Supplementary Information

Thermally healable and reprocessable polymethacrylate networks based on diol-mediated metathesis of 6-membered boronic esters

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Part-I. Synthesis of model compounds, monomers, and crosslinkers

5,5-Dimethyl-2-phenyl-1,3,2-dioxaborinane (A1-B1). Phenylboronic acid (1.22 g, 10 mmol) and 2,2-dimethyl-1,3-propanediol (1.04 g, 10 mmol) were charged into a round flask containing magnesium sulfate (3.6 g, 30 mmol), and then diethyl ether (20 mL) was added. After stirring at ambient temperature for 8 h, the reaction mixture was filtered and evaporated to remove diethyl ether under reduced pressure. The residue was purified by sublimation, affording a white powder in 96% yield. Anal. Calcd. ($C_{11}H_{15}BO_2$): C, 69.52; H, 7.96. Found: C, 69.57; H, 8.09. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.81-7.79 (d, J = 8 Hz, 2H), 7.44-7.40 (m, 1H), 7.36-7.32 (m, 2H), 3.77 (s, 4H), 1.02 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 133.82, 130.68, 127.58, 72.32, 31.90, 21.93. HRMS: m/z calcd for $C_{11}H_{15}BO_2$ M^+ 190.1160, found 190.1158.

5,5-Diethyl-2-(p-tolyl)-1,3,2-dioxaborinane (A2-B2). This compound was prepared as a white powder in 95% yield, following the same synthetic procedure as for **A1-B1**. Anal. Calcd. ($C_{14}H_{21}BO_2$): C, 72.44; H, 9.12. Found: C, 72.43; H, 9.24. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.72-7.70 (d, J = 8 Hz, 2H), 7.20-7.18 (d, J = 8 Hz, 2H), 3.86 (s, 4H), 2.38 (s, 3H), 1.46-1.40 (q, J = 8 Hz, 4H), 0.91-0.87 (t, J = 8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.65, 133.88, 128.39, 69.37, 36.75, 23.24, 21.67, 7.26. HRMS: m/z calcd for $C_{14}H_{21}BO_2$ M^+ 232.1629, found 232.1628.

4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)benzyl methacrylate (M1). 4-(Hydroxymethyl) phenylboronic acid (15.2 g, 0.10 mol) and 2,2-dimethyl-1,3-propanediol (11.45 g, 0.11 mol) were charged into a round flask containing freshly activated molecular sieves (0.4 nm, 5 g), and then toluene (120 mL) was added. The reaction was carried out at 120 °C for 24 h until the reaction system became clear. The reaction solution was filtered and evaporated to remove toluene under reduced pressure, affording a white powder (**S1**) in 96% yield. **S1** (11 g, 50 mmol) was dissolved in anhydrous DCM (60 mL), followed by adding 6.1 g of triethylamine (TEA, 60 mmol). After cooling to 0 °C, 6.3 g (60 mmol) of methacryloyl chloride in 5 mL dried DCM was added dropwise within 1 h. Then, the reaction mixture was warmed to room temperature, stirred for 10 h, and filtered. The filtrate was concentrated on a rotary evaporator and diluted by ethyl acetate, and washed with brine thrice. After drying over $MgSO_4$, the organic solution was concentrated again and purified by silica column chromatography using petroleum ether and ethyl acetate (v/v = 30/1) as the eluent. **M1** was obtained as a white crystal in 55% yield. Anal. Calcd. ($C_{16}H_{21}BO_4$): C, 66.69; H, 7.35. Found: C, 66.80; H, 7.39. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.81-7.79 (m, 2H), 7.37-7.35 (m, 2H), 6.16 (s, 1H), 5.58 (s, 1H), 5.20 (s, 2H),

3.77 (s, 4H), 1.97 (s, 3H), 1.02 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.24, 138.44, 136.24, 134.08, 127.06, 125.81, 72.32, 66.40, 31.90, 21.90, 18.37 (**Fig. S1**). HRMS: m/z calcd for $C_{16}H_{21}BO_4$ $(M+NH_4)^+$ 306.1871, found 306.1871.

(5-Ethyl-2-phenyl-1,3,2-dioxaborinan-5-yl)methyl methacrylate (M2). M2 was synthesized following a similar procedure as for the preparation of **M1**. Phenyl boronic acid (12.2 g, 0.1 mol) and trimethylol propane(14.78 g, 0.11 mol) were charged into a round flask containing freshly activated molecular sieves (0.4 nm, 5 g), and then toluene (120 mL) was added. The reaction was carried out at 120 °C for 24 h until the reaction system became clear. The reaction solution was filtered and evaporated to remove toluene under reduced pressure, affording a white powder (**S2**)in 97% yield. **S2** (11 g, 50 mmol) was dissolved in anhydrous DCM (60 mL), followed by adding 6.1 g TEA (60 mmol). After cooling to 0 °C, 6.3 g (60 mmol) of methacryloyl chloride in 5 mL dried DCM was added dropwise within 1 h. Then, the reaction mixture was warmed to room temperature, stirred for 10 h, and filtered. The filtrate was concentrated on a rotary evaporator and diluted by ethyl acetate, and washed with brine thrice. After drying over $MgSO_4$, the organic solution was concentrated and purified by silica column chromatography using petroleum ether and ethyl acetate (v/v = 30/1) as the eluent. **M2** was obtained as a white crystal in 48% yield. Anal. Calcd. ($C_{16}H_{21}BO_4$): C, 66.69; H, 7.35. Found: C, 66.34; H, 7.35. ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 7.70-7.33 (m, 5H), 6.07 (s, 1H), 5.70 (s, 1H), 4.11 (s, 2H), 4.03-3.93 (m, 4H), 1.89 (s, 3H), 1.47-1.41 (q, J = 8 Hz, 2H), 0.89-0.85 (t, J = 8 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ 166.78, 136.03, 134.01, 131.29, 128.07, 126.69, 66.47, 63.71, 38.00, 23.61, 18.41, 7.61 (**Fig. S2**). HRMS: m/z calcd for $C_{16}H_{21}BO_4$ $(M+NH_4)^+$ 306.1871, found 306.1868.

(5-Ethyl-2-(4-((methacryloyloxy)methyl)phenyl)-1,3,2-dioxaborinan-5-yl) methyl methacrylate (L1). L1 was also synthesized in a similar manner to **M1**. 4-(Hydroxymethyl) phenylboronic acid (15.2 g, 0.10 mol) and trimethylol propane(14.78 g, 0.11 mol) were charged into a round flask containing freshly activated molecular sieves (0.4 nm, 5 g), and then toluene (120 mL) was added. The reaction was carried out at 120 °C for 24 h until the reaction system became clear. The reaction solution was filtered and evaporated to remove toluene under reduced pressure, affording a white powder (**S3**) in 97% yield. **S3** (12.5 g, 50 mmol) was dissolved in anhydrous DCM (60 mL), followed by adding 12.1 g TEA (120 mmol). After cooling to 0 °C, 12.6 g (120 mmol) of methacryloyl chloride in 10 mL dried DCM was added dropwise within 1 h. Then, the reaction mixture was warmed to room temperature, stirred for 10 h, and filtered. The filtrate was concentrated on a rotary evaporator and diluted by ethyl

acetate, and washed with brine thrice. After drying over $MgSO_4$, the organic solution was concentrated and purified by silica column chromatography using petroleum ether and ethyl acetate (v/v = 30/1) as the eluent. **L1** was obtained as colorless oil in 46% yield. Anal. Calcd. ($C_{21}H_{27}BO_6$): C, 65.30; H, 7.05. Found: C, 65.24; H, 7.11. ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 7.71-7.69 (m, 2H), 7.37-7.35 (m, 2H), 6.09-6.07 (m, 2H), 5.72-5.69 (m, 2H), 5.19 (s, 2H), 4.11 (s, 2H), 4.03-3.94 (m, 4H), 1.91-1.89 (m, 6H), 1.47-1.41 (q, J = 8 Hz, 2H), 0.89-0.85 (t, J = 8 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ 166.76, 139.28, 136.21, 136.03, 134.19, 127.30, 126.67, 126.56, 66.48, 66.13, 63.68, 38.02, 23.60, 18.47, 18.40, 7.61 (**Fig. S3**). HRMS: m/z calcd for $C_{21}H_{27}BO_6$ $(M+NH_4)^+$ 404.2239, found 404.2236.

1,4-Phenylenebis(methylene) bis(2-methylacrylate) (L2). 1,4-Benzene dimethanol (2.76 g, 0.02 mol) was dissolved in anhydrous DCM (40 mL), followed by adding 4.8 g TEA (48 mmol). After cooling to 0 °C, 5 g (48 mmol) of methacryloyl chloride in 5 mL dried DCM was added dropwise within 1 h. Then, the reaction mixture was warmed to room temperature, stirred for 10 h, and filtered. The filtrate was concentrated on a rotary evaporator and diluted by ethyl acetate, and washed with brine thrice. After drying over $MgSO_4$, the organic solution was concentrated and purified by silica column chromatography using petroleum ether and ethyl acetate (v/v = 30/1) as the eluent. **L2** was obtained as a white crystal in 65% yield. Anal. Calcd. ($C_{16}H_{18}O_4$): C, 70.06; H, 6.61. Found: C, 69.99; H, 6.68. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.38 (s, 4H), 6.16-6.15 (m, 2H), 5.60-5.58 (m, 2H), 5.19 (s, 4H), 1.97 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.19, 136.18, 136.09, 128.21, 125.90, 66.04, 18.36 (**Fig. S4**). HRMS: m/z calcd for $C_{16}H_{18}O_4$ $(M+NH_4)^+$ 292.1543, found 292.1544.

2,3-Dihydroxypropyl methacrylate (D1). DL-1,2-isopropylideneglycerol (13.2 g, 100 mmol) was dissolved in anhydrous DCM (120 mL), followed by adding 12.1 g TEA (120 mmol). After cooling to 0 °C, 12.6 g (120 mmol) of methacryloyl chloride in 5 mL dried DCM was added dropwise within 1 h. Then, the reaction mixture was warmed to room temperature, stirred for 10 h, and filtered. The filtrate was concentrated on a rotary evaporator and diluted by ethyl acetate, and washed with brine thrice. After drying over $MgSO_4$, the organic solution was concentrated to afford a slightly yellow liquid (**S4**). **S4** was dissolved in 240 mL of CH_3OH/1.0 M HCl (v/v = 1/1) and stirred at room temperature for 4h. The solution pH was then adjusted to 7.0 using 2 M NaOH. The solution was concentrated and extracted with ethyl acetate. The organic phase was concentrated and purified by silica column chromatography using petroleum ether and ethyl acetate (v/v = 1/1) as the eluent. **D1** was obtained as a slightly yellow oil in 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.14 (s, 1H), 5.61 (s, 1H), 4.23-

4.22 (m, 2H), 4.00-3.93 (m, 1H), 3.74-3.70 (m, 1H), 3.63-3.59 (m, 1H), 3.40 (s, 2H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.74, 135.82, 126.41, 70.24, 65.42, 63.44, 18.25 (**Fig. S5**). HRMS: m/z calcd for $C_7H_{12}O_4$ $(M+H)^+$ 161.0808, found 161.0810.

5,6-Dihydroxyhexyl methacrylate (D2). 1,2,6-hexanetriol (13.41 g, 100 mmol) was dissolved in acetone (200 mL) in the presence of $MgSO_4$ (24 g, 200 mmol). Then p-toluenesulfonic acid (pTSA, 1.46 g, 8 mmol) was added slowly and the mixture was stirred at room temperature for 24 h. Sodium bicarbonate ($NaHCO_3$, 1.34 g, 16 mmol) was added and the stirring was continued for 3 h at room temperature. The mixture was filtered, concentrated to obtain a white slurry. Water (150 mL) was added and the organic phase was extracted with dichloromethane. The organic phase was concentrated to afford **S5** as a slightly yellow liquid. **S5** (9 g, 50 mmol) was dissolved in anhydrous DCM (60 mL), followed by adding 6.1 g TEA (60 mmol). After cooling to 0 ^{o}C, 6.1 g (60 mmol) of methacryloyl chloride in 5 mL dried DCM was added dropwise within 1 h. Then, the reaction mixture was warmed to room temperature, stirred for 10 h, and filtered. The filtrate was concentrated on a rotary evaporator and diluted by ethyl acetate, and washed with brine thrice. After drying over $MgSO_4$, the organic solution was concentrated. **S6** was obtained as slightly yellow liquid. **S6** was dissolved in 120 mL of CH_3OH/1.0 M HCl (v/v = 1/1) and stirred at room temperature for 4 h. The solution pH was then adjusted to 7.0 using 2 M NaOH. The solution was concentrated and extracted with ethyl acetate. The organic phase was concentrated and purified by silica column chromatography using petroleum ether and ethyl acetate (v/v = 1/1) as the eluent. **D2** was obtained as a slightly yellow oil in 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.10 (s, 1H), 5.56 (s, 1H), 4.18-4.14 (t, J=8 Hz, 2H), 3.74-3.68 (m, 1H), 3.66-3.63 (m, 1H), 3.46-3.41 (m, 1H), 2.75 (s, 2H), 1.94 (s, 3H), 1.79-1.40 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.58, 136.43, 125.37, 72.02, 66.75, 64.46, 32.67, 28.64, 22.07, 18.34 (**Fig. S6**). HRMS: m/z calcd for $C_{10}H_{18}O_4$ $(M+H)^+$ 203.1278, found 203.1279.

