

Supplementally Material

## **Self- and Cross-fusing of Furan-based Polyurea Gels Dynamically Cross-linked with Maleimides**

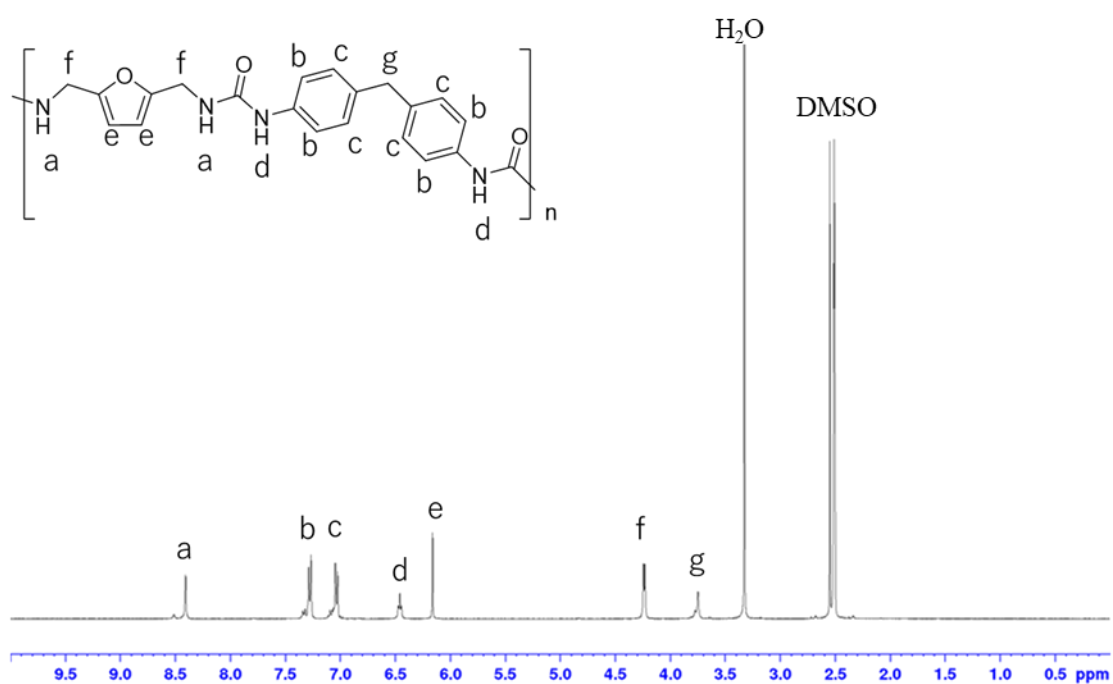
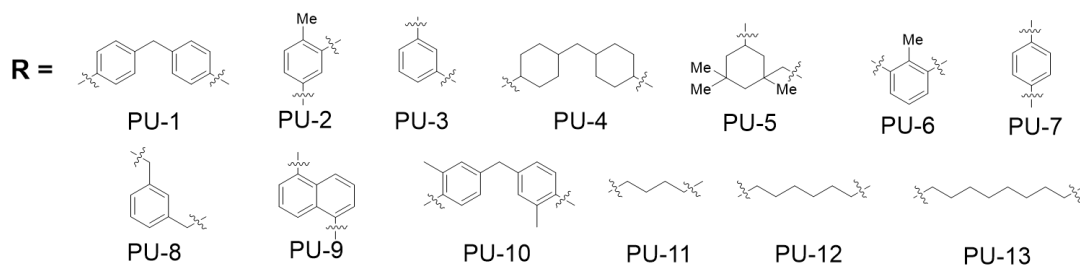
