Supporting information

Transparent, Self-Recoverable, Highly Tough, Puncture and Tear Resistant Polyurethane Supramolecular with Fast Self-healing Capacity via "Hard-soft" Hard Domain Design

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Synthesis of 5-(2-hydroxyethyl)-6-methyl-2-aminouracil (HMIC)

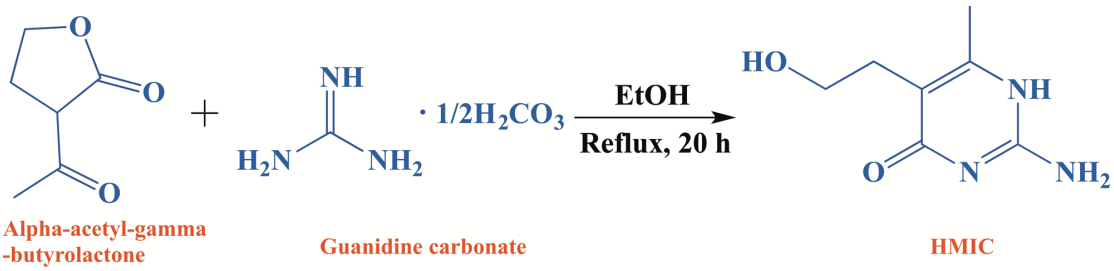

Figure S1. Schematic synthesis route of HMIC

The synthesis process of HMIC was according to a previously study [1]. As shown in Figure S1, a mixture of alpha-acetyl-gamma-butyrolactone (21.51 ml, 0.2 mol) and guanidine carbonate (18.00 g, 0.2 mol) was refluxed in absolute alcohol (200 ml) in the presence of triethylamine (55.34 ml, 0.4 mol) for 20 h. The mixture first became clear, then turned into milk white and finally turned into pale-yellow precipitate suspension. The resulting precipitate was filtered using a Büchner funnel to yield a pale-yellow solid, which was further washed with alcohol for three times. The resulting solid was dissolved in distilled water and then was titrated

with hydrochloric acid to a pH of 7. The neutral suspension was filtered again to yield a white solid, which was further washed with alcohol and distilled water for three times. Finally, the resulting powder was dried under vacuum to obtain HMIC (yield: 40 %). ^{1}H NMR (400 Hz, DMSO): δ 10.79 (s, 1H), 6.32 (s, 2H), 4.53 (t, 1H), 3.35 (d, 2H), 2.44 (t, 2H), 2.06 (s, 3H). FTIR: 3377 cm^{-1} (NH_2), 3117,3043 cm^{-1} (NH), 1641 cm^{-1} (C=O), 1048 cm^{-1} (C-O).

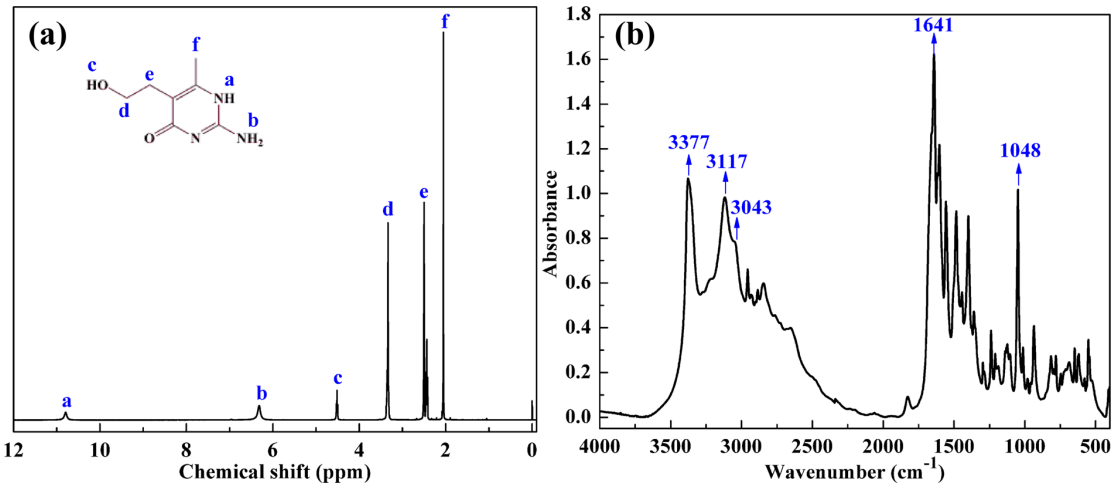

Figure S2. The (a) ^{1}H NMR and (b) FTIR spectra of HMIC

Synthesis of 3-(3-(tert-butyl)-4-hydroxy-5-methylphenyl)propanoic acid (AC)

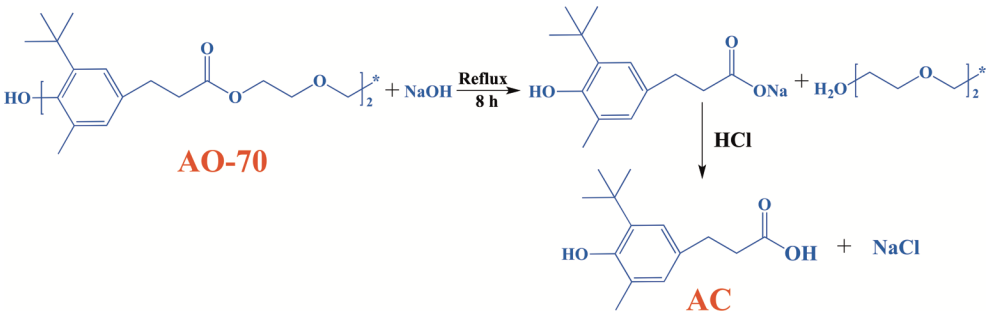

Figure S3. Schematic synthesis route of AC

The synthesis process of AC was according to our previous work [2]. As shown in Figure S3, a mixture of AO-70 (176.04 g, 0.3 mol) and NaOH (96 g, 2.4 mol) was refluxed in distilled water (800 ml) for 8 h under nitrogen atmosphere. The mixture became a yellow solution along with the reaction proceeded. The resulting yellow solution was first extracted with dichloromethane (25 ml) for two times, then was titrated with hydrochloric acid to a pH of 3, which resulted in a white precipitate suspension. After stewing overnight, the resulting precipitate was filtered using a Büchner funnel to yield a white solid, which was further washed with distilled water to a pH of 7. Finally, the resulting powder was dried in oven to obtain AC (yield: 95 %).^{1}H NMR (400 Hz, $CDCl_3$): δ 6.97 (d, 1H), 6.85 (d, 1H), 4.66 (s, 1H), 2.86 (t, 2H), 2.64 (t, 2H), 2.23 (s, 3H), 1.40 (s, 9H). FTIR: 3543 cm^{-1} (Ph-OH), 3117,1694 cm^{-1} (C=O).