3-Hydroxy-2-(hydroxymethyl)-2-methylpropyl methacrylate (D3). D3 was prepared from 1,1,1-tris (hydroxy methyl)ethane by following the similar procedure as for the preparation of D2. D3 was obtained as a slightly yellow oil in 44% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.15 (s, 1H), 5.62 (s, 1H), 4.27 (s, 2H), 3.62-3.54 (q, J=12Hz, 4H), 2.80 (s, 2H), 1.96 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.23, 135.95, 126.36, 67.79, 66.73, 40.92, 18.32, 16.87 (**Fig. S7**). HRMS: m/z calcd for $C_9H_{16}O_4$ $(M+H)^+$ 189.1121, found 189.1117.

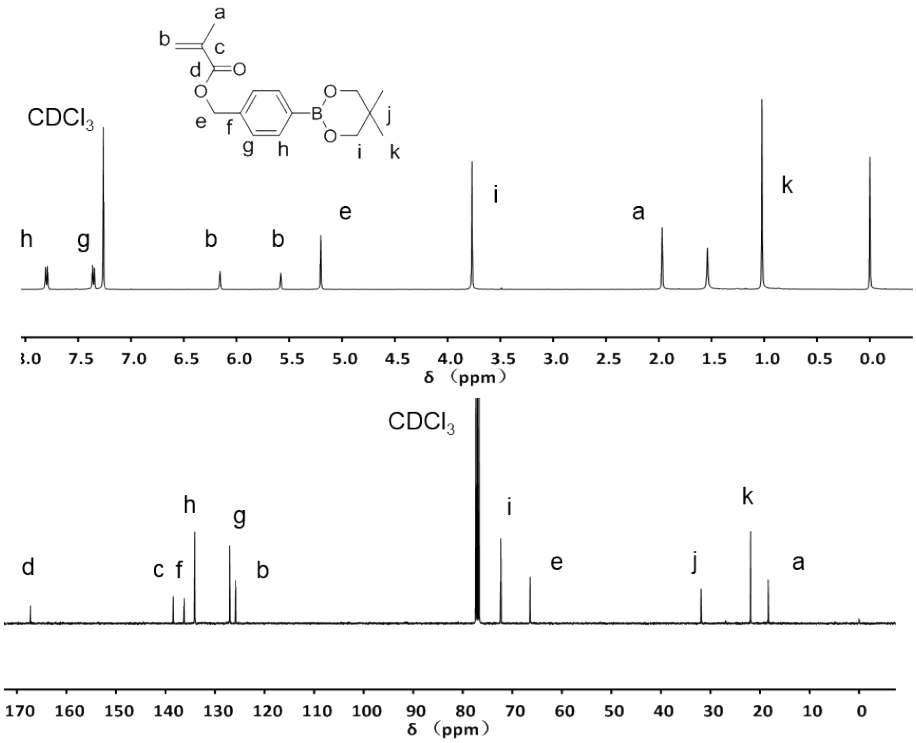

Fig. S1 ^{1}H NMR and ^{13}C NMR spectra of **M1** in $CDCl_3$.

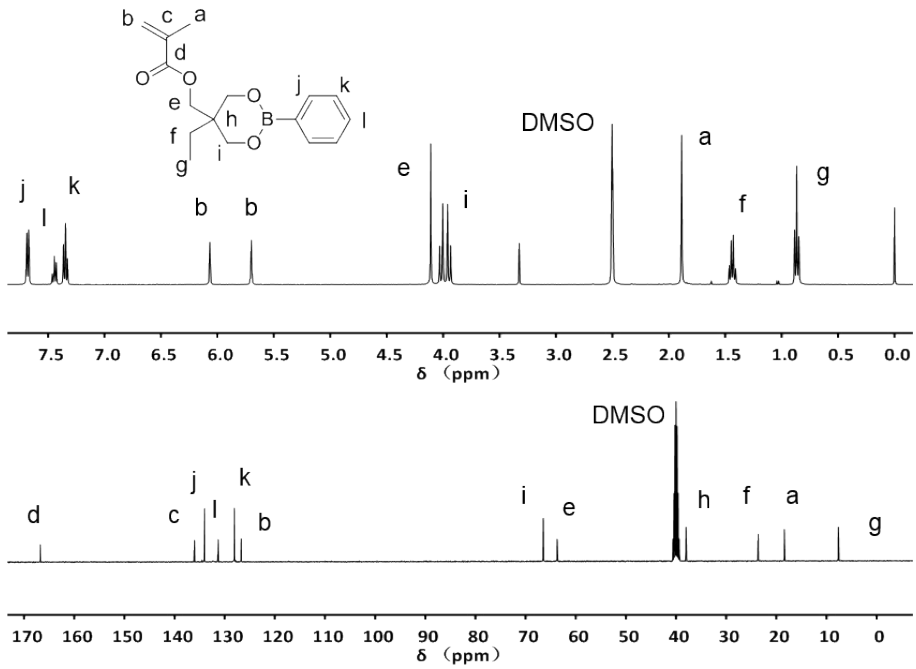

Fig. S2 ^{1}H NMR and ^{13}C NMR spectra of **M2** in DMSO-d_6.

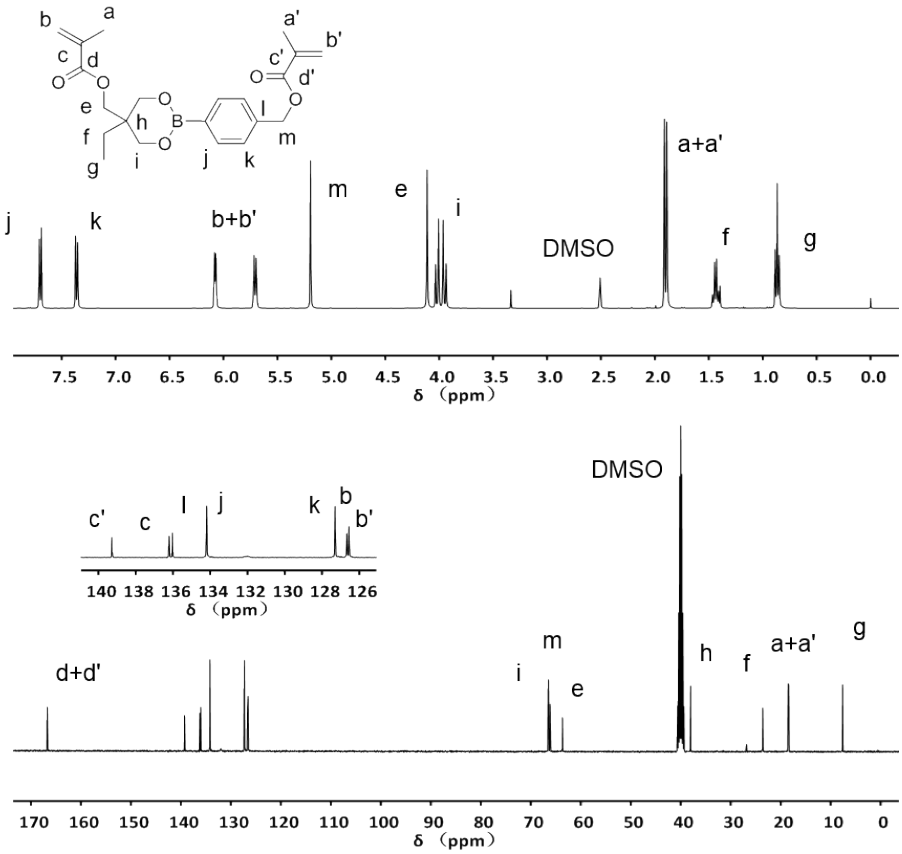

Fig. S3 ^{1}H NMR and ^{13}C NMR spectra of **L1** in DMSO-d_6.

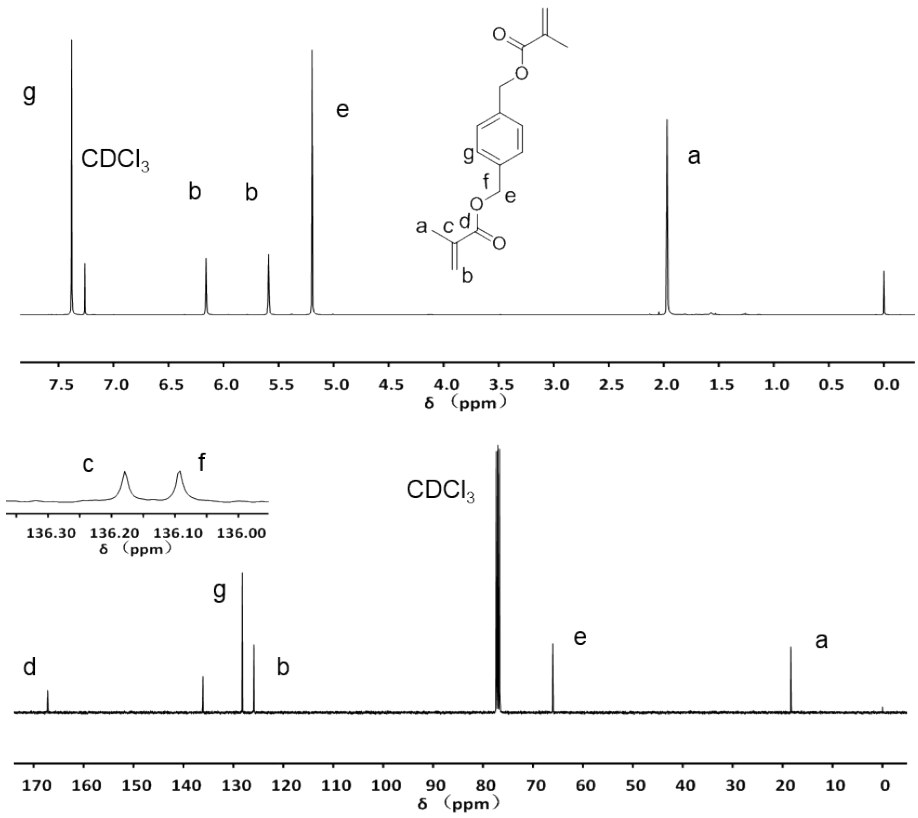

Fig. S4 ^{1}H NMR and ^{13}C NMR spectra of **L2** in $CDCl_3$.

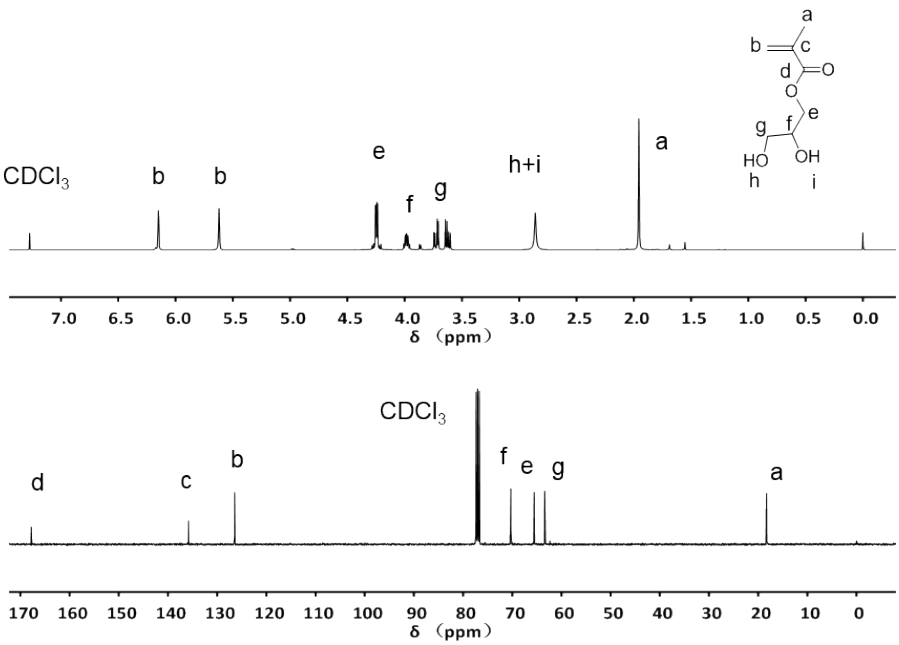

Fig. S5 ^{1}H NMR and ^{13}C NMR spectra of **D1** in $CDCl_3$.

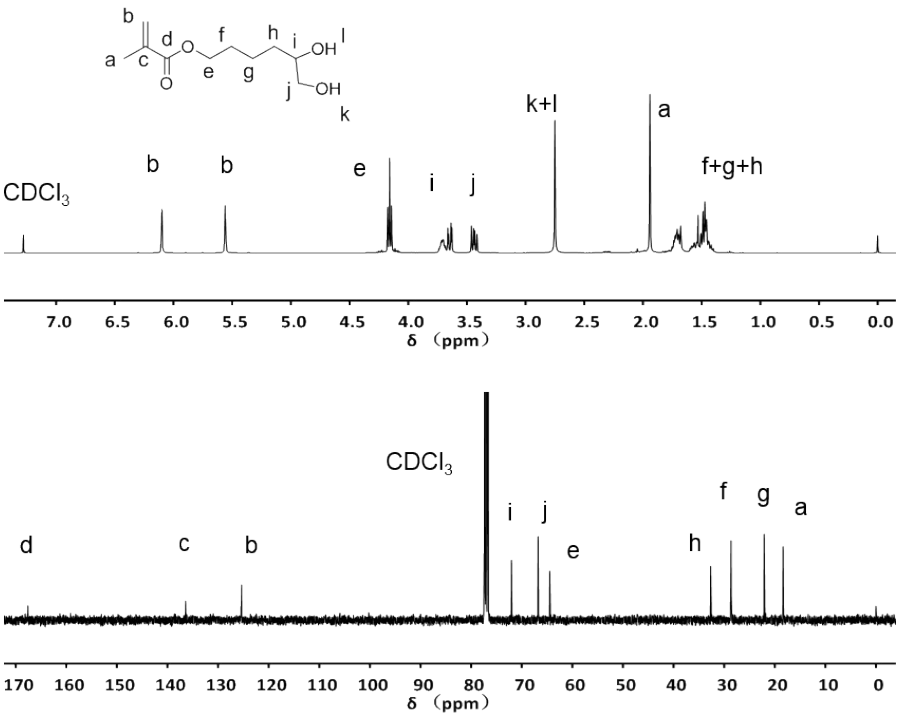

Fig. S6 ^{1}H NMR and ^{13}C NMR spectra of **D2** in $CDCl_3$.