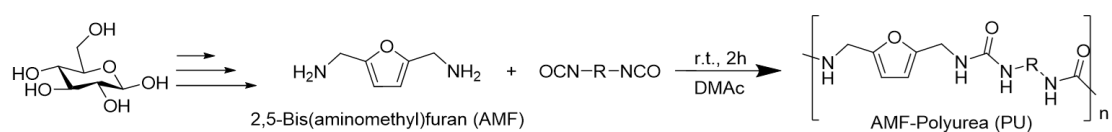
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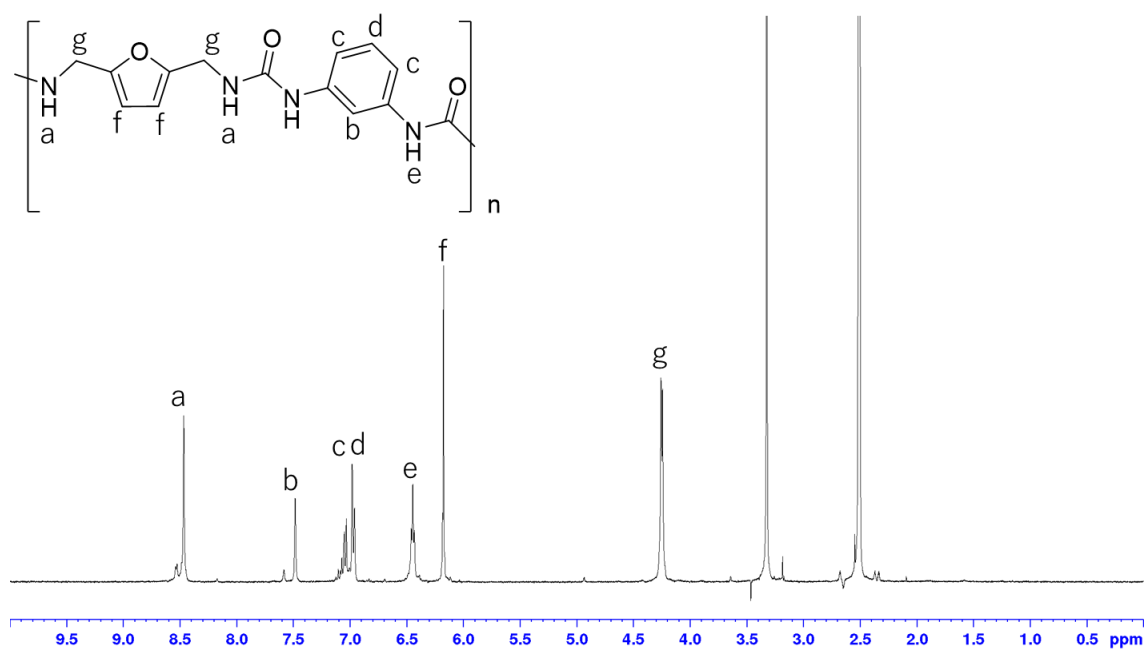
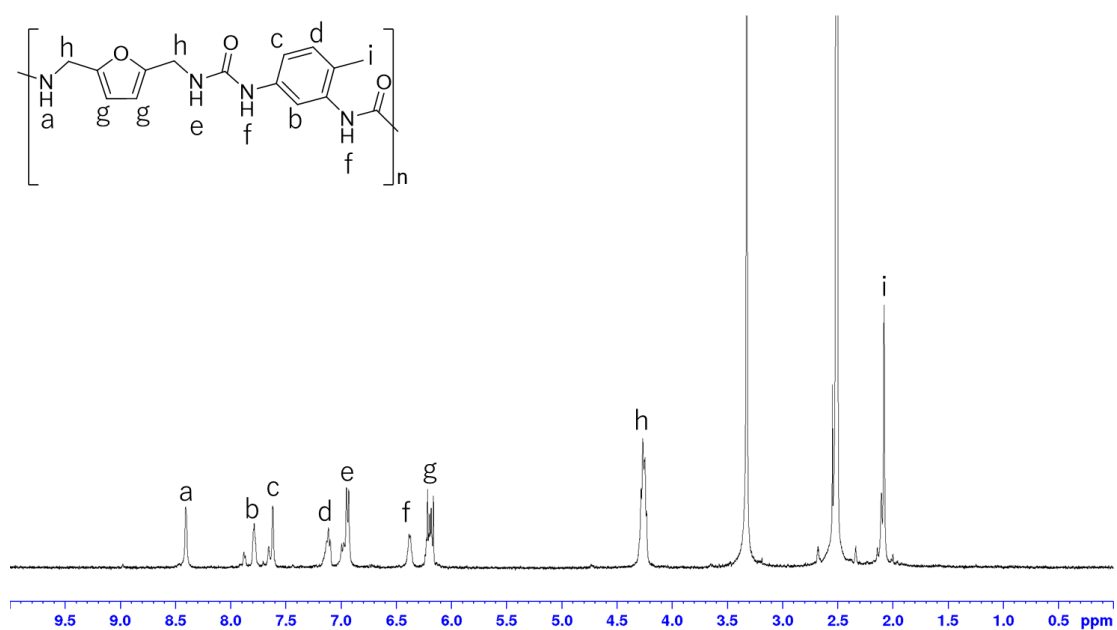
\*Correspondence author