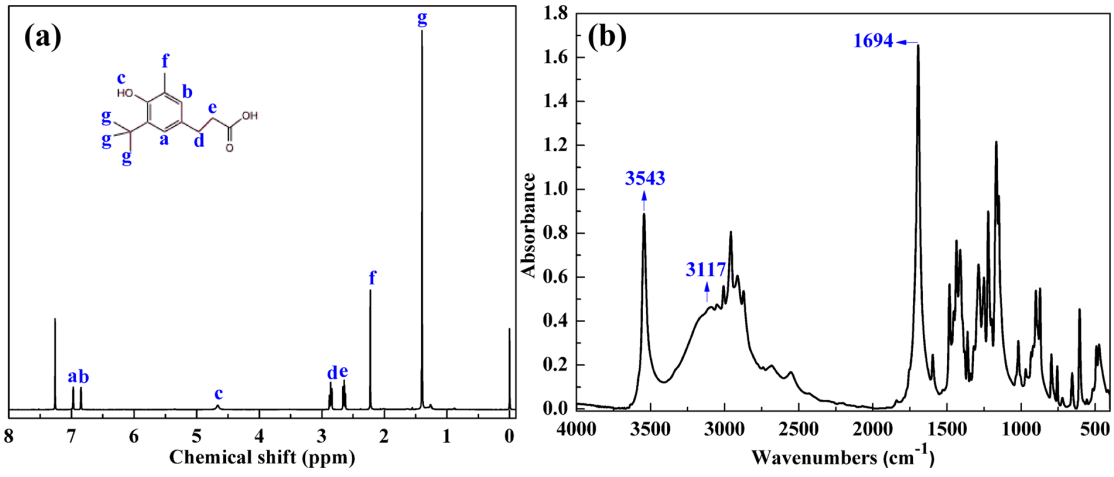

Figure S4. The (a) ^{1}H NMR and (b) FTIR spectra of AC

Synthesis of 3-(allyloxy)propyl 3-(3-(tert-butyl)-4-hydroxy-5-

methylphenyl)propanoate (ES)

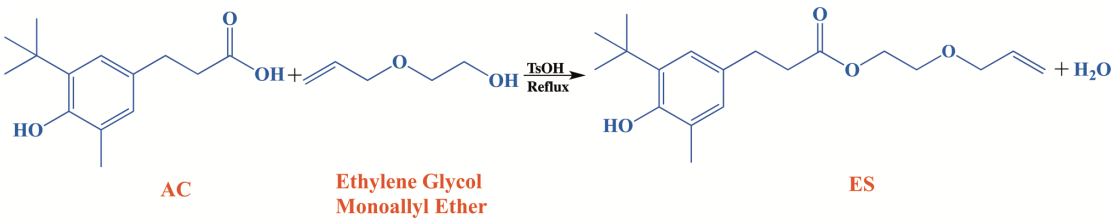

Figure S5. Schematic synthesis route of ES

The synthesis process of ES was shown in Figure S5. A mixture of AC (64.9 g, 0.275 mol) and ethylene glycol monoallyl ether (26. 74 ml, 0.25 mol) was refluxed in cyclohexane (150 ml) with P-toluenesulfonic acid (0.5 g, 2 wt% of ethylene glycol monoallyl ether) as catalyzer for 8 h under nitrogen atmosphere. The product water was removed through the water separator. The resulting solution was washed with saturated sodium bicarbonate aqueous solution for three times, then the cyclohexane was removed through the rotary evaporation, which resulted in an oily product. After stewing at room temperature for 2 days, the oily product turned into solid, i.e. ES (yield: 90 %). ^{1}H NMR (400 Hz, DMSO): δ 7.86 (s, 1H), 6.83 (d, 1H), 6.77 (d, 1H), 5.86 (ddt, 1H), 5.24 (dq, 1H), 5.14 (m, 1H), 4.12 (dd, 2H), 3.94 (dd, 2H), 3.55 (dd, 2H), 2.70 (t, 2H), 2.55 (t, 2H), 2.13 (s, 3H), 1.33 (s, 9H). FTIR: 3471 cm^{-1} (OH), 1735 cm^{-1} (C=O), 1648 cm^{-1} (C=C), 1176, 1045, 929 cm^{-1} (C-O-C).

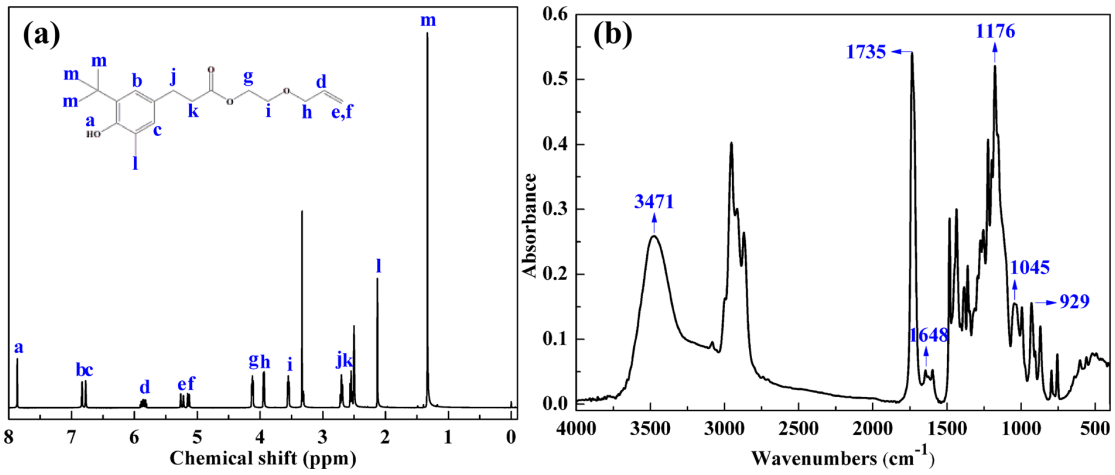

Figure S6. The (a) ^{1}H NMR and (b) FTIR spectra of ES

Synthesis of 3-(2-((2,3-dihydroxypropyl)thio)ethoxy)propyl 3-(3-(tert-butyl)-4-hydroxy-5-methylphenyl)propanoate (GL)