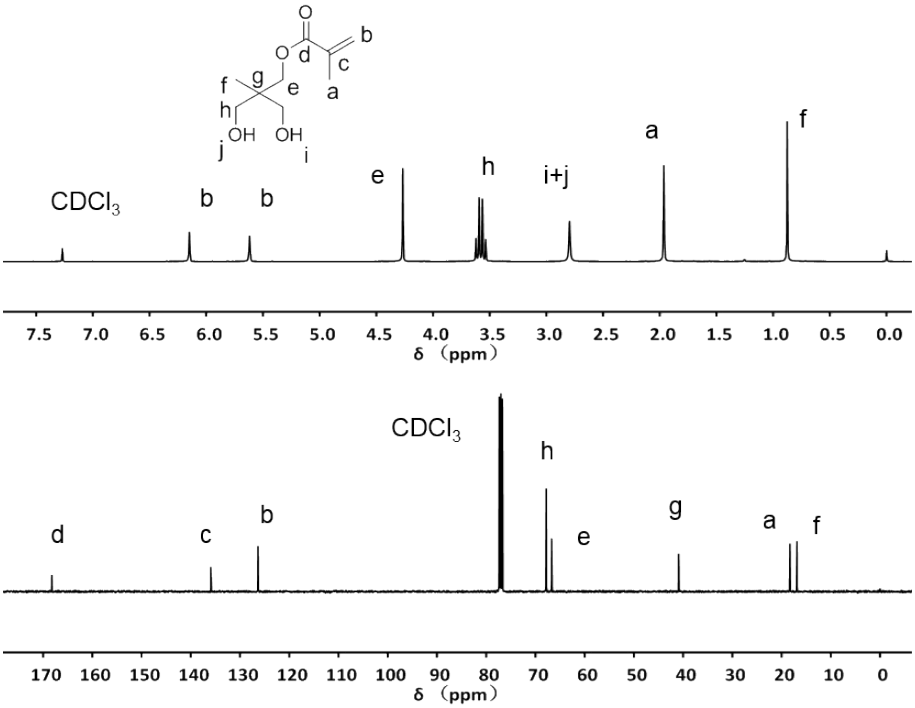

Fig. S7 ^{1}H NMR and ^{13}C NMR spectra of **D3** in $CDCl_3$.

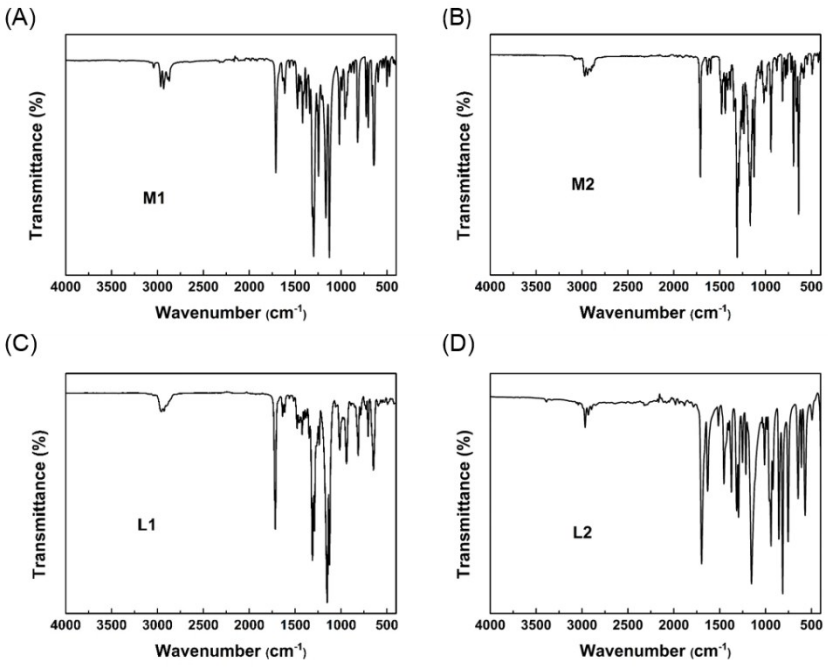

Fig. S8 ATR-IR spectra of monomers and crosslinkers.

Part-II. Metathesis of model compounds

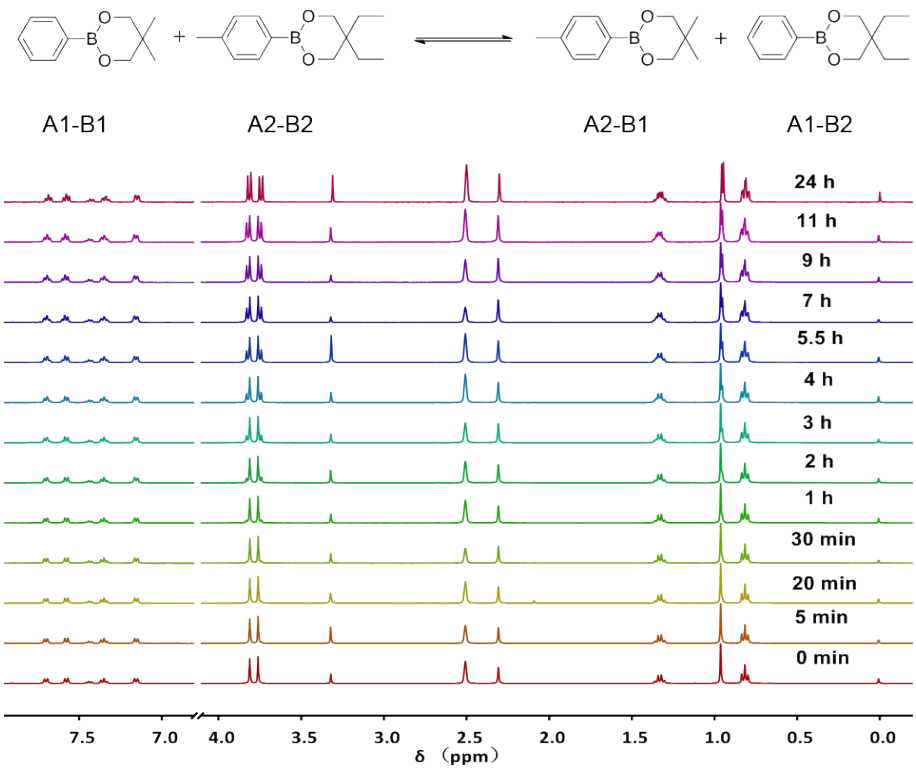

Fig. S9 Time-dependent ^{1}H NMR spectra of the reaction mixture of **A1-B1** and **A2-B2** in bulk at 100 °C.

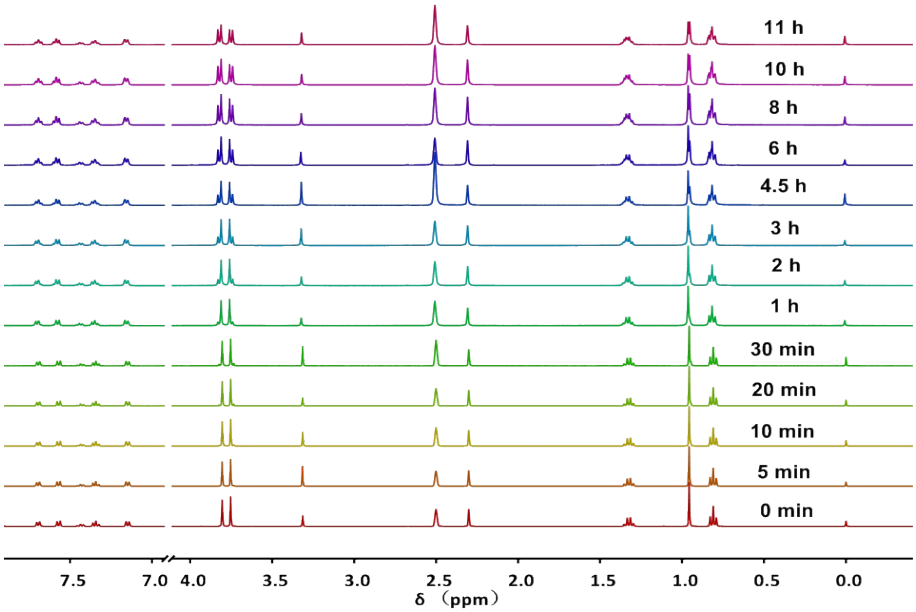

Fig. S10 Time-dependent ^{1}H NMR spectra of the reaction mixture of **A1-B1** and **A2-B2** in bulk at 120 °C .

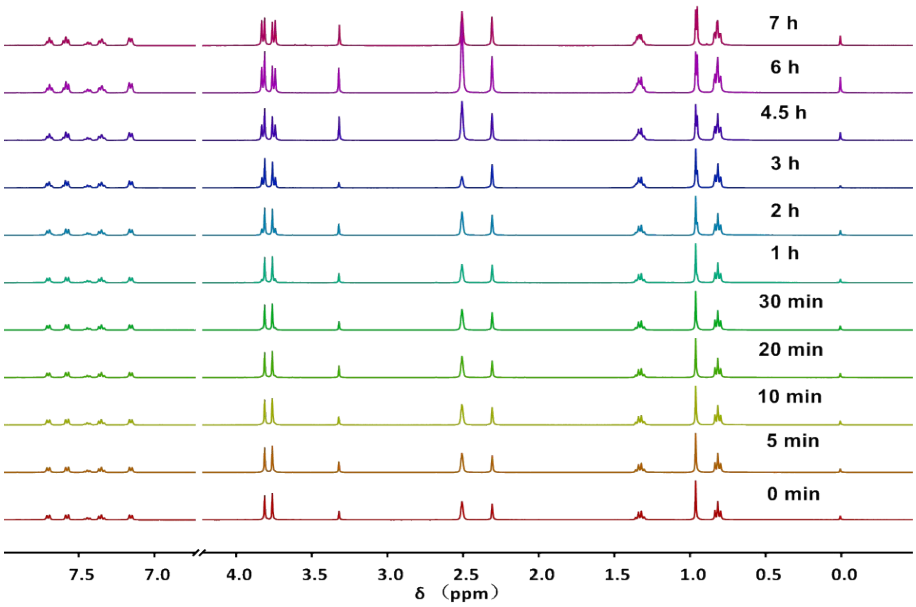

Fig. S11 Time-dependent ^{1}H NMR spectra of the reaction mixture of **A1-B1** and **A2-B2** in bulk at 135 °C .

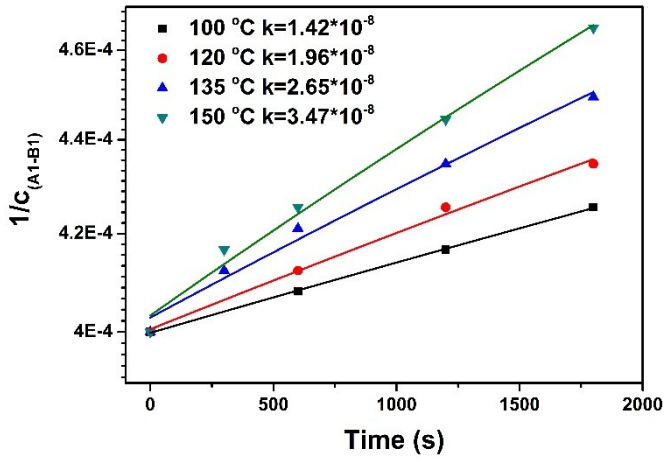

Fig. S12 Kinetic plot of $1/C_{[\mathbf{A1\text{-}B1}]}$ versus time for the reaction of **A1-B1** and **A2-B2** at different temperatures.

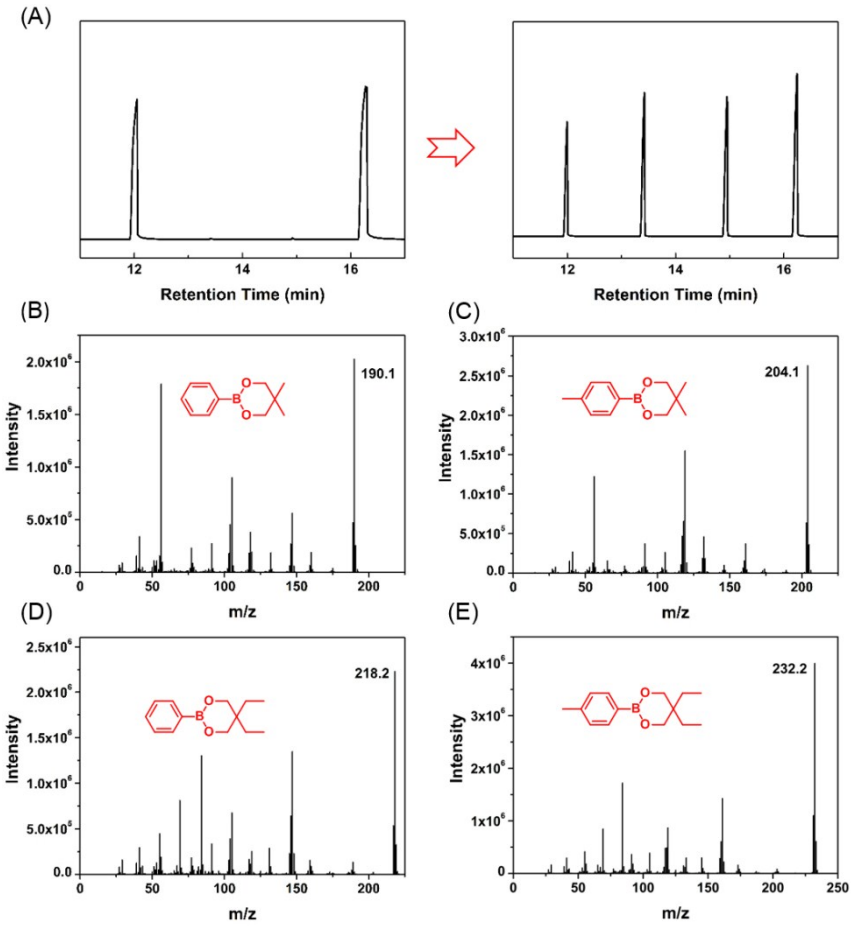

Fig. S13 (A) Gas chromatography traces of the reaction mixture of **A1-B1** and **A2-B2** in bulk at 0 min (left) and 180 min (right), 150 °C. Electron impact mass spectrometry of the four components in the reaction mixture (A) **A1-B1**, (B) **A2-B1**, (C) **A1-B2**, and (D) **A2-B2**.