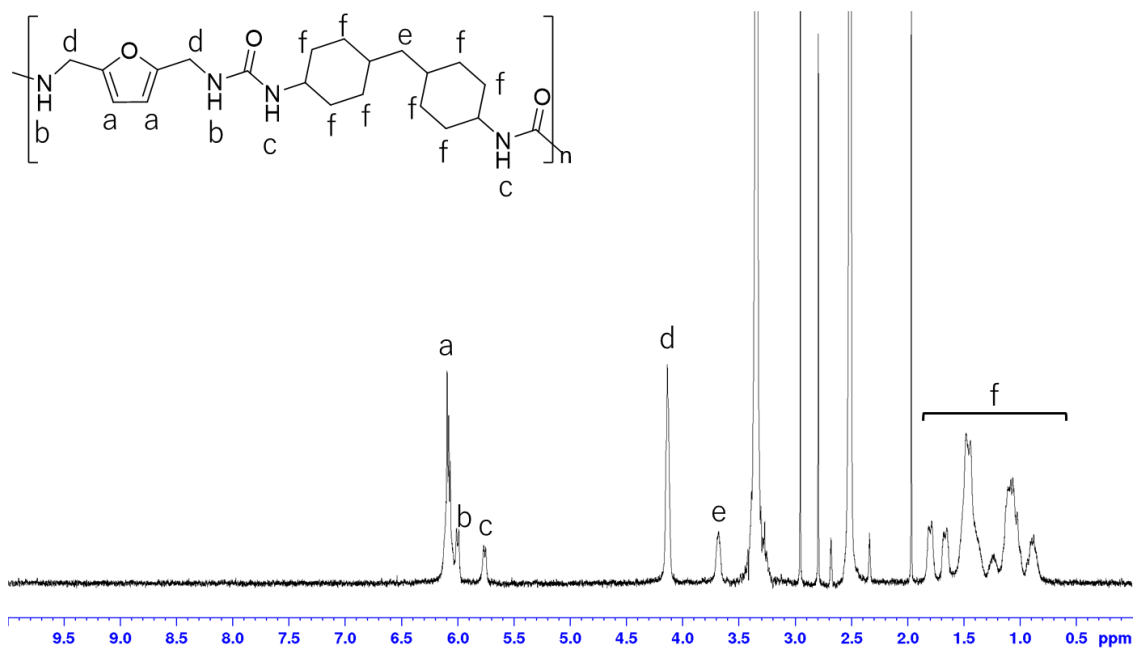
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**Scheme S1.** Syntheses of polyureas from 2,5-bis(aminomethyl)furan and various diisocyanates.