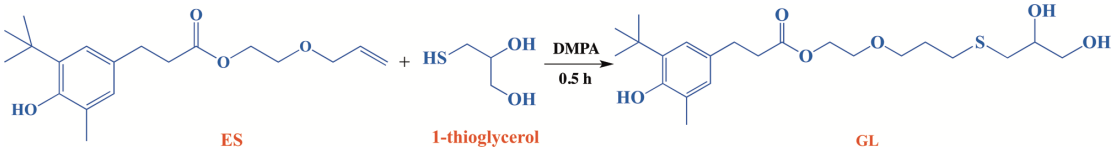

Figure S7. Schematic synthesis route of GL

The synthesis process of GL was shown in Figure S7. ES (16 g, 0.05 mol) and 2,2-dimethoxy-2-phenylacetophenone (0.08 g, 0.5 wt% of ES) was added into a quartz flask with tetrahydrofuran (40 ml). After injecting nitrogen for 10 min, 1-thioglycerol (5.19 ml, 0.06 mol) was added into the flask and the solution was irradiated by UV light at 365 nm for 0.5 h. After the irradiation, the tetrahydrofuran was removed through the rotary evaporation. The resulting oil was dissolved again in dichloromethane (10 ml) and was washed with distilled water for five times. Then anhydrous sodium sulfate was added into the dichloromethane solution. After stewing

for 24 h, the solvent was removed through the rotary evaporation and resulting an oily product, i.e. GL (yield: 92 %). ^{1}H NMR (400 Hz, $CDCl_3$): δ 6.96 (m, 1H), 6.84 (d, 1H), 5.11 (s, 1H), 4.24 (dd, 2H), 3.77 (m, 1H), 3.64 (m, 2H), 3.57 (m, 2H), 3.54 (d, 2H), 2.86 (t, 2H), 2.65 (m, 6H), 2.22 (s, 3H), 1.86 (t, 2H), 1.41 (s, 9H). FTIR: 3438 cm^{-1} (OH), 1732 cm^{-1} (C=O), 1177 cm^{-1} (C-O-C), 1034 cm^{-1} (C-S-C).

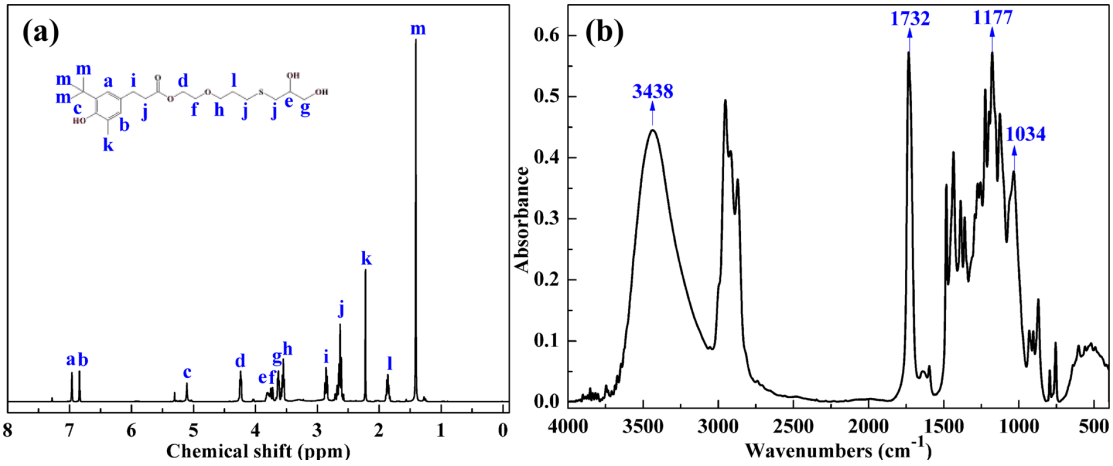

Figure S8. The (a) ^{1}H NMR and (b) FTIR spectra of GL

Synthesis of 2-Amino4-hydroxy-6-methylpyrimidine (MIC)

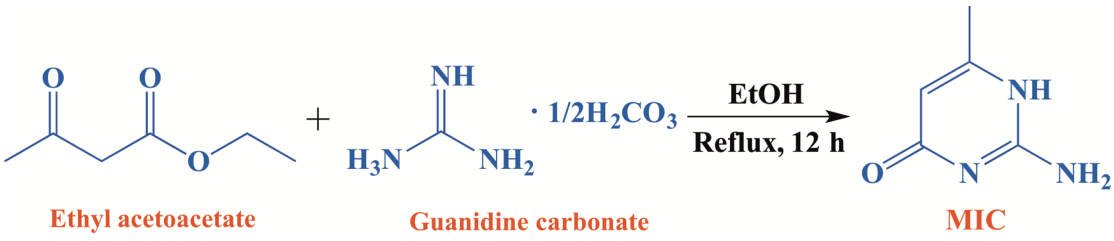

Figure S9. Schematic synthesis route of MIC

The synthesis process of MIC was according to a previously study [3]. As shown in Figure S9, a mixture of ethyl acetoacetate (31.58 ml, 0.25 mol) and guanidine carbonate (18.00 g, 0.2 mol) was refluxed in absolute alcohol (250 ml) for 12 h under nitrogen atmosphere. The mixture turned

into white precipitate suspension along with the reaction proceeded. The resulting precipitate was filtered using a Büchner funnel to yield a white solid, which was further washed with alcohol, distilled water and acetone for two times. Finally, the resulting powder was dried under vacuum to obtain MIC (yield: 85 %). ^{1}H NMR (400 Hz, DMSO): δ 10.71 (s, 1H), 6.49 (s, 2H), 5.39 (s, 1H), 1.98 (s, 3H). FTIR: 3333 cm^{-1} (NH_2), 3072,2946 cm^{-1} (CH_3), 1664 cm^{-1} (C=O), 1497 cm^{-1} (NH).