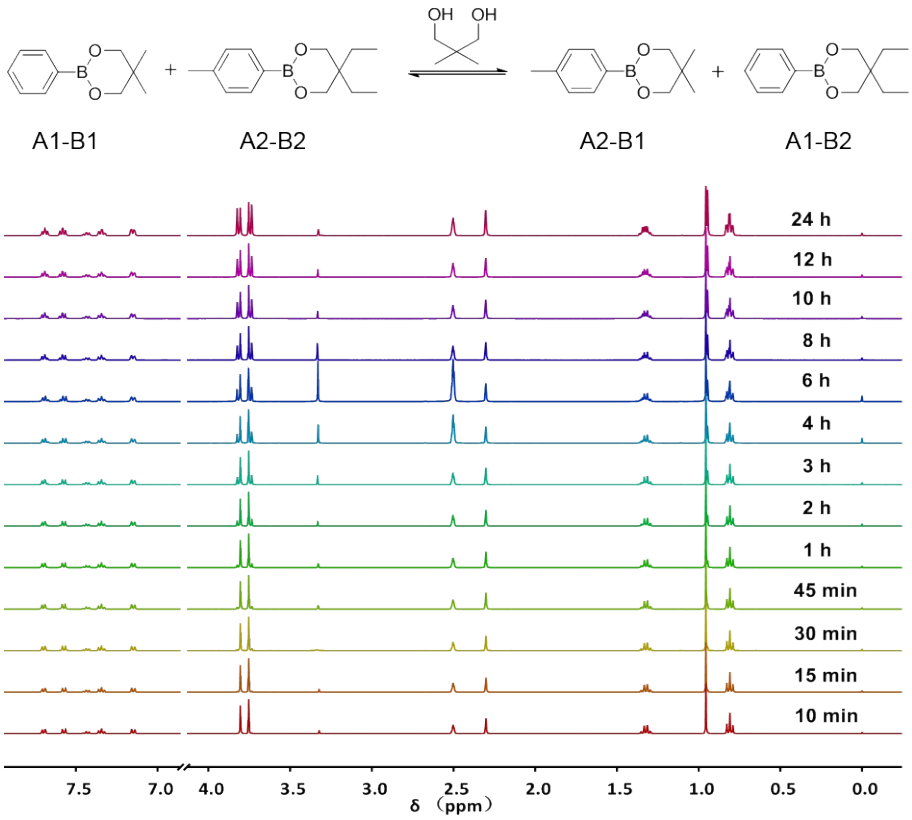

Fig. S14 Time-dependent ^{1}H NMR spectra of the reaction mixture of **A1-B1** and **A2-B2** with 1 mol% neopentyl glycol in bulk at 50 °C.

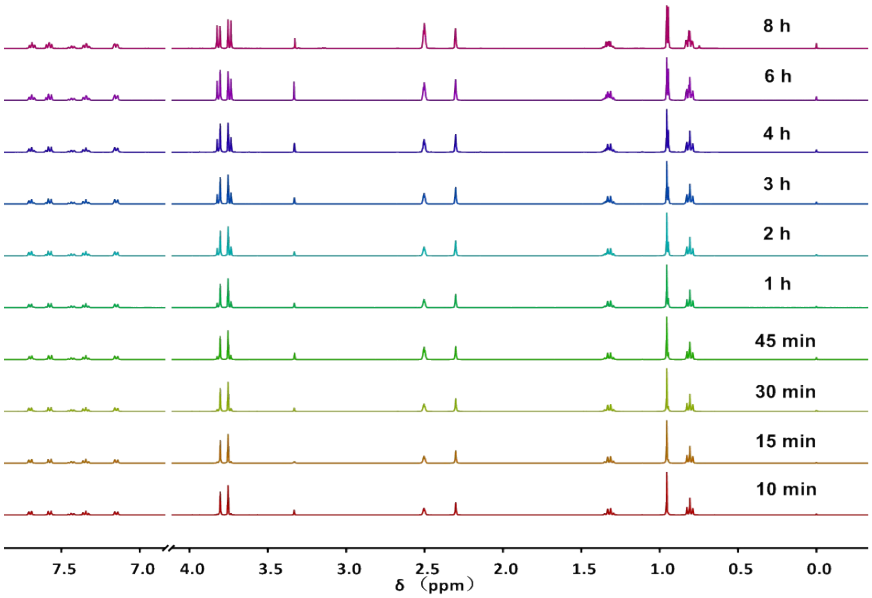

Fig. S15 Time-dependent ^{1}H NMR spectra of the reaction mixture of **A1-B1** and **A2-B2** with 1 mol% neopentyl glycol in bulk at 125 °C.

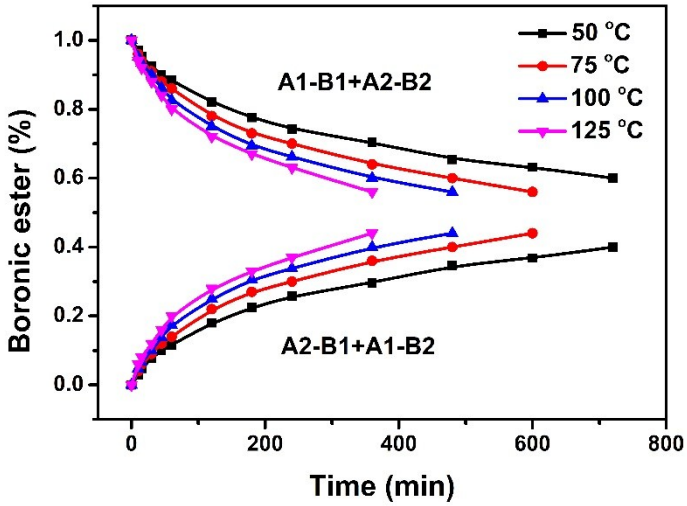

Fig. S16 Consumption and formation of dioxaborinanes as a function of time for the reaction of **A1-B1** and **A2-B2** with 1 mol% neopentyl glycol in bulk.

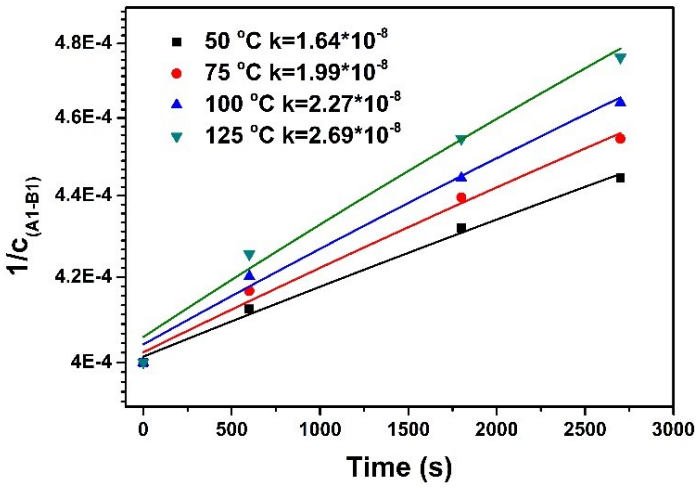

Fig. S17 Kinetic plots of $1/C_{[\mathbf{A1\text{-}B1}]}$ versus time for the reaction of **A1-B1** and **A2-B2** with 1 mol% neopentyl glycol at different temperatures.

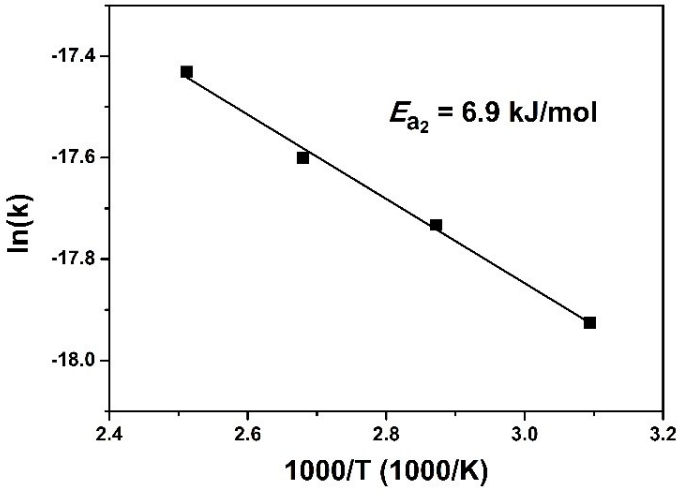

Fig. S18 Temperature-dependent kinetics provides an Arrhenius activation energy of 6.9 kJ/mol for the metathesis of the dioxaborinanes with 1 mol% neopentyl glycol.

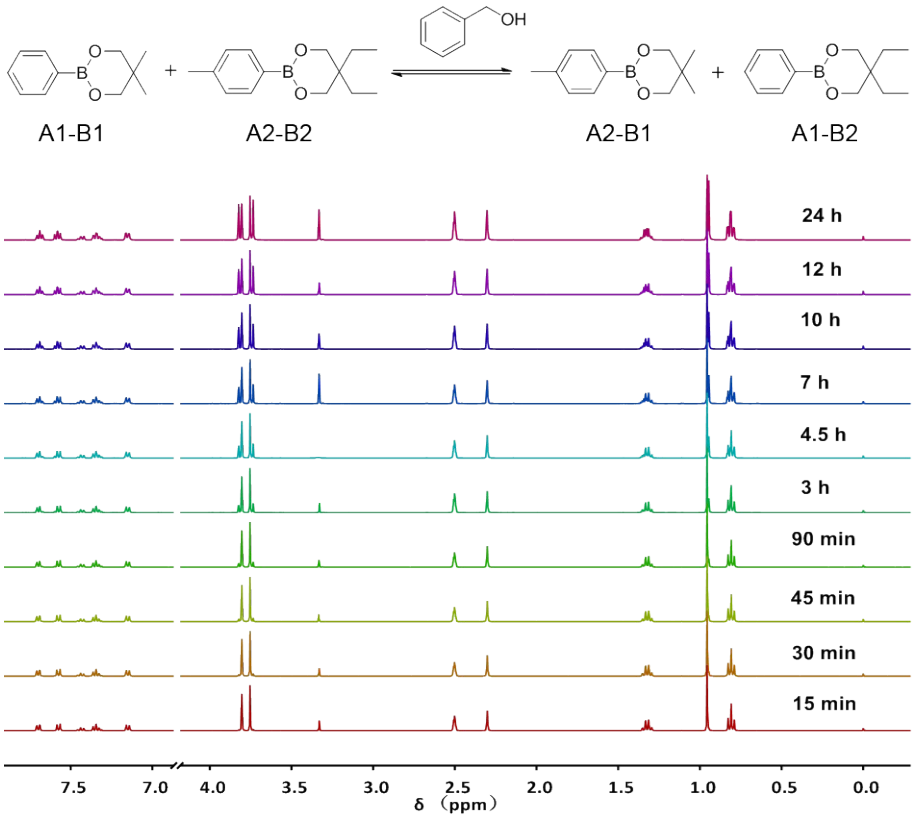

Fig. S19 Time-dependent ^{1}H NMR spectra of the reaction mixture of **A1-B1** and **A2-B2** with 2 mol% benzyl alcohol in bulk at 50 °C.

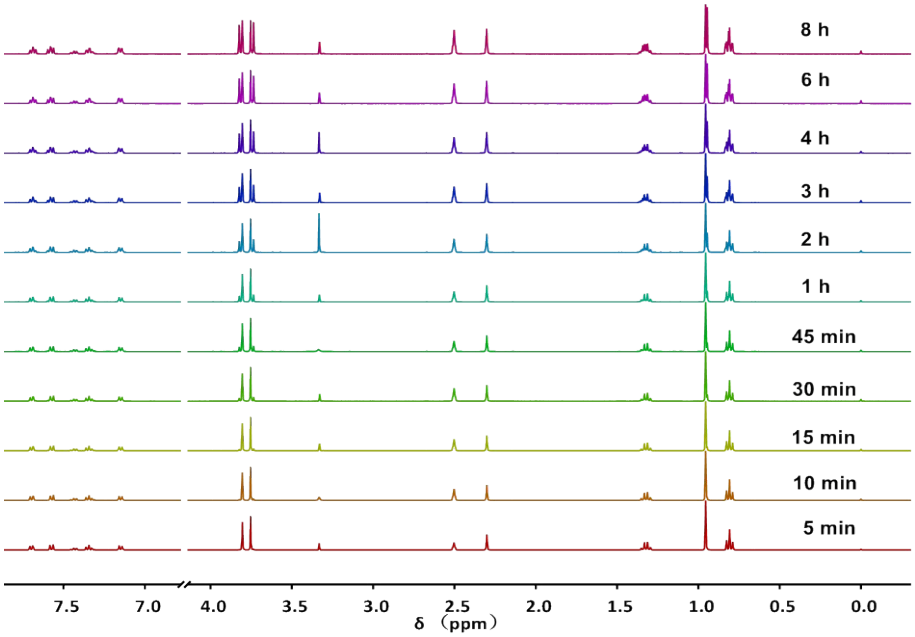

Fig. S20 Time-dependent ^{1}H NMR spectra of the reaction mixture of **A1-B1** and **A2-B2** with 2 mol% benzyl alcohol in bulk at 125 °C.