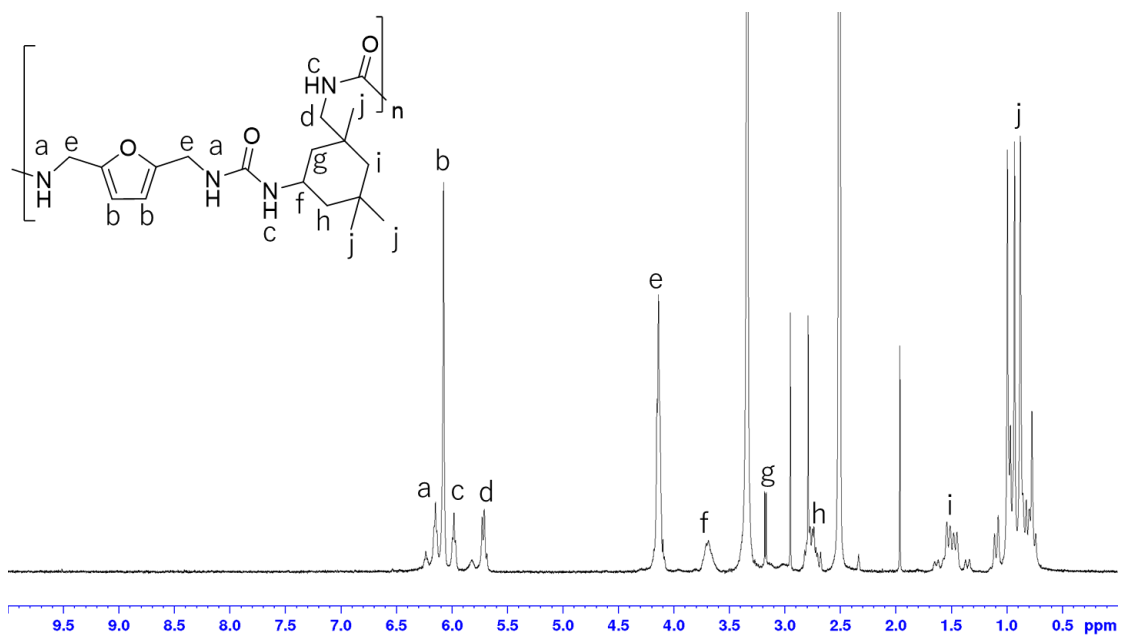


**Figure S1**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ) spectrum of PU-1.

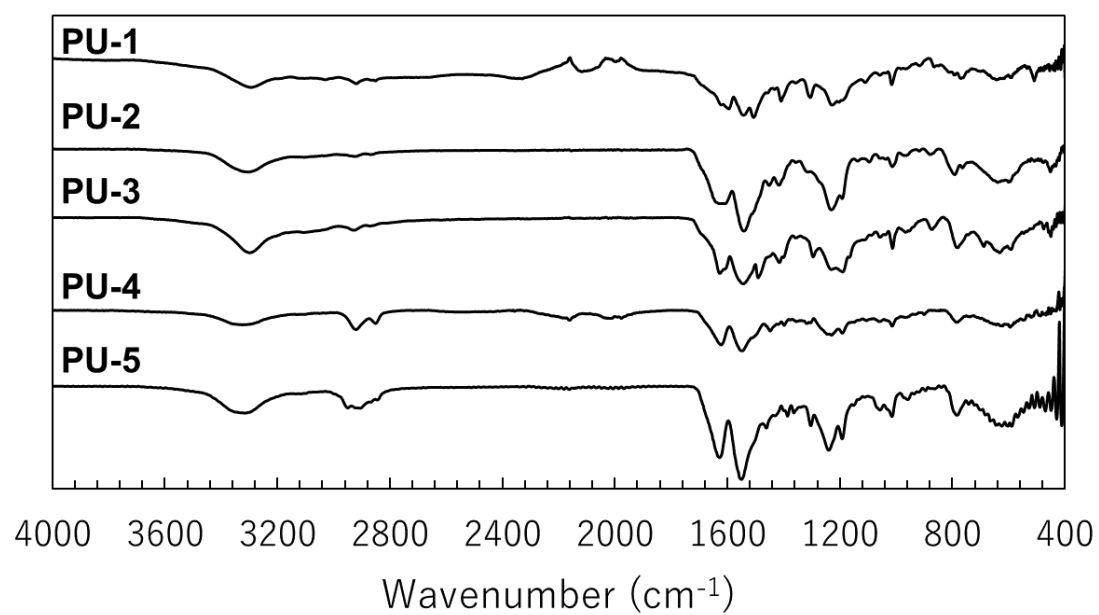




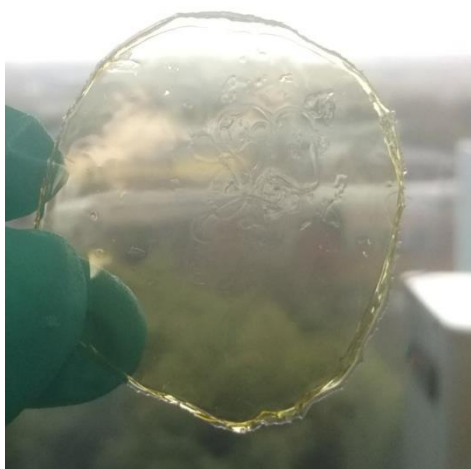
**Figure S4**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ) spectrum of PU-4.