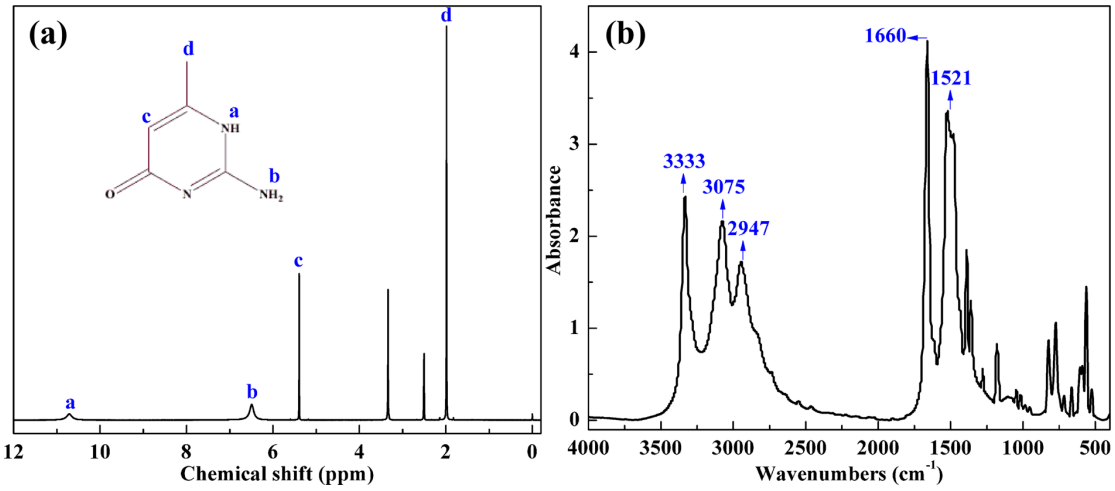

Figure S10. The (a) ^{1}H NMR and (b) FTIR spectra of MIC

Synthesis of 2-(6-isocyanato-hexylamino)-6-methyl-4[1H]-pyrimidone (UPy)

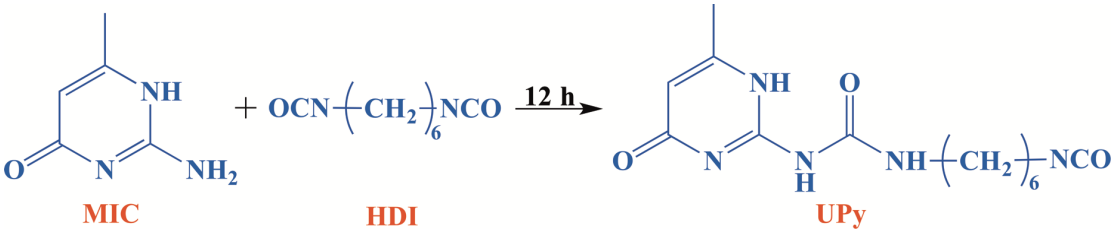

Figure S11. Schematic synthesis route of UPy

The synthesis process of UPy was according to a previously study [3]. As shown in Figure S11, a mixture of MIC (5.82 g, 0.046 mol) and hexamethylene diisocyanate (51.95 ml, 0.32 mol) was refluxed for 12 h under nitrogen atmosphere. The resulting precipitate was filtered using a Büchner funnel to yield a white solid, which was further washed with petroleum ether for a few times. Finally, the resulting powder was dried under vacuum to obtain UPy (yield: 94 %). ^{1}H NMR (400 Hz, $CDCl_3$): δ 13.11 (s, 1H), 11.86 (s, 1H), 10.17 (s, 1H), 5.82 (s, 1H), 3.27 (ddd, 4H), 2.23 (s, 3H), 1.63, 1.40 (m, dp, 8H). FTIR: without 3333 cm^{-1} (NH_2), 2280 cm^{-1} (NCO), 1700 cm^{-1} (new C=O), 1583 cm^{-1} (amide Ⅱ).

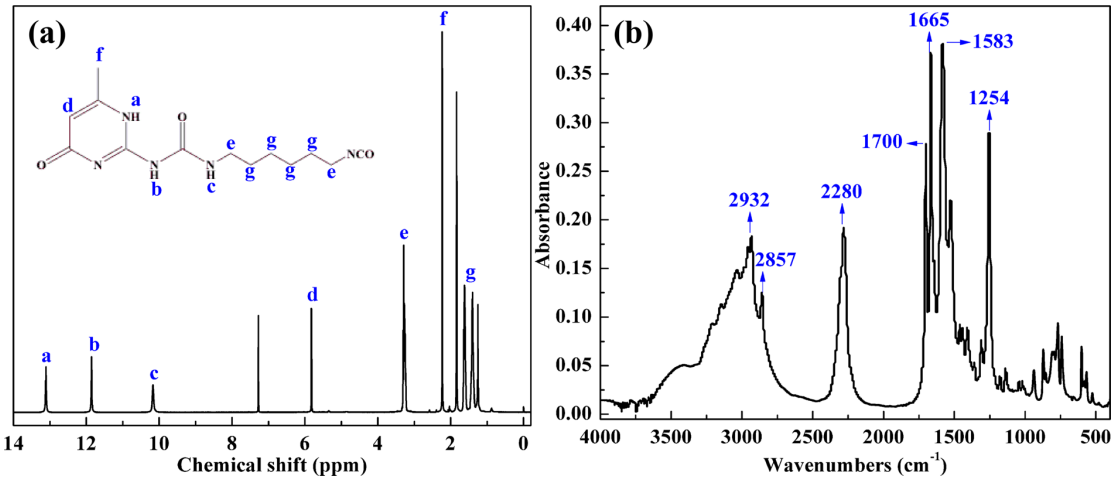

Figure S12. The (a) ^{1}H NMR and (b) FTIR spectra of UPy

Preparation of MWCNTs-UPy

The preparation process of MWCNTs-UPy was according to a previously study [4]. A mixture of MWCNTS-OH (1.009 g, 0.0018 mol) and UPy (1.021 g, 0.0036 mol) with DBTDL (1 drop) as catalyzer was heated at 80 ℃

for 6 h under nitrogen atmosphere. The resulting precipitate was filtered using a Büchner funnel to yield a solid, which was further washed with DMF and dichloromethane for three times. Finally, the resulting powder was dried under vacuum to obtain MWCNTs-UPy.