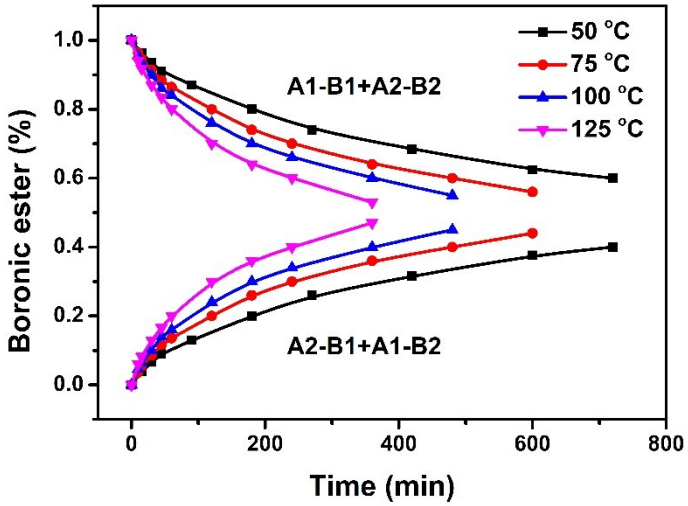

Fig. S21 Consumption and formation of dioxaborinanes as a function of time for the reaction of **A1-B1** and **A2-B2** with 2 mol% benzyl alcohol in bulk.

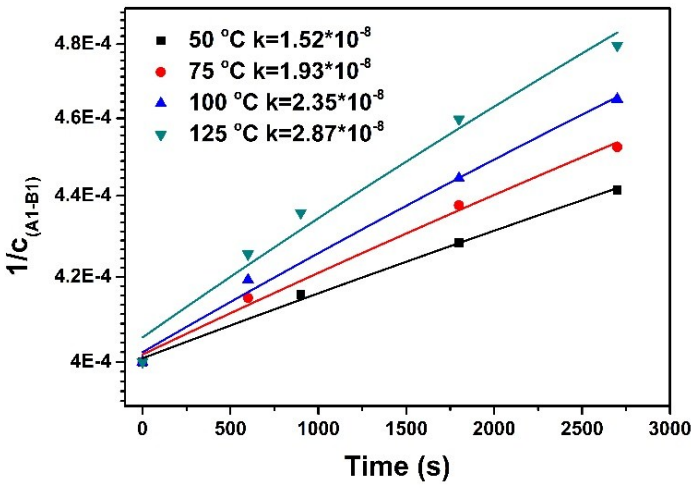

Fig. S22 Kinetic plots of $1/C_{[\mathbf{A1\text{-}B1}]}$ versus time for the reaction of **A1-B1** and **A2-B2** with 2 mol% benzyl alcohol in bulk at different temperatures.

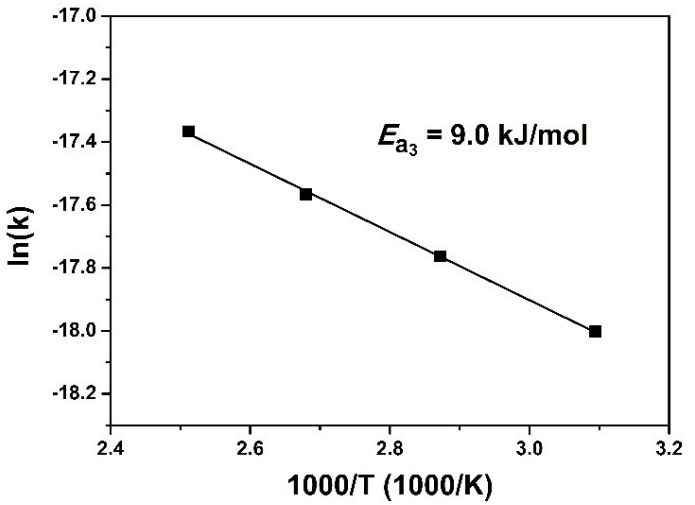

Fig. S23 Temperature-dependent kinetics provides an Arrhenius activation energy of 9.0 kJ/mol for the metathesis of the dioxaborinane with 2 mol% benzyl alcohol.

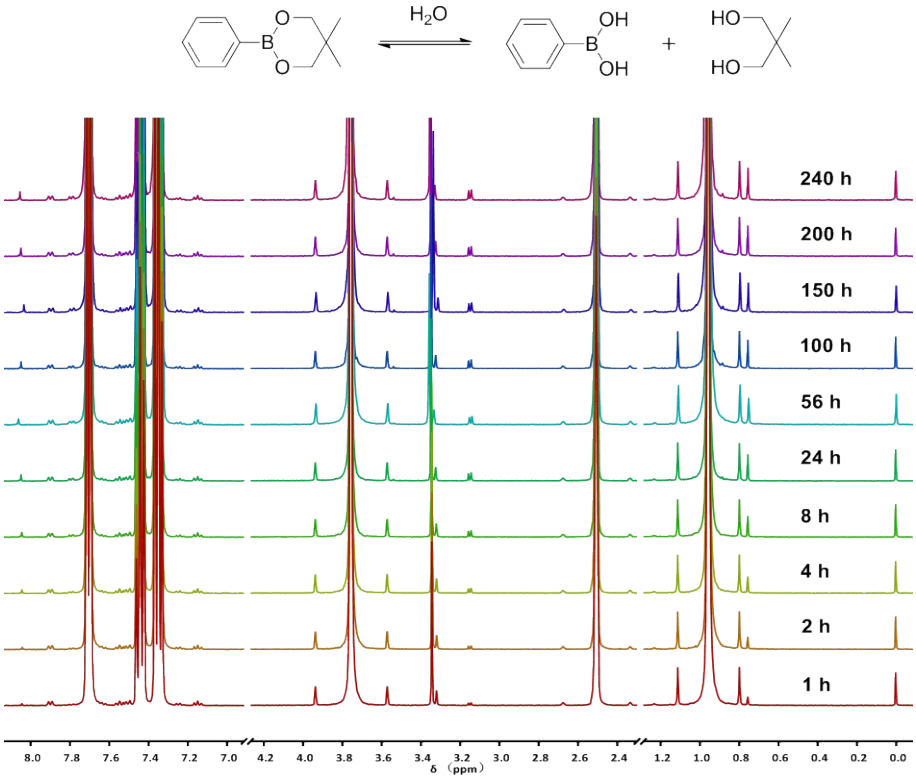

Fig. S24 Time-dependent ^{1}H NMR spectra of **A1-B1** in DMSO-d_6 at 20 ^{o}C.

Table S1 Effect of structure and content of alcohols, temperature, and concentration of boronic esters on metathesis rate.

Entry	Conc. [a] /mol/L	Alcohol content [b]	T /°C	Equilibrium percentage /% [c]				Equilibrium time /h [d]
				A1-B1	**A2-B2**	**A2-B1**	**A1-B2**	
1	5	0	100	25	25	25	25	24
2	5	A (1 mol%)	100	25	25	25	25	11
3	5	A (1 mol%)	50	25	25	25	25	24
4	5	A (3 mol%)	50	25	25	25	25	0.5
5	5	A (10 mol%)	50	27	23	27	23	0.17
6	5	C (2 mol%)	50	25	25	25	25	24
7	0.13	0	50	/	/	/	/	＞480
8	0.13	A (10 mol%)	80	27	23	27	23	24
9	0.13	A (10 mol%)	50	27	23	27	23	48
10	0.13	A (10 mol%)	20	27	23	27	23	120
11	0.13	A (20 mol%)	50	28	22	28	22	48
12	0.27	A (10 mol%)	50	27	23	27	23	24
13	0.13	B (10 mol%)	50	25	25	25	25	48
14	0.13	B (10 mol%)	20	25	25	25	25	120

[a] Total concentration of dioxaborinanes in the reaction mixture. The metathesis reaction was carried out in bulk or in DMSO-d_6. As shown in **Fig.S24**, DMSO-d_6 contained a small amount of water, but the hydrolysis ratio of **A1-B1** was less than 0.4% for 10 days at 20 °C. So the trace water in DMSO-d_6 had little effect on the metathesis reaction under the conditions for NMR tests. [b] Molar percentage of excess alcohol compared to the total content of dioxaborinanes. A, B, C denote neopentyl glycol, 1,2-propylene glycol, and benzyl alcohol, respectively. [c] The relative percentages of four dioxaborinanes at equilibrium. [d] Time needed to reach equilibrium. It should be noted that the real equilibrium time may be slightly shorter than the indicated value.

Part-III. Syntheses and dynamic crosslinking of linear copolymers

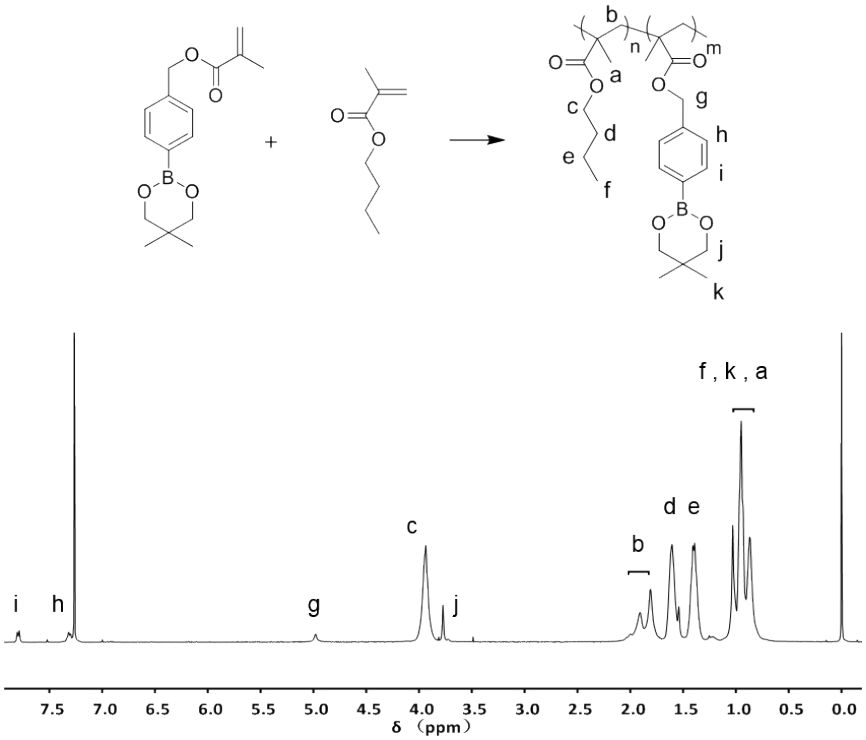

Fig. S25 ^{1}H NMR spectrum of copolymer **P1**.

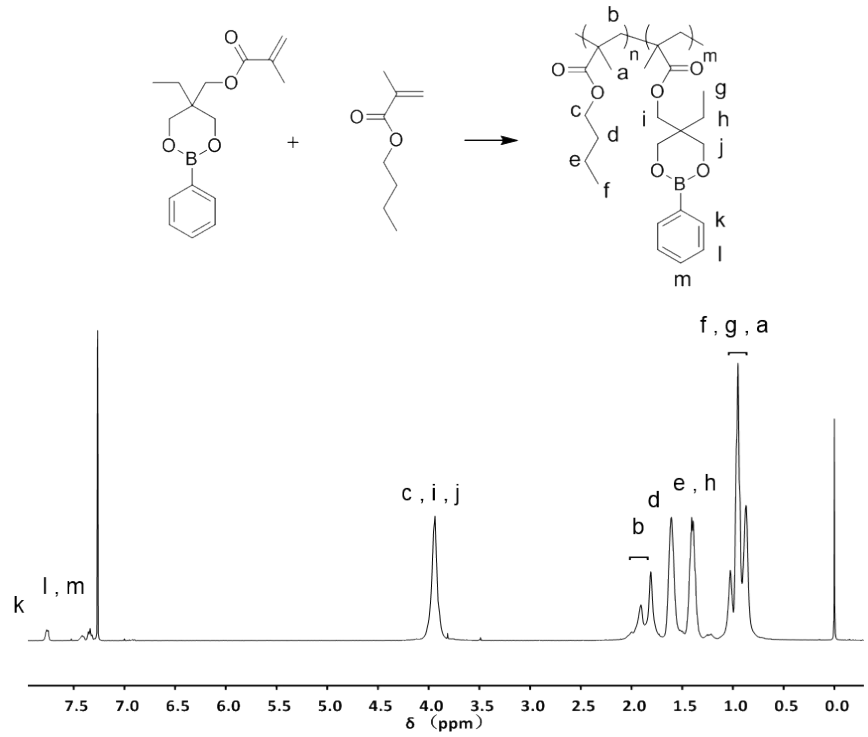

Fig. S26 ^{1}H NMR spectrum of copolymer **P2**.

