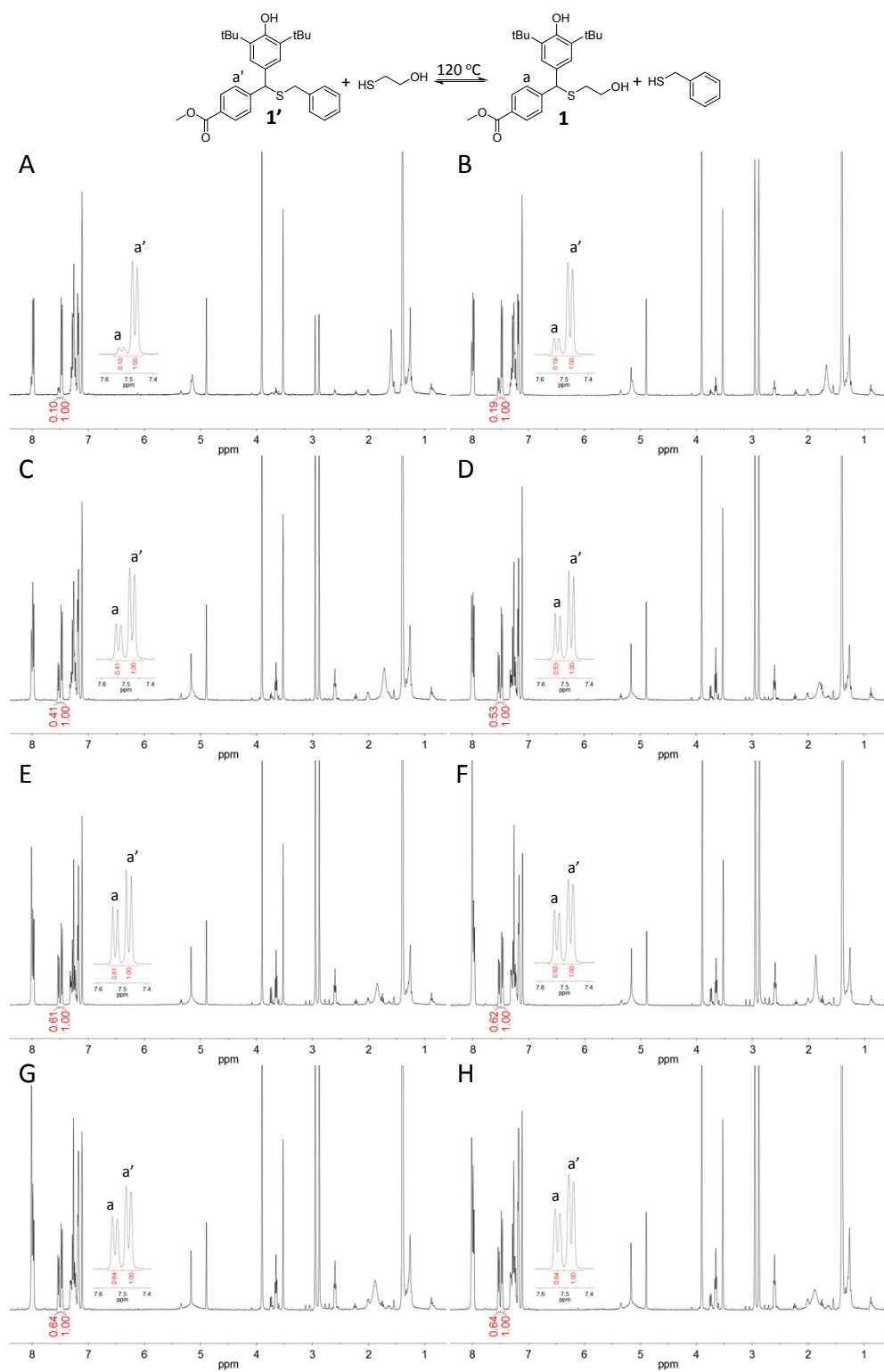
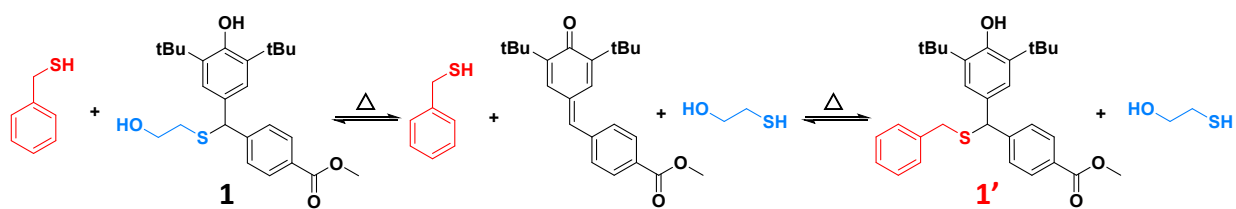
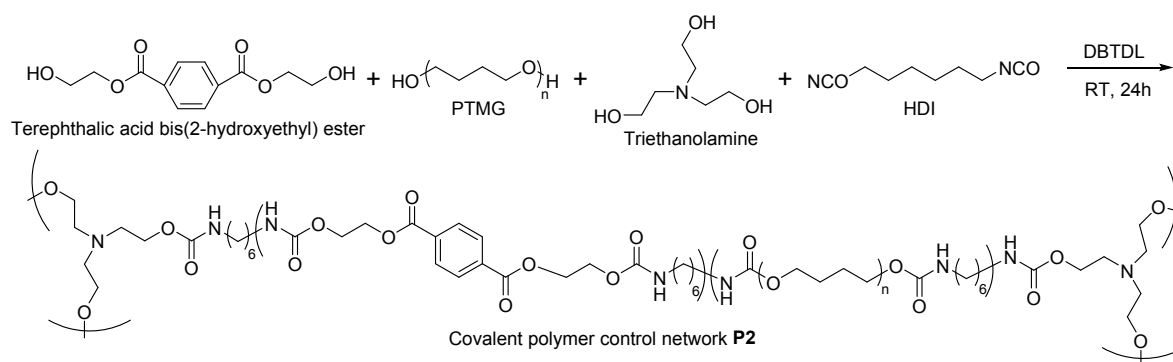