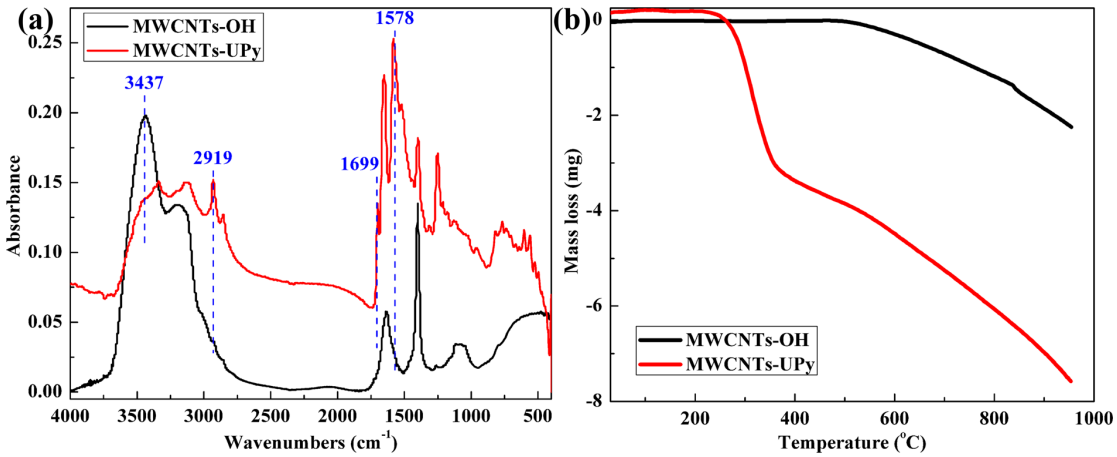

Figure S13. The (a) FTIR and (b) TGA spectra of MWCNTs-OH and MWCNTs-UPy

In Figure S13 (a), the disappearance of 3437 cm^{-1} (OH) peak and the appearance of 2919 (CH_2), 1699 (C=O) and 1578 cm^{-1} (amide Ⅱ) peak in MWCNTs-UPy compared with MWCNTs-OH, indicated the successful modification of MWCNTs. In Figure S13 (b), the weight loss of MWCNT-UPy from 200 ºC to 1000 ºC was attributed to the decomposition of ureidopyrimidinone and ureido groups.

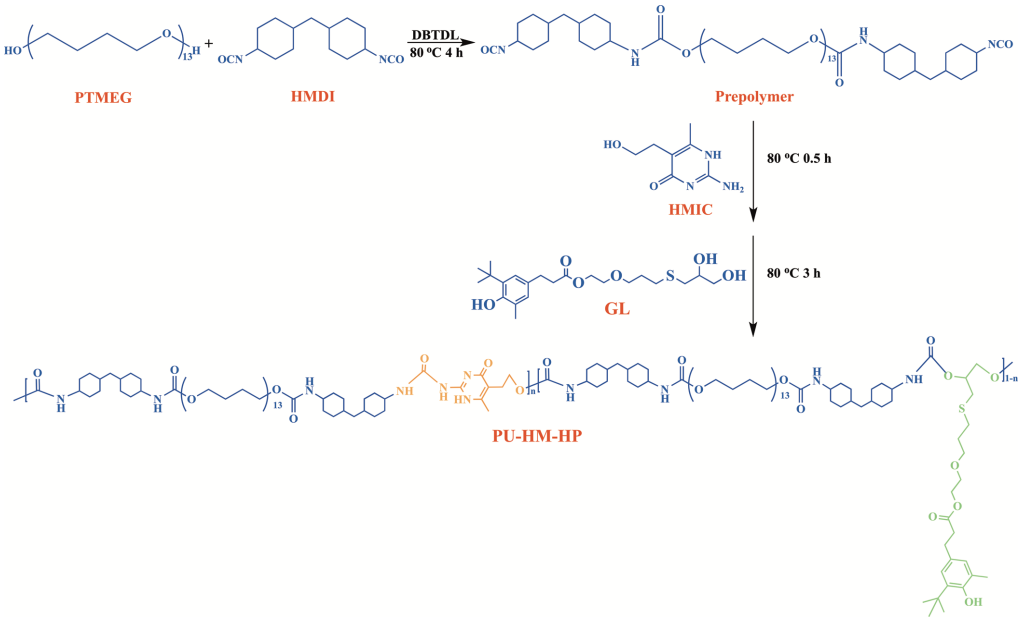

Figure S14. Schematic synthesis route of PU-HM-HP

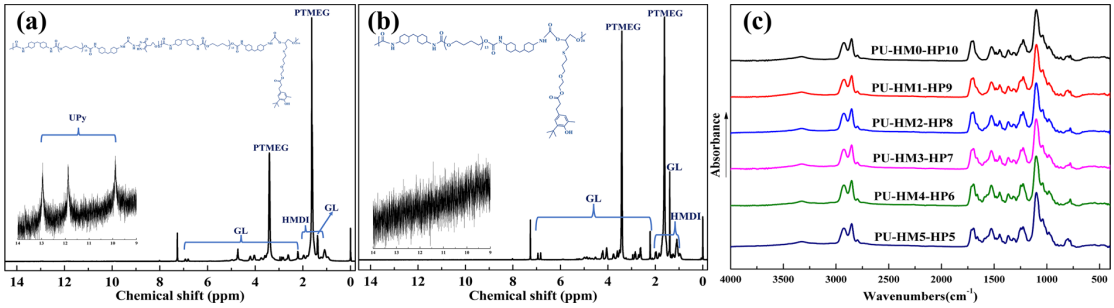

Figure S15. (a) the ^{1}H NMR spectra of PU-HM4-HP6, (b) the ^{1}H NMR spectra of PU-HM0-HP10 and (c) the FTIR spectra of PU-HM-HP

Table S1. The assignment of the FTIR investigation of PU-HM-HP

Wavenumber (cm^{-1})	**Assignment**
3442	H-bond *v* (OH)
3328	H-bond *v* (NH)
2926	v_a (CH_2)

2852	ν_s (CH_2)
1716	Free ν (C=O) urethane amide I
1695	H-bond ν (C=O) urethane amide I
1528	H-bond ν (C-N) + δ (N-H) amide II
1444	Free ν (C-N) + δ (N-H) amide II
1365	w (C-H) in CH_2
1226	ν (C-N) + δ (N-H) amide III
1100	ν (C-O-C)