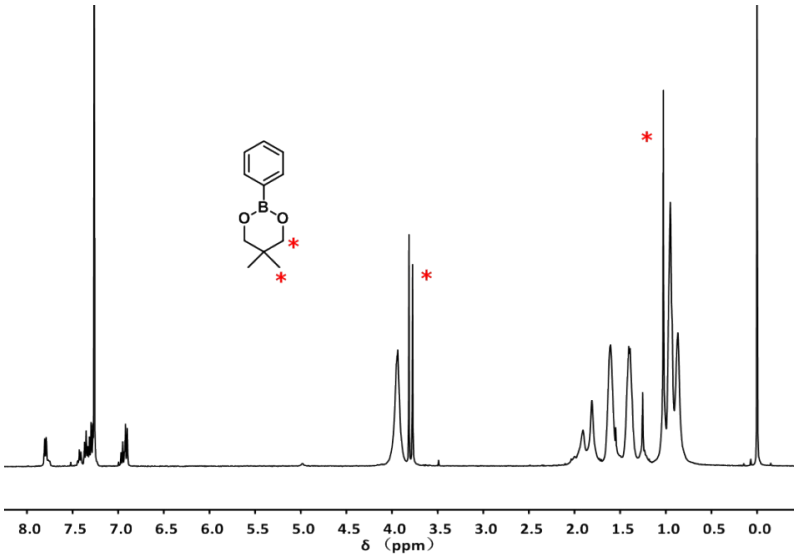

Fig. S27 ^{1}H NMR spectrum of the gel swollen in $CDCl_3$.

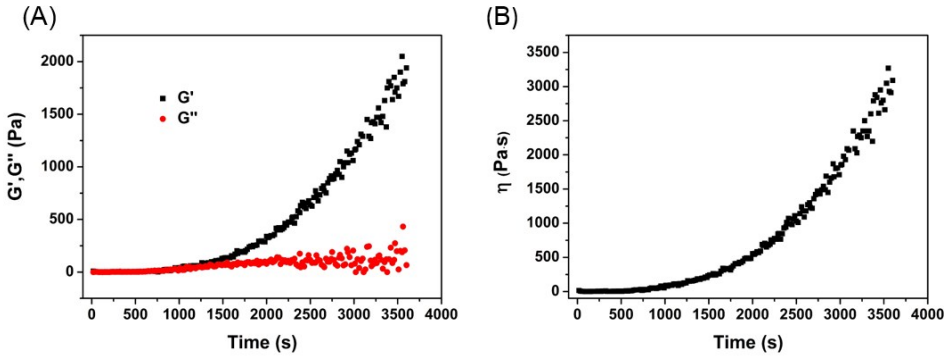

Fig. S28 The change of storage modulus (G'), loss modulus (G") and viscosity with time during gelation at 100 °C. (The mixed solution of P1 and P2 in anisole was 20 wt%.)

Part-IV. Characterization of the structure, and thermal and mechanical properties of crosslinked networks without diols

Table S2 Thermal and Mechanical properties of test groups and control groups

Sample	Linker ratio /%	$T_{d,5\%}$ /°C	T_g [a] /°C	GF [b] /%	σ [c] /MPa	ε [c] /%	E [c] /MPa	Toughness /MJ/m^3 [c]	
								Pristine	Healed [d]
N1a	1	271	34	96 ± 2	2.4 ± 0.2	262 ± 15	35.4 ± 1.1	4.8 ± 0.2	4.6 ± 0.2
N1b	3	289	47	95 ± 4	7.7 ± 0.6	86 ± 6	301.7 ± 24.8	6.5 ± 0.2	6.4 ± 0.3
N2a	1	277	31	96 ± 3	1.3 ± 0.2	216 ± 14	2.9 ± 0.4	1.9 ± 0.2	/
N2b	3	273	46	95 ± 5	6.5 ± 0.3	105 ± 20	209.2 ± 37.2	5.9 ± 1.2	/
N3a	1	271	27	98 ± 1	0.8 ± 0.1	167 ± 24	0.9 ± 0.1	0.7 ± 0.1	/
N3b	3	277	36	96 ± 4	5.3 ± 0.3	99 ± 1	136.1 ± 24.3	4.3 ± 0.4	/

[a] T_g measured by DSC. [b] Gel fraction determined by swelling tests at 40 °C. [c] Mechanical properties including breaking strength (σ), strain at break (ε), and Young's modulus (E) measured by uniaxial tension tests. [d] Healing conditions: 150 °C, 8 h for **N1a** and 12 h for **N1b**.

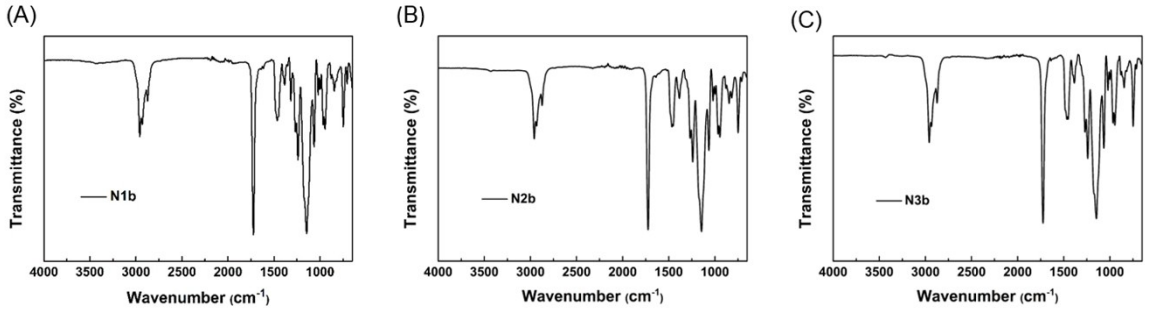

Fig. S29 ATR-IR spectra of polymer networks (A) **N1b,** (B) **N2b**, and (C) **N3b**.

Swelling Test

Anisole was used as a good solvent for the swelling tests. A piece of each network material (8 mm in diameter and 1 mm in thickness) was immersed in 3 mL anisole at 40 °C for 6 h. The swollen sample was weighed at the desired intervals after blotting excess liquid on the surface. Swelling ratio and gel fraction were defined as follows:

$$\text{Swelling ratio} = (M_s - M_d)/M_d;\ \text{Gel fraction} = M_e/M_d$$

wherein M_d, M_s, M_e denote the mass of the pristine dry sample, the swollen sample, and the dried sample after extraction with anisole. The experiments was carried out in triplicate.

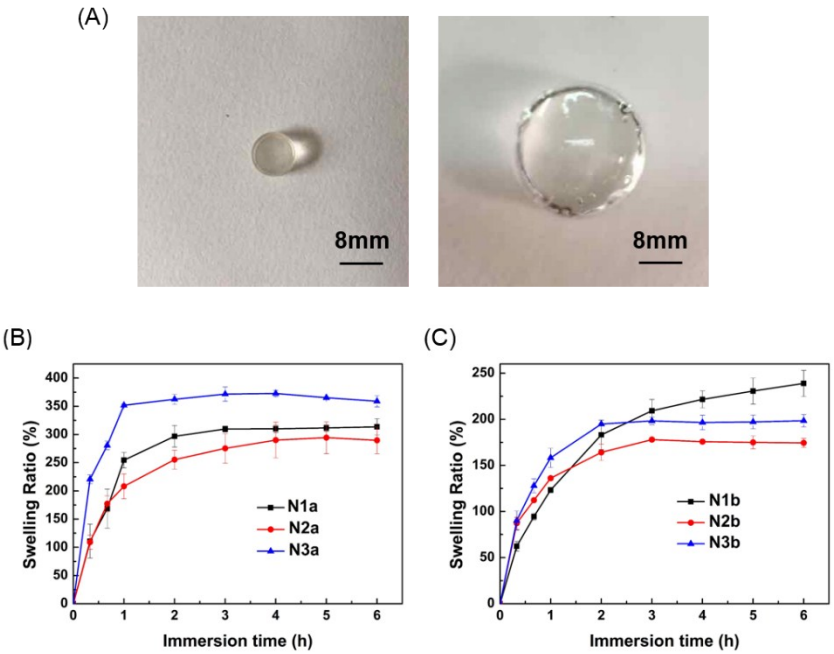

Fig. S30 (A) photographs of pristine and anisole-swollen samples of **N1a**. (B, C) Swelling ratio versus time during swelling of (B) **N1a**, **N2a** and **N3a**, and (C) **N1b**, **N2b** and **N3b** in anisole, 40 °C.

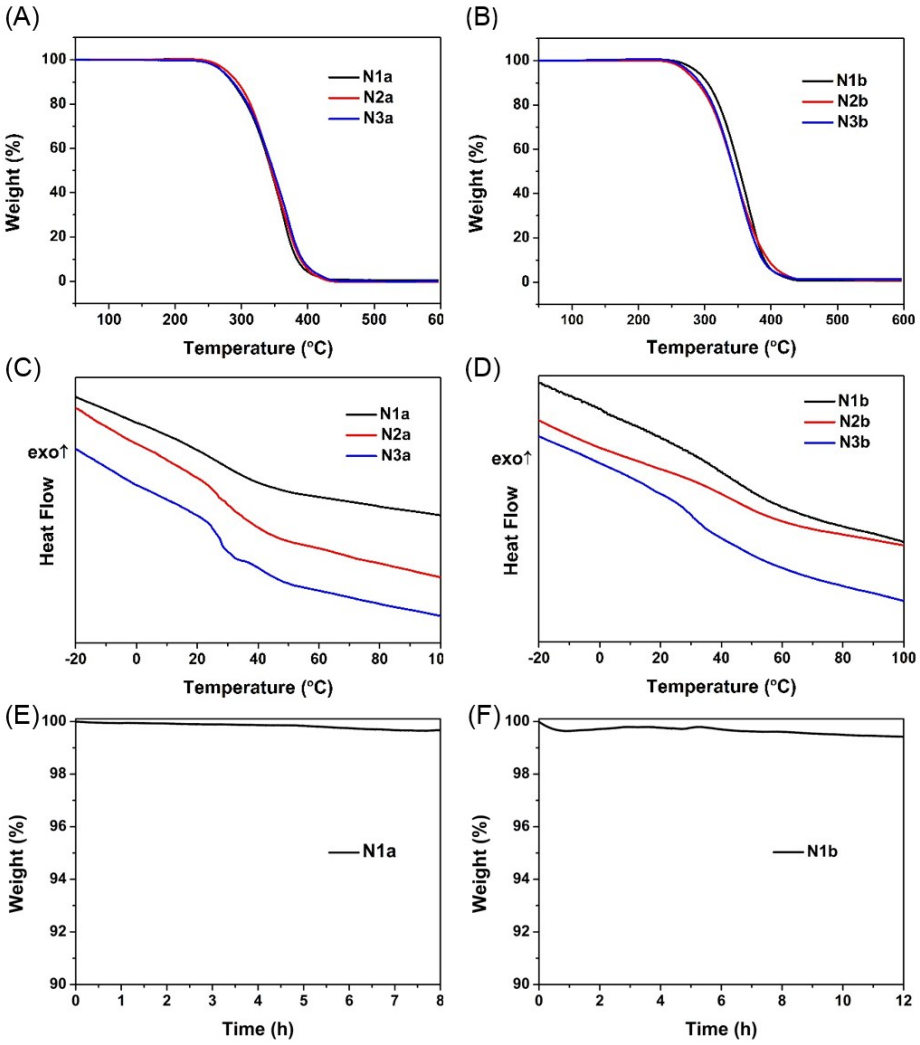

Fig. S31 (A, B) Thermal gravimetric analyses of the polymer networks. (C, D) DSC curves of the polymer networks. (E, F) Isothermal TGA curves of the polymer networks under nitrogen atmosphere at 150 °C.

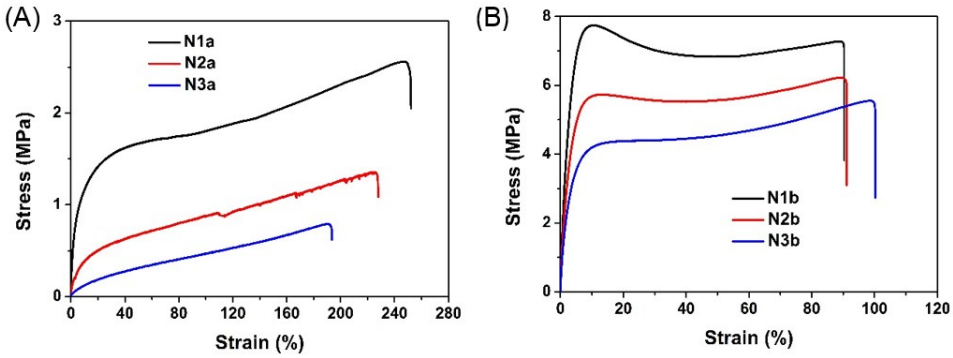

Fig. S32 Stress-strain curves of polymer networks (A) **N1a**, **N2a** and **N3a**, and (B) **N1b**, **N2b** and **N3b** under a stretching speed of 3 mm/min at room temperature.

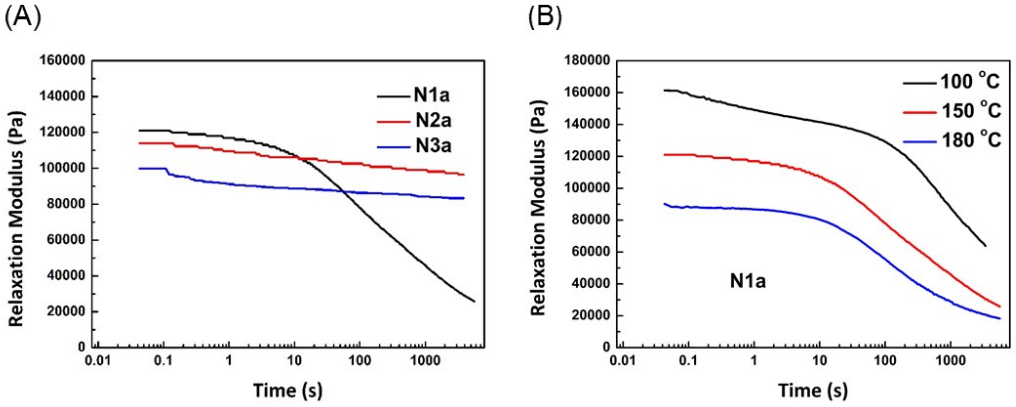

Fig. S33 (A) Stress relaxation behavior of **N1a**-**N3a** at 150 °C (before normalization). (B) Stress relaxation behavior of **N1a** at varied temperatures (before normalization).

