Supporting information

## A self-healing polyurethane elastomer with excellent mechanical property based on phase-locked dynamic imine bonds

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**Figure S1** The stress-strain curves and the sample appearances of PUI samples based on different diisocyanates: HDI for PUI-H; MDI for PUI-M; HMDI for PUI-HM; TDI for PUI-T; IPDI for PUI-IP.



Figure S2 The <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and FTIR spectra of imine-diol.



**Figure S3** The <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and FTIR spectra of bis(2-hydroxylethylthio-)-p-xylene (BHETX).



Figure S5 The <sup>1</sup>H-NMR spectrum of control sample PU-0.



Figure S6 The GPC curves of all the PU samples



Figure S7 the WAXD patterns of all the PU samples



Figure S8 The 2D SAXS patterns of PU-0 (a) and PUI-3 (b)



**Figure S9** Stress-strain curves of PUI-2 and PUI-3 dog-boned films aged 7 days in desiccator or under ambient conditions ( $28 \pm 4^{\circ}C$ ,  $70 \pm 20\%$ RH)



**Figure S10** Optical images of scratch healing processes of different PUI samples at various conditions: (a) PUI-1 healing at 50°C; (b) PUI-3 healing at 50°C; (c) PUI-3 healing at 70°C; (d) PUI-4 healing at 100°C; (e) PU-0 healing at 80°C.



**Figure S11** Temperature sweep curves of PUI-2 (a) and PU-0 (b) at various temperatures, Van Gurp-Palmen-plots of PUI-2 (c) and PU-0 (d) and the constructed master curves of PUI-2 (e) and PU-0 (f) referenced to 50°C.

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Sample	$T_{\rm d}$ (°C)	<i>T</i> <sub>m1</sub> (°C)	<i>T</i> <sub>m2</sub> (°C)
PUI-1	277.4	333.7	408.3
PUI-2	276.8	328.4	406.7
PUI-3	280.0	325.5	409.8
PUI-4	278.0	322.0	419.5
PUI-5	271.1	318.0	432.6
PU-0	294.5	341.2	391.3

Table S1 Thermal properties of all the PU samples measured by TGA

**Table S2** Healing efficiencies of different PUI samples at various temperatures for 2 h of healing

Sample	Temperature (°C)	Healing efficiency of tensile strength $\eta_{\sigma}$ (%)	Healing efficiency of elongation at break $\eta_{e}$ (%)	Healing efficiency of toughness $\eta_W$ (%)
PUI-2	35	58.7	80.0	45.8
PUI-2	50	60.8	78.4	47.7
PUI-2	60	80.4	96.8	74.3
PUI-2	70	95.9	97.7	89.1
PUI-3	35	48.6	65.8	37.7
PUI-3	50	59.6	68.0	46.4
PUI-3	60	65.0	71.3	51.4
PUI-3	70	76.3	82.4	66.2
PUI-3	80	95.9	98.5	94.9
PUI-4	80	36.7	29.3	16.8
PUI-4	100	95.8	98.0	93.9
PU-0	80	91.6	103.3	98.6

Time (min)	Healing efficiency of tensile strength $\eta_{\sigma}$ (%)	Healing efficiency of elongation at break $\eta_{\epsilon}$ (%)	Healing efficiency of toughness η <sub>W</sub> (%)
5	55.2	65.2	42.1
10	62.3	76.4	50.1
20	74.3	84.0	65.1
40	84.9	89.5	79.5
60	89.0	95.1	86.7
120	95.9	98.5	94.9

Table S3 Healing efficiencies of PUI-3 samples at 80°C for different healing time