subscript a = antisymmetric, subscript s = symmetric

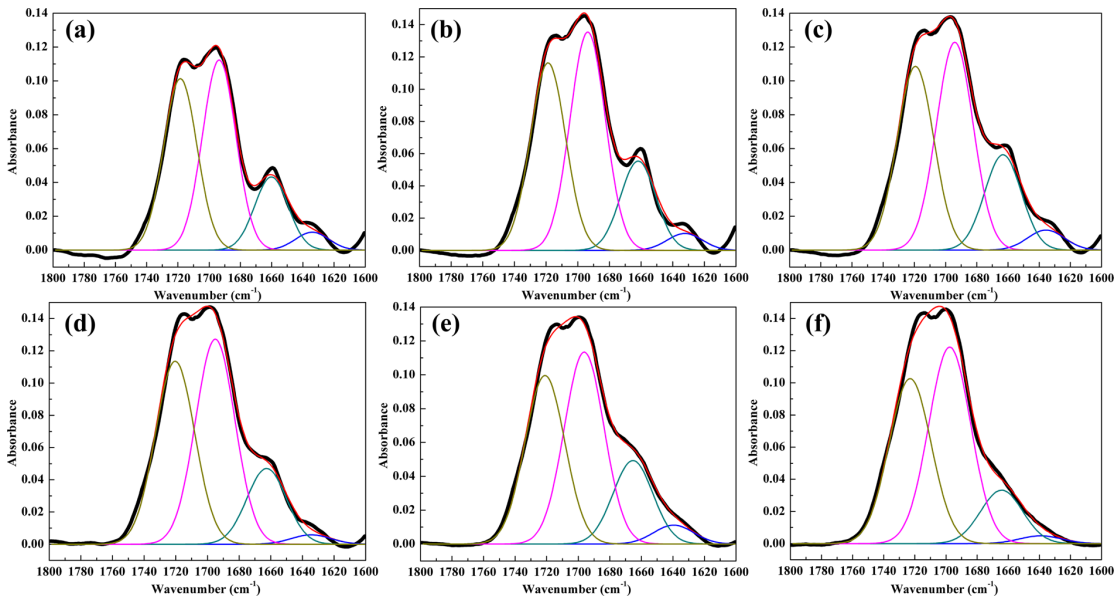

Figure S16. Peak fitting curves in the 1600-1800 cm^{-1} region: (a) PU-HM5-HP5, (b) PU-HM4-HP6, (c) PU-HM3-HP7, (d) PU-HM2-HP8, (e) PU-HM1-HP9 and (f) PU-HM0-HP10

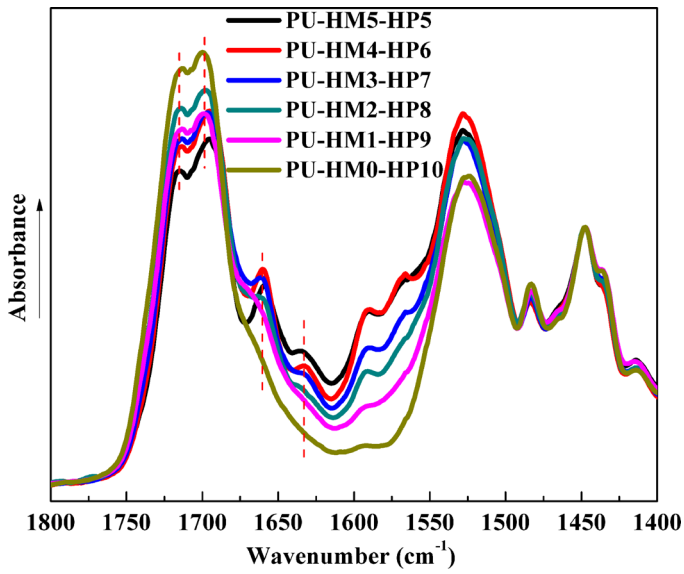

Figure S17. FTIR spectra of different PU samples, and the absorbance is normalized according to the peak height at 1447 cm^{-1} ($\delta_a(CH_2)$)

Figure S18. Optical images of PU-HM4-HP6 that can recover its original length after being stretched to 650 % strain

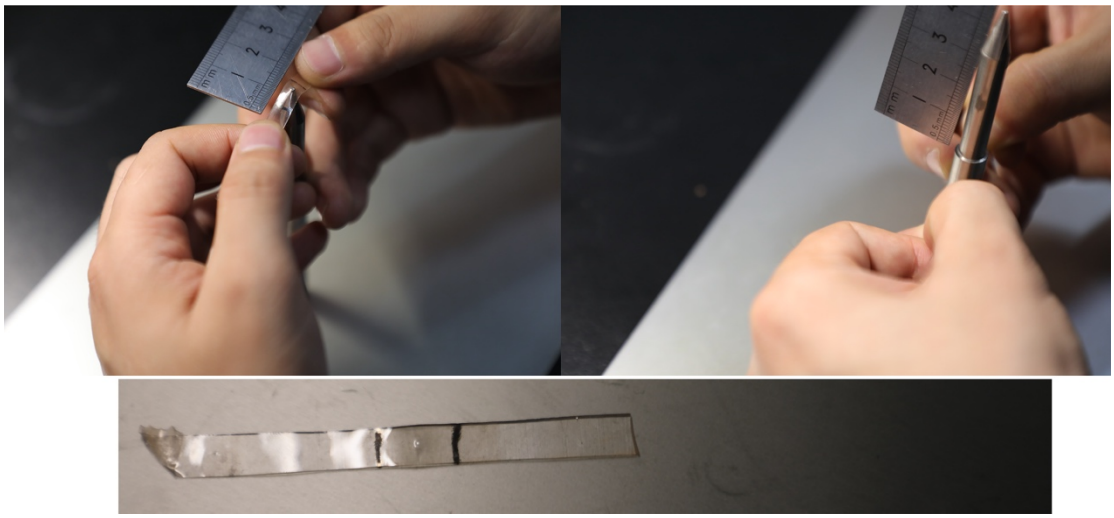

Figure S19. Optical images of PU-HM4-HP6 that can tolerate puncture

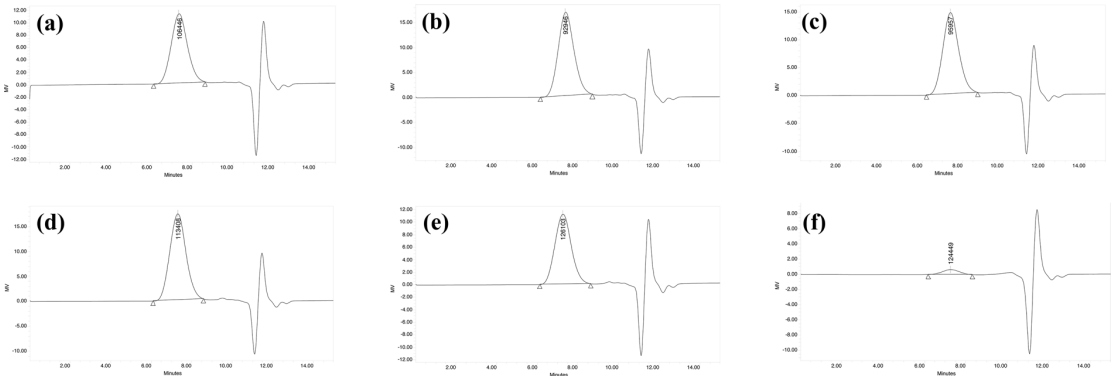

Figure S20. GPC curves of the elastomers: (a) PU-HM5-HP5, (b) PU-HM4-HP6, (c) PU-HM3-HP7, (d) PU-HM2-HP8, (e) PU-HM1-HP9 and (f) PU-HM0-HP10