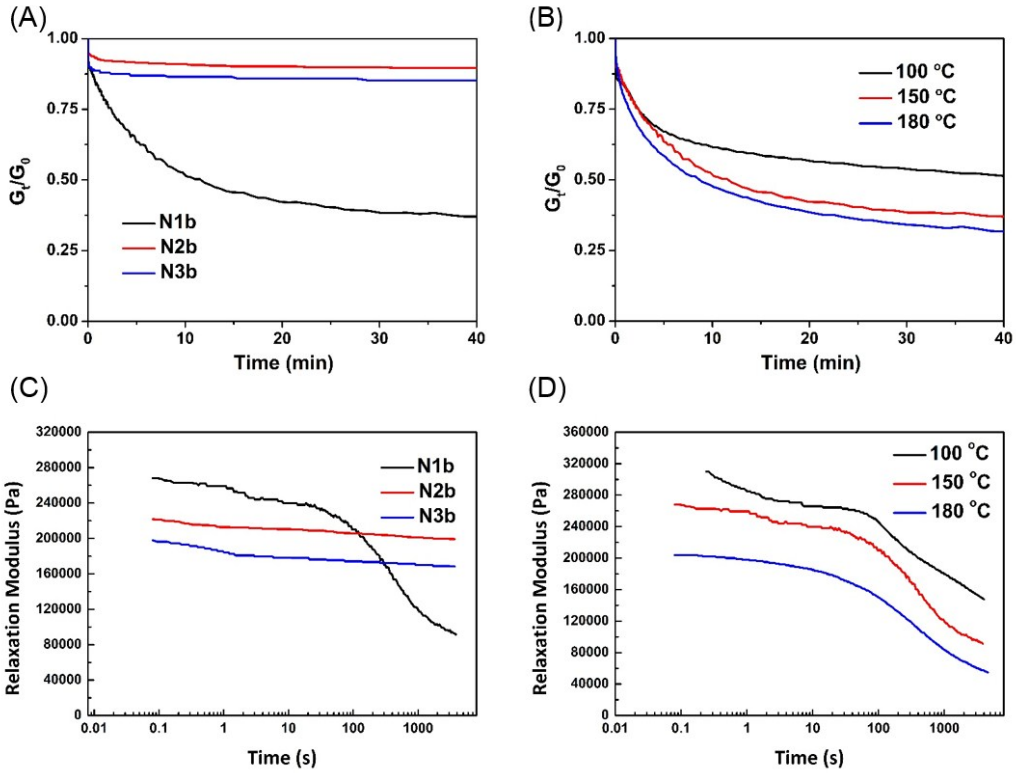

Fig. S34 (A, C) Stress relaxation behavior of the **N1b**-**N3b** networks at 150 °C. (B, D) Stress relaxation behavior of **N1b** at varied temperatures. The curves in C and D represent the native data before normalization.

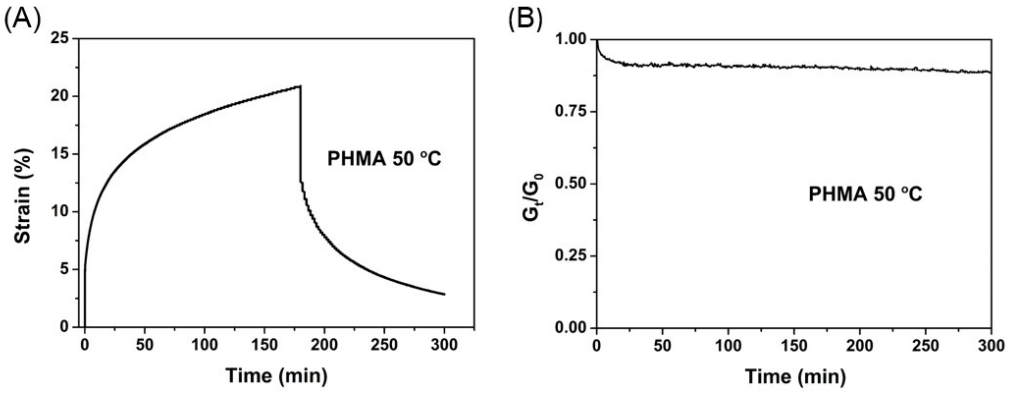

Fig. S35 (A) Creep recovery and (B) stress relaxation behaviors of poly(hexyl methacrylate) network crosslinked by 1 mol% **L1**. For creep recovery test, a loading of 5000 Pa was applied for 180 min and then released.

Part-V. Characterization of the structure, thermal, mechanical and self-healing properties of crosslinked networks with pendent diols

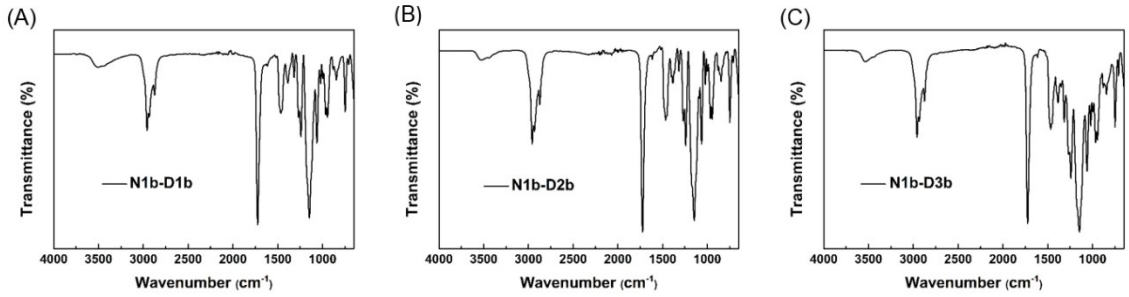

Fig. S36 ATR-IR spectra of the dynamic polymer networks with excess pendent diols.

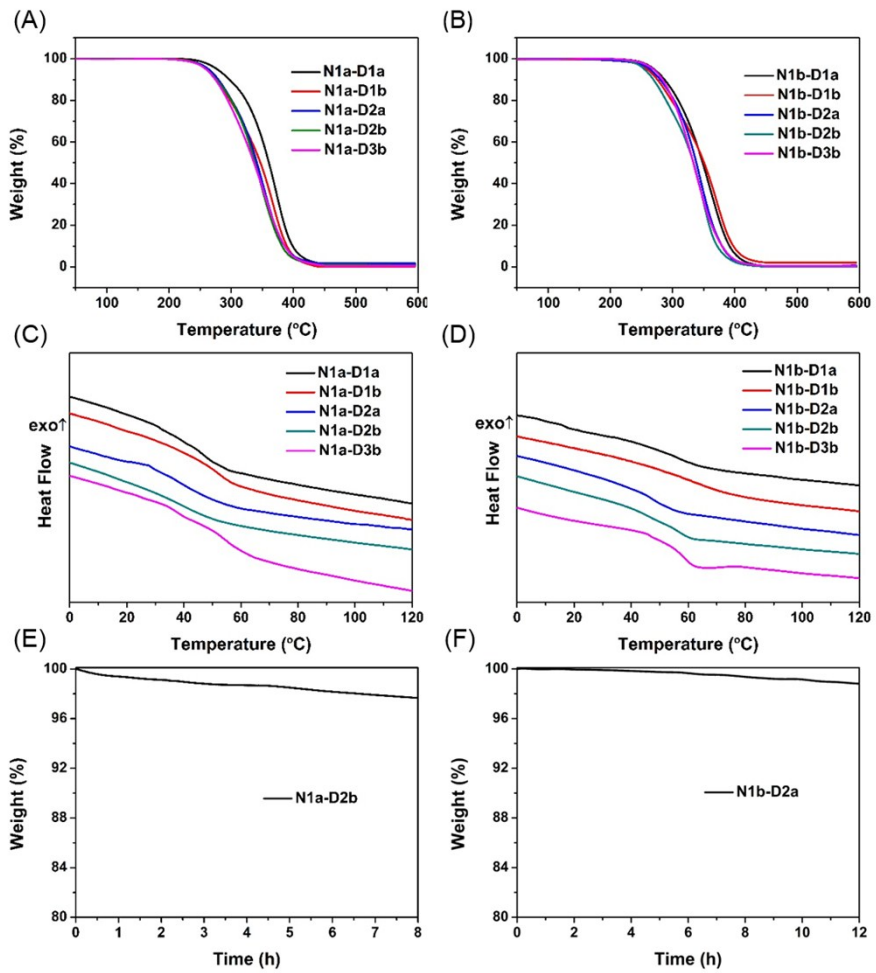

Fig. S37 (A, B) Thermal gravimetric analyses and (C, D) DSC curves of the polymer networks with excess pendent diols. (E, F) Isothermal TGA curves of the polymer networks under nitrogen atmosphere at 150 °C.

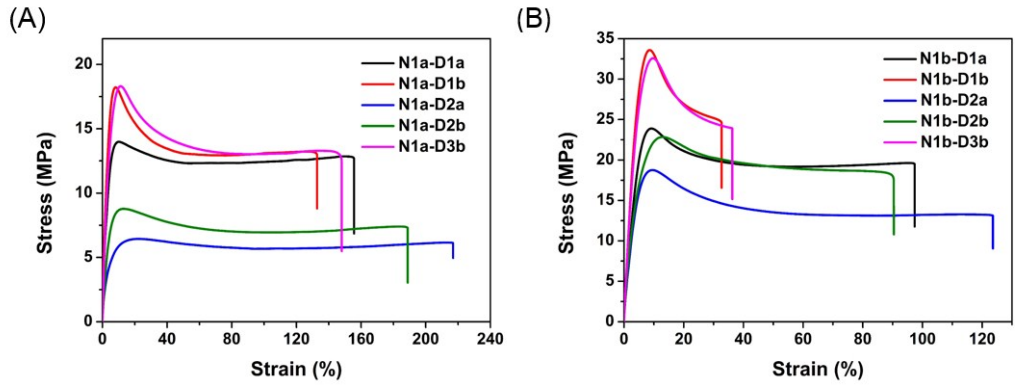

Fig. S38 Stress-strain curves of the diol-containing polymer networks under a stretching speed of 3mm/min at room temperature.

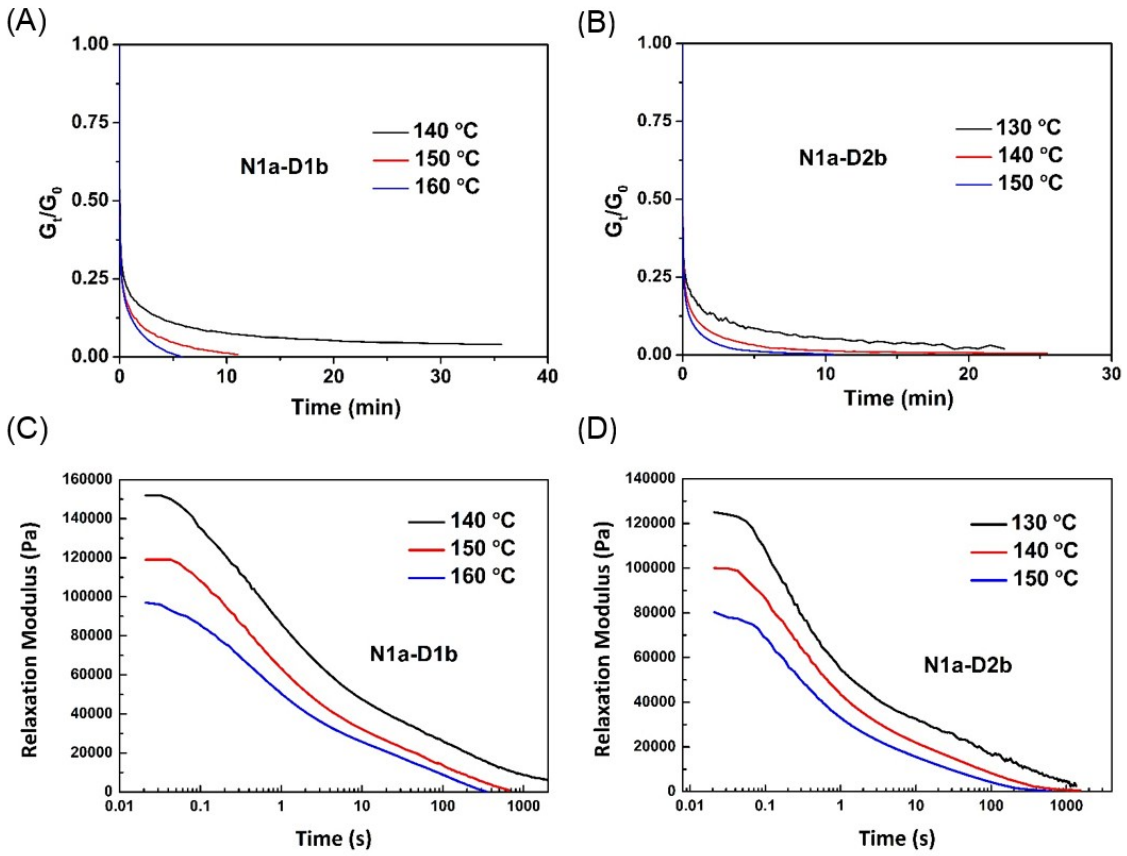

Fig. S39 Stress-relaxation behavior of the diol-containing networks (A, C) **N1a-D1b** and (B, D) **N1a-D2b** at different temperatures. The curves in C and D represent the native data before normalization.