Figure S3. $^1\text{H-NMR}$ spectra (in CDCl_3) of the dynamic exchange reaction of adduct **1'** (1 equiv) and 2-mercaptoethanol (1 equiv) at $120\text{ }^\circ\text{C}$ in DMF solution with reaction time of 5 min (A), 10 min (B), 30 min (C), 1 h (D), 2 h (E), 3 h (F), 4 h (G) and 5 h (H). The equilibrium content of adduct **1** = $A_a / (A_a + A_{a'})$.



Scheme S1. Proposed mechanism of dynamic quinone methide-thiol chemistry under thermal stimulus.



Scheme S2. Synthesis of the covalent polymer control network P2.

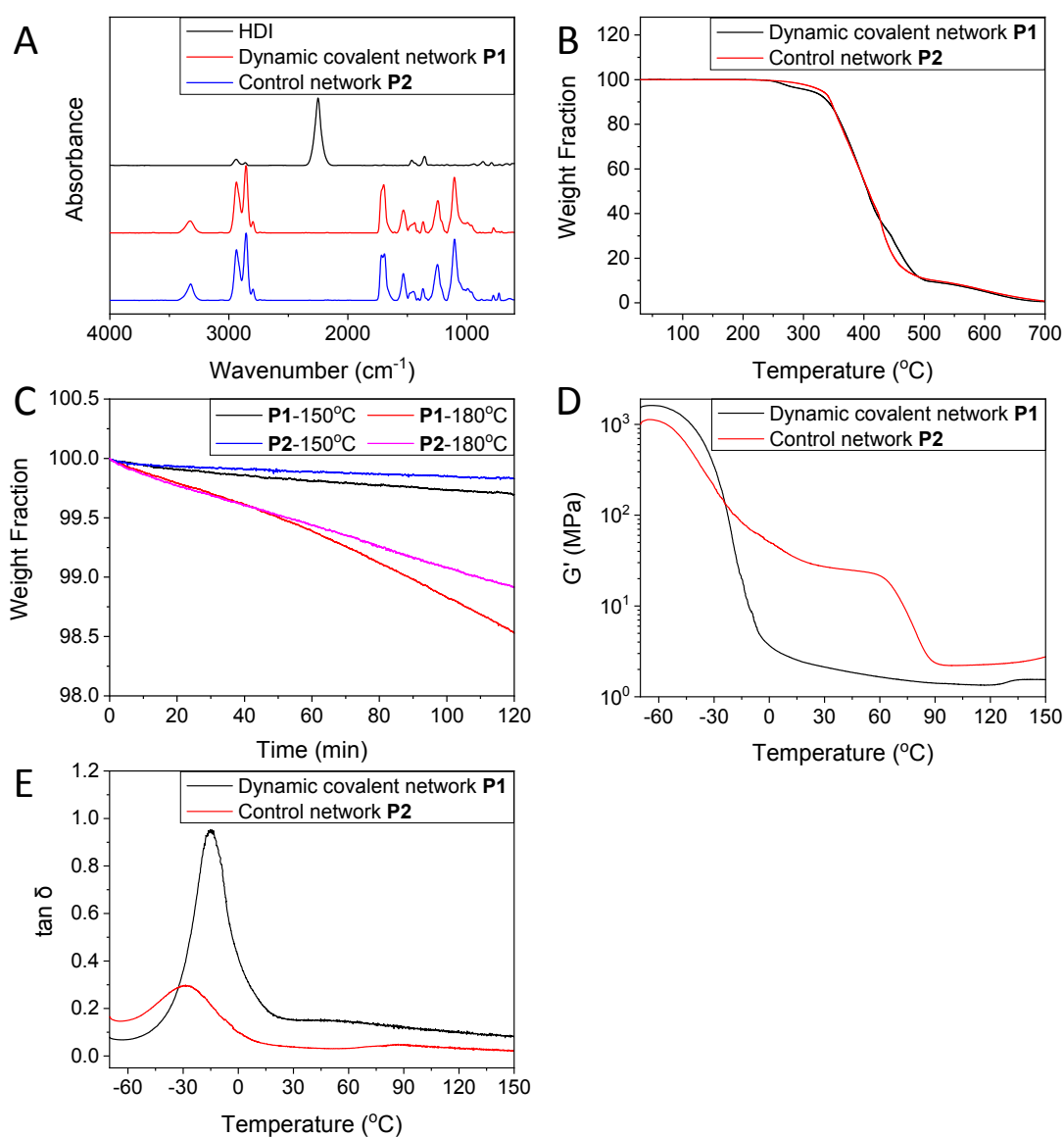


Figure S4. ATR-IR spectra (A), TGA (B), isothermal TGA at 150 $^{\circ}\text{C}$ and 180 $^{\circ}\text{C}$ for 120 min (C), temperature dependence of storage modulus (G') (D), and temperature dependence of loss factor ($\tan \delta$) (E) of the dynamic covalent polymer network **P1** and the covalent polymer network **P2**.

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

Sample	Original		Condition	Healed		Recovery	
	Stress of break (MPa)	Strain of break (%)		Stress of break (MPa)	Strain of break (%)	Stress (%)	Strain (%)