**Figure S5**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ) spectrum of PU-5.



**Figure S6** IR spectra of PU-1 to PU-5 using AMF and various diisocyanates.



**Figure S7** Films of synthesized PU-1 using AMF.

**Table S1** Molecular weight, thermal, mechanical, and optical properties of the obtained PU-1 to 5

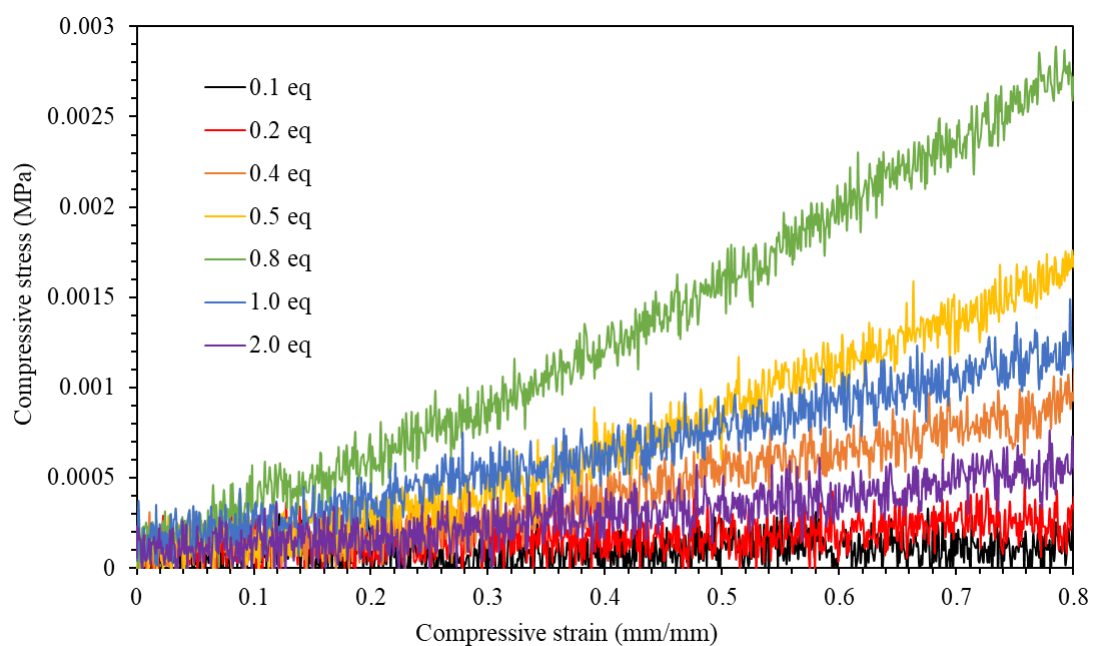
| Polymer | $M_n^a$           | $M_w^a$           | $M_w/M_n^a$ | $T_{d5} / ^\circ\text{C}^b$ | $T_{d10} / ^\circ\text{C}^b$ | $T_g / ^\circ\text{C}^c$ | Strength,<br>$\sigma / \text{MPa}$ | Young's<br>modulus,<br>$E / \text{GPa}$ | Elongation at<br>break,<br>$\varepsilon / \%$ |
|---------|-------------------|-------------------|-------------|-----------------------------|------------------------------|--------------------------|------------------------------------|---|---|
| PU-1    | $7.4 \times 10^3$ | $2.1 \times 10^4$ | 2.84        | 280                         | 290                          | 190                      | 65                                 | 0.8                                     | 8.6   |
| PU-2    | $16 \times 10^3$  | $94 \times 10^4$  | 6.01        | 280                         | 290                          | <i>N.D.</i> <sup>f</sup> | 25                                 | 0.5                                     | 6.8   |
| PU-3    | $8.8 \times 10^3$ | $2.0 \times 10^4$ | 2.39        | 270                         | 285                          | 175                      | 38                                 | 0.7                                     | 8.4   |
| PU-4    | $8.0 \times 10^3$ | $2.0 \times 10^4$ | 2.65        | 310                         | 320                          | 210                      | 16                                 | 0.3                                     | 8.9   |
| PU-5    | $3.0 \times 10^3$ | $1.0 \times 10^4$ | 3.46        | 300                         | 310                          | 205                      | 5                                  | 0.2                                     | 2.7   |

a) Determined by SEC measurement using DMF LiBr solution b) 5 % and 10 % weight loss temperatures,  $T_{d5}$  and  $T_{d10}$ , were obtained from TGA curve scanned at a heating rate of 10  $^\circ\text{C} / \text{min}$  under  $\text{N}_2$  atmosphere. c)  $T_g$  was obtained from DSC curve scanned at a heating rate of 10  $^\circ\text{C} / \text{min}$  under  $\text{N}_2$  atmosphere. d) Not detected

**Table S2** Weight loss temperature and glass-transition temperature of the synthesized PUs using AMF and various diisocyanates.