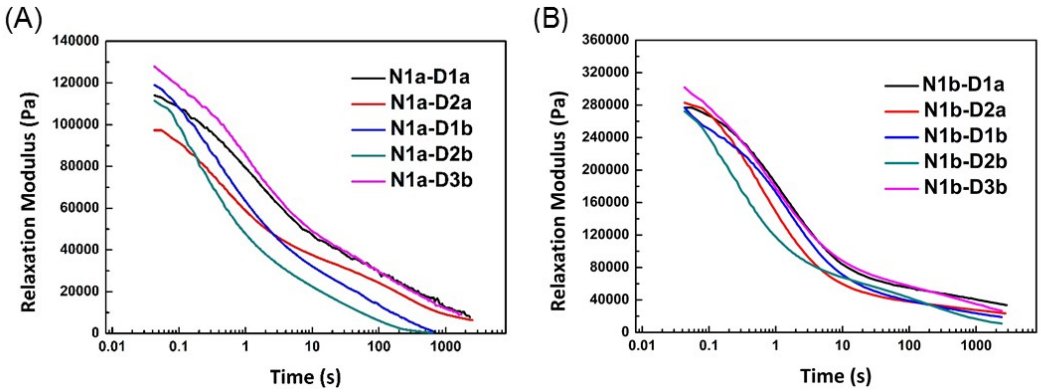

Fig. S40 Stress-relaxation behavior of the networks with excess diols at 150 °C before the normalization.

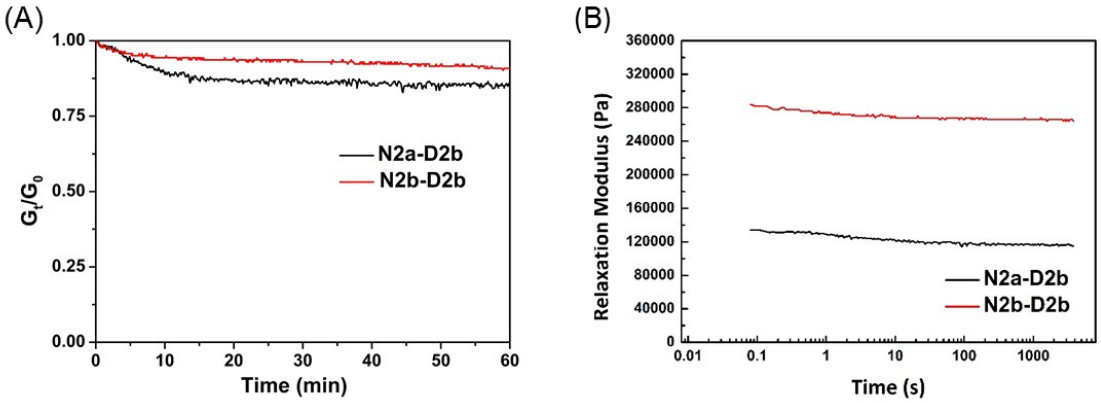

Fig. S41 Stress-relaxation behavior of the diol-containing non-dynamic networks **N2a-D2b** and **N2b-D2b** at 150°C. The curves in B represent the native data before normalization.

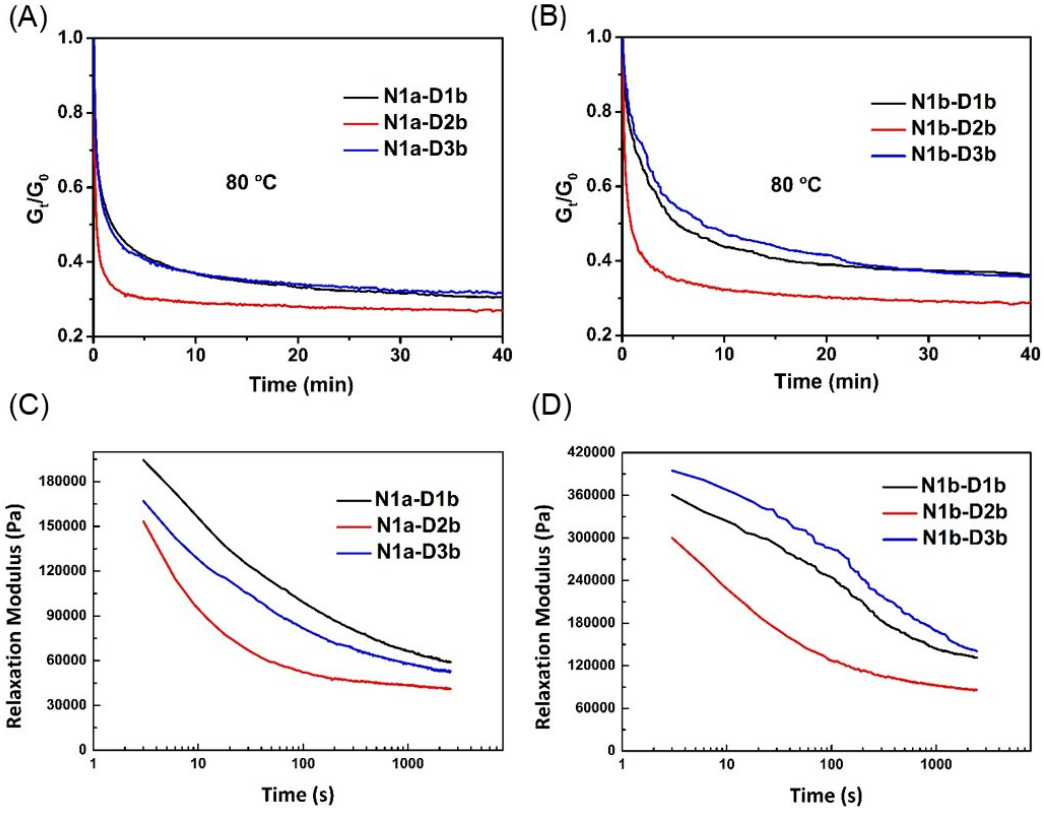

Fig. S42 Stress-relaxation behavior of the diol-containing networks at 80 °C. (A, B) Normalized curves and (C, D) the native date before normalization. The data points were taken at equal intervals instead of logs, so the abscissa started from 1 instead of 0.01.

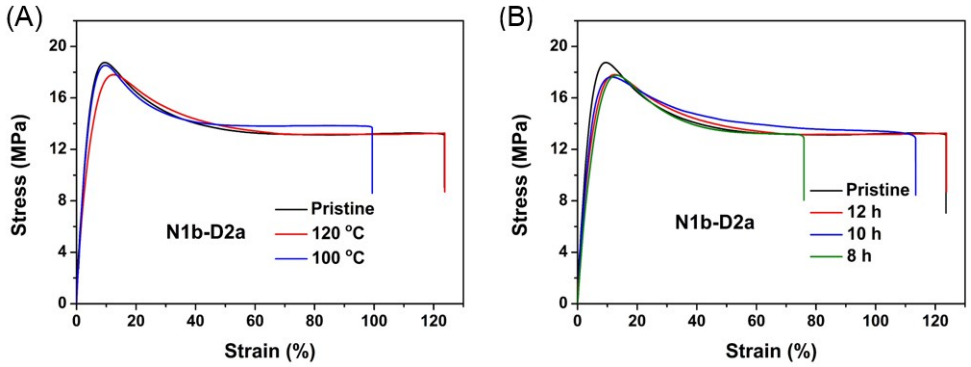

Fig. S43 Stress-strain curves of **N1b-D2a** healed (A) for 12 h at different temperatures and (B) for varied times at 120 °C.

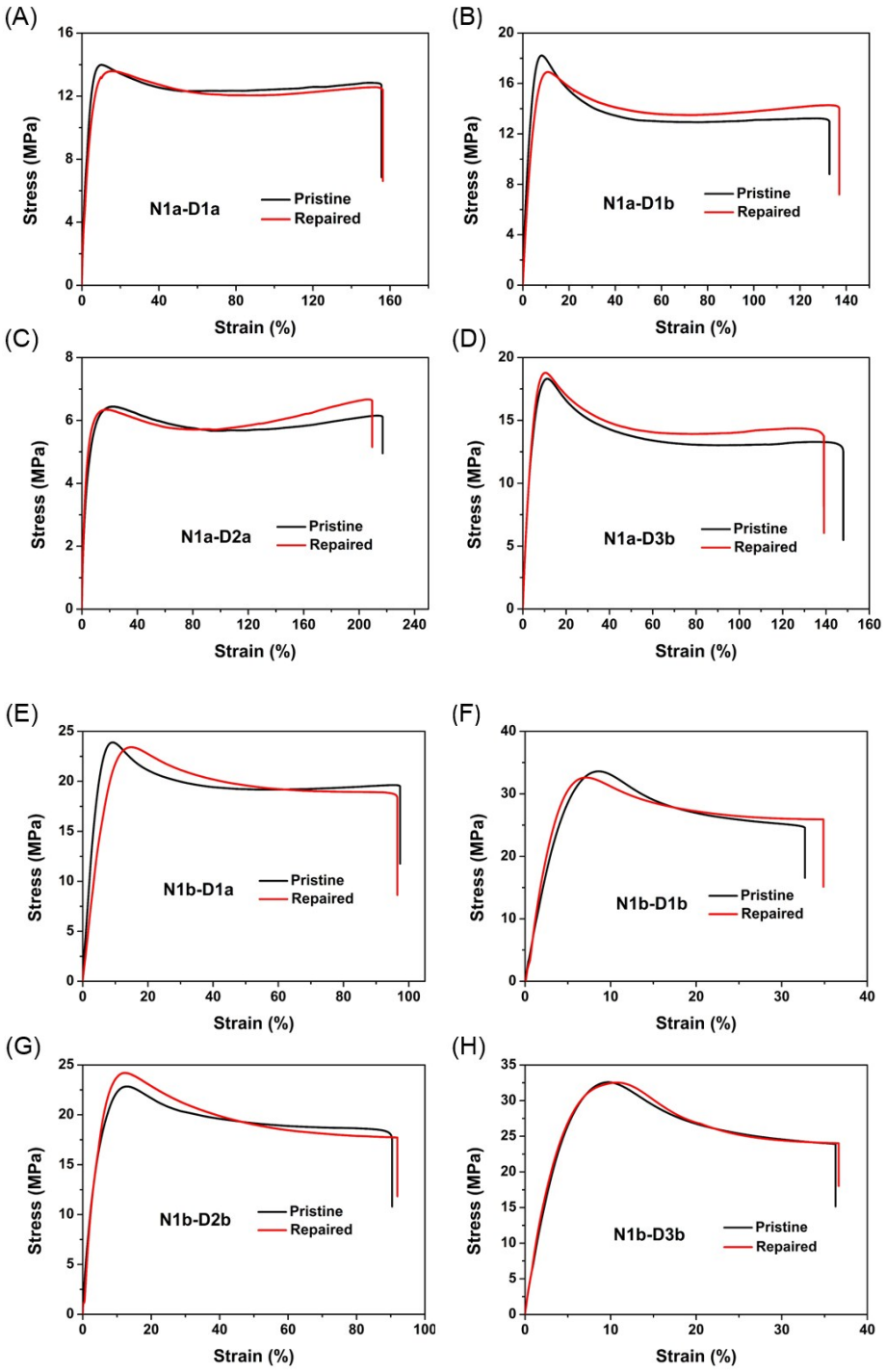

Fig. S44 Stress-strain curves of (A-D) **N1a** series networks healed at 120 °C for 8 h and (E-H) **N1b** series networks healed at 120 °C for 12 h. The pristine samples were tested under the same conditions.

Part-VI. Hydrolytic stability tests of crosslinked networks

To evaluate the water absorbability and hydrolytic stability, the crosslinked polymer networks were submerged in deionized water at ambient temperature for 24 h. The changes in mass and mechanical properties were measured after wiping the surface water.

Table S3 Mass of samples before and after submerging in water

	N1a	**N1b**	**N1a-D2a**	**N1a-D2b**	**N1b-D2a**	**N1b-D2b**
Before (g)	0.1089	0.0993	0.0940	0.0865	0.0809	0.1225
After (g)	0.1092	0.0989	0.0943	0.0868	0.0811	0.1222
Δ mass (%)	0.28	-0.40	0.32	0.35	0.25	-0.25

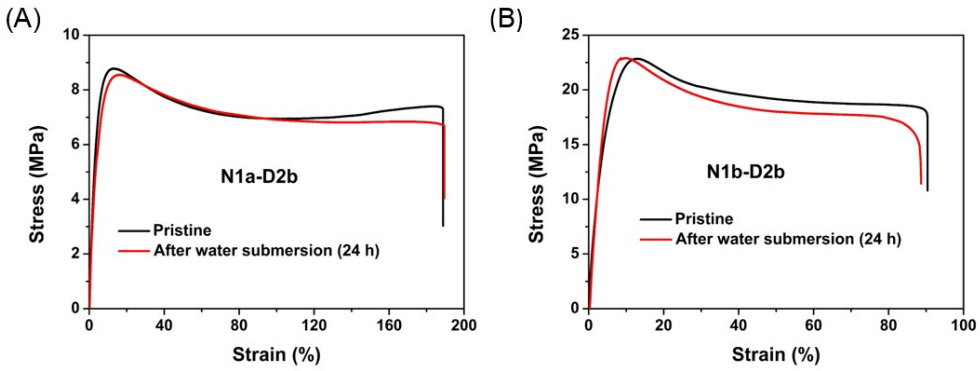

Fig. S45 Stress-strain curves of (A) **N1a-D2b** and (B) **N1b-D2b** before and after submerging in water for 24 h at ambient temperature.