P1			120 °C-4 h	12.66 ± 0.80	2108 ± 84	98	93
	12.90 ± 0.34	2255 ± 71	150 °C-0.5 h	12.66 ± 0.71	2149 ± 80	98	95
			30 °C-4 h	2.55 ± 0.14	1316 ± 21	20	58
P2	20.08 ± 1.68	2762 ± 142	120 °C-4 h	7.44 ± 0.51	1190 ± 73	37	43
			150 °C-0.5 h	5.97 ± 0.41	1091 ± 5	30	40

**Figure S5.** Photograph of self-healed **P1** samples (120 °C, 4 h) after tensile experiment, which did not break at the repair sites.**Table S2.** Mechanical properties of original and recycled dynamic covalent polymer network **P1**.

Sample	Stress of break (MPa)	Strain of break (%)	Storage modulus (MPa)	T _g (°C)
Original (P1)	12.90 ± 0.34	2255 ± 71	1615	-15
Recycle 1	12.16 ± 0.86	2107 ± 137	1757	-14
Recycle 2	12.23 ± 0.99	2065 ± 132	1649	-15
Recycle 3	12.15 ± 0.94	2035 ± 183	1749	-15

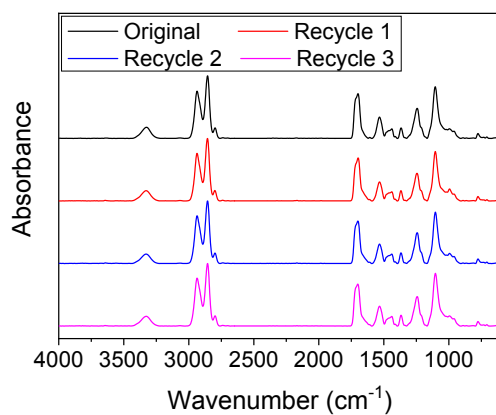


Figure S6. ATR-IR spectra of the original and the recycled **P1**.

References

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2. A. Takahashi, R. Goseki and H. Otsuka, *Angew. Chem. Int. Ed.*, 2017, **56**, 2016-2021.
3. K. Imato, A. Takahara and H. Otsuka, *Macromolecules*, 2015, **48**, 5632-5639.