|       | $T_{d1} (^\circ\text{C})^{(a)}$ | $T_{d5} (^\circ\text{C})^{(a)}$ | $T_{d10} (^\circ\text{C})^{(a)}$ | $T_g (^\circ\text{C})^{(b)}$ |
|-------|---------------------------------|---------------------------------|----------------------------------|------------------------------|
| PU-1  | 250                             | 280                             | 290                              | 190                          |
| PU-2  | 240                             | 280                             | 290                              | <i>N.D.</i> <sup>(c)</sup>   |
| PU-3  | 245                             | 270                             | 285                              | 175                          |
| PU-4  | 290                             | 310                             | 320                              | 210                          |
| PU-5  | 280                             | 300                             | 310                              | 205                          |
| PU-6  | 245                             | 270                             | 280                              | <i>N.D.</i> <sup>(c)</sup>   |
| PU-7  | 250                             | 280                             | 290                              | <i>N.D.</i> <sup>(c)</sup>   |
| PU-8  | 270                             | 295                             | 300                              | 150                          |
| PU-9  | 250                             | 280                             | 295                              | <i>N.D.</i> <sup>(c)</sup>   |
| PU-10 | 255                             | 290                             | 300                              | <i>N.D.</i> <sup>(c)</sup>   |
| PU-11 | 270                             | 290                             | 305                              | 115                          |
| PU-12 | 280                             | 300                             | 310                              | <i>N.D.</i> <sup>(c)</sup>   |
| PU-13 | 275                             | 300                             | 310                              | <i>N.D.</i> <sup>(c)</sup>   |

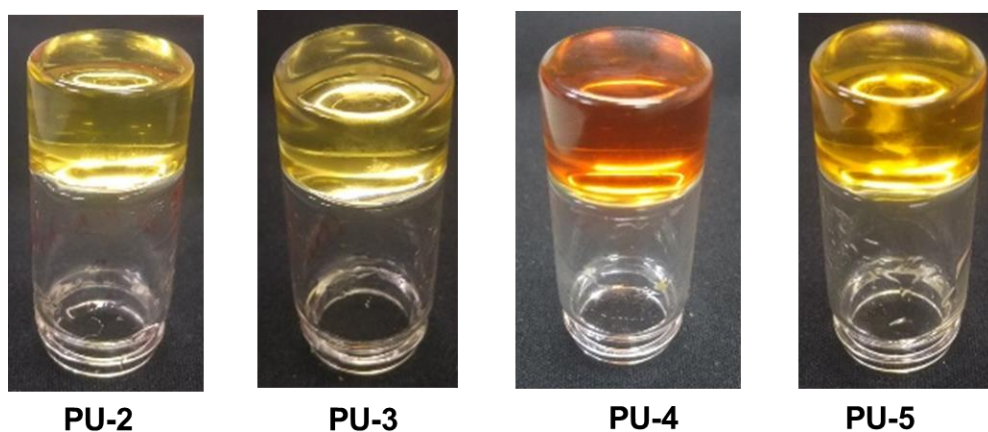
(a) 5 % and 10 % weight loss temperatures,  $T_{d1}$ ,  $T_{d5}$  and  $T_{d10}$ , were obtained from TGA curve scanned at a heating rate of 10  $^\circ\text{C} / \text{min}$  under  $\text{N}_2$  atmosphere. (b)  $T_g$  was obtained from DSC curve scanned at a heating rate of 10  $^\circ\text{C} / \text{min}$  under  $\text{N}_2$  atmosphere. (c) Not detected



**Figure S8** Stress-strain curves of PU-1 gels with different of amount of BMI addition.

**Table S3** Mechanical properties of obtained PU-1 gels

| Amount of<br>BMI(mol%) | Elastic moduli<br>$E_0$ (kPa) |
|------------------------|-------------------------------|
| 0.1                    | $0.12 \pm 0.01$               |
| 0.2                    | $0.18 \pm 0.05$               |
| 0.4                    | $0.73 \pm 0.04$               |
| 0.5                    | $0.72 \pm 0.07$               |
| 0.8                    | $0.78 \pm 0.2$                |
| 1.0                    | $0.51 \pm 0.03$               |
| 2.0                    | $0.18 \pm 0.04$               |



**Figure S9** Photographs of gelation of various PUs

**Table S4** Mechanical properties of obtained polyurea gels and recovery of mechanical properties by DA reaction.

| Amount of BMI(mol%) | Compressive strength, $\sigma$ (kPa) | Compressive strength after self-healing, $\sigma$ (kPa) | Compression strain, $\varepsilon$ (mm/mm) | Compression strain after self-healing, $\varepsilon$ (mm/mm) |
|---------------------|--------------------------------------|---|---|--|
| 10                  | 17.2                                 | 23.2  | 0.9                                       | 0.8  |
| 50                  | 39.4                                 | 60.5  | 0.6                                       | 0.6  |
| 80                  | 23.9                                 | 15.5  | 0.5                                       | 0.4  |
| 100                 | 33.6                                 | 38.4  | 0.6                                       | 0.6  |