Table S2. The number-average molecular weight, weight-average molecular weight and polydispersity indexes of PU-HM-HP elastomers

Sample name	Mn (Daltons)	Mw (Daltons)	Polydispersity
PU-HM5-HP5	72787	144307	1.982601
PU-HM4-HP6	61534	120120	1.952097

PU-HM3-HP7	63500	125813	1.981293
PU-HM2-HP8	78465	155829	1.985958
PU-HM1-HP9	85341	172490	2.021174
PU-HM0-HP10	91599	182223	1.989358

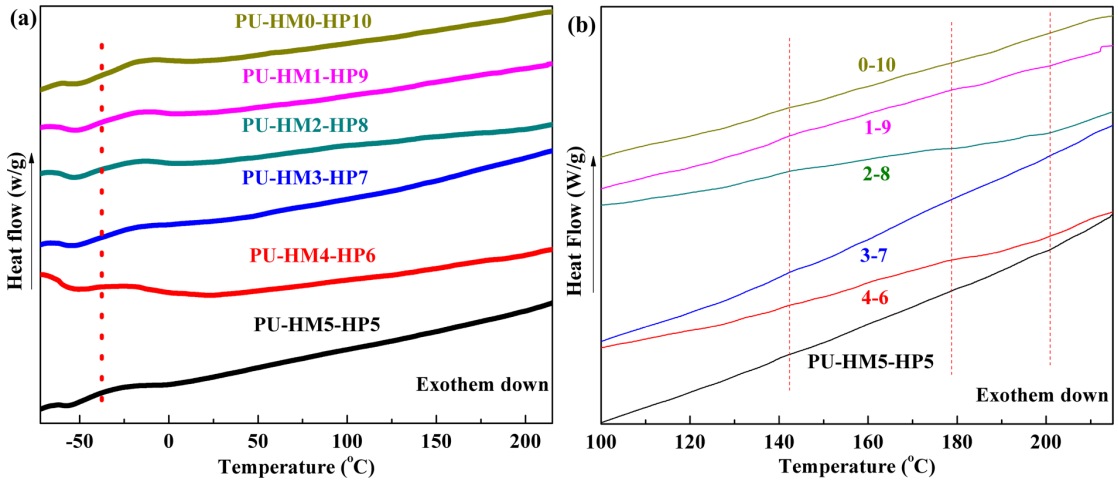

Figure S21. DSC curves of PU-HM-HP elastomers

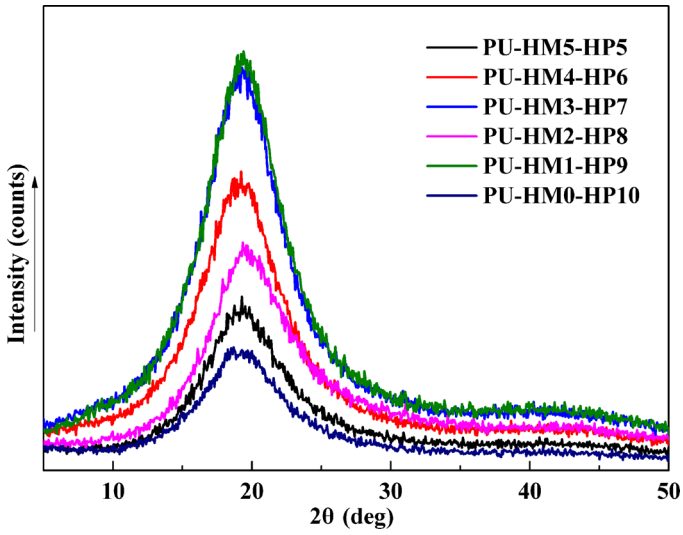

Figure S22. XRD curves of PU-HM-HP elastomers

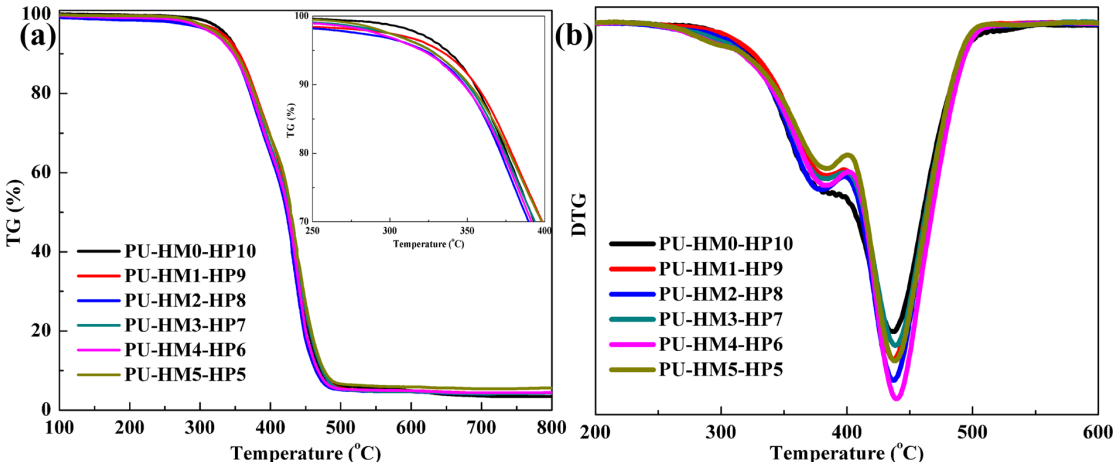

Figure S23. (a) TG and (b) DTG curves of PU-HM-HP elastomers

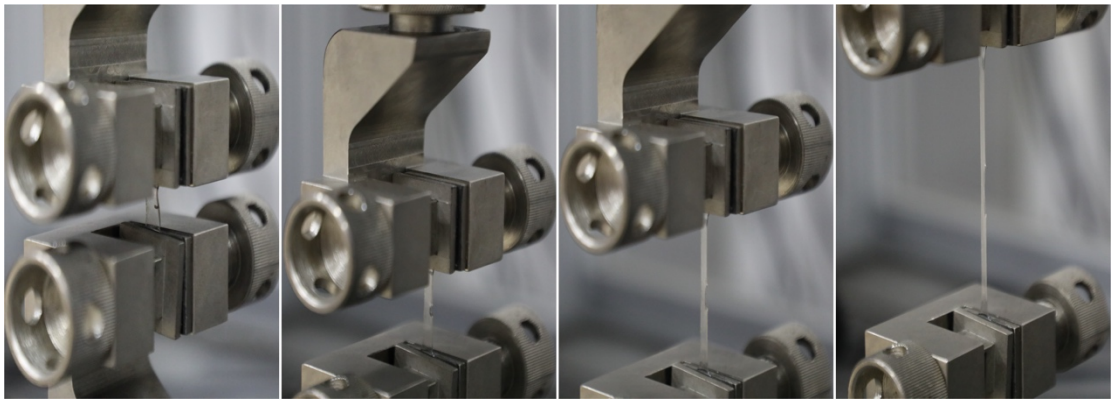

Figure S24. Optical images of the single-edge-notched PU-HM4-HP6 sample from 0 % to 800 % strain

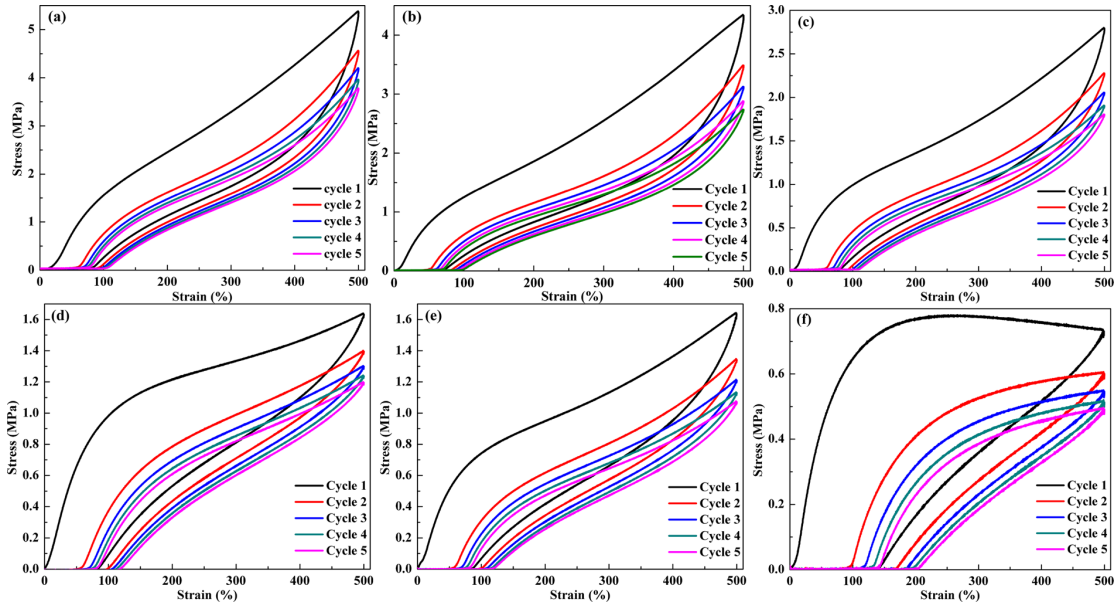

Figure S25. Five successive loading-unloading process with a strain of 500 % in every cycle of PU-HM-HP elastomers: (a) PU-HM5-HP5, (b) PU-HM4-HP6, (c) PU-HM3-HP7, (d) PU-HM2-HP8, (e) PU-HM1-HP9 and (f) PU-HM0-HP10

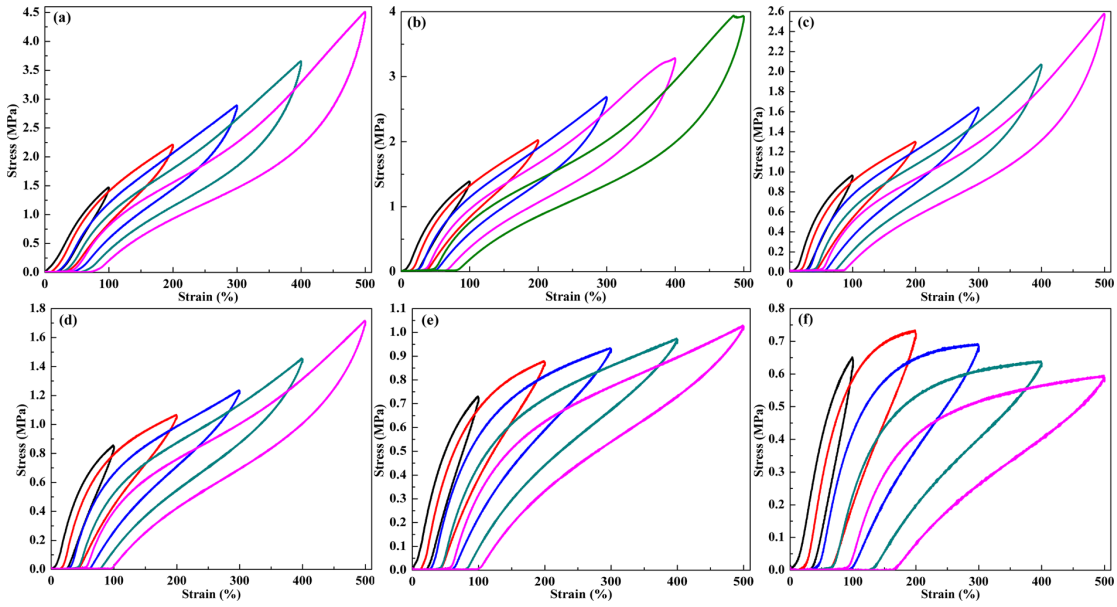

Figure S26. Loading-unloading process under 100 % to 500 % strains of PU-HM-HP elastomers: (a) PU-HM5-HP5, (b) PU-HM4-HP6, (c) PU-

HM3-HP7, (d) PU-HM2-HP8, (e) PU-HM1-HP9 and (f) PU-HM0-HP10

Supporting References

[1] F. Wang, Z. Yang, J. Li, C. Zhang and P. Sun, *ACS Macro Lett.,* 2021, **10**, 510-517.

[2] K. Xu, Q. Hu, J. Wang, H. Zhou and J. Chen, *Polymers,* 2019, **11**, 884.

[3] J. Hu, R. Mo, X. Jiang, X. Sheng and X. Zhang, *Polymer,* 2019, **183**, 121912.

[4] X. Dai, L. B. Huang, Y. Du, J. Han, Q. Zheng, J. Kong and J. Hao, *Adv. Funct. Mater.,* 2020, **30**, 1910723.