Supporting Information

Self-Healing Polymers with PEG Oligomer Side Chains Based on Multiple H-Bonding and Adhesion Properties

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PHEA-UPy, b) $PPEG_{360}$-UPy and c) $PPEG_{500}$-UPy copolymers.

Table S1. Summary of polar and dispersion components of SEs of the prepared copolymers.

Synthesis

Synthesis of RAFT agent 2-(((dodecylthio)carbonothioyl)thio)-2-methylpropanoic acid (C_{12}TTC)

The RAFT agent C_{12}TTC was synthesized according to previously published work.[1] ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 0.86 (t, 3H, CH_3), 1.37-1.20 (m, 20H, CH_2), 1.62 (s, 6H, CH_3), 3.30 (t, 2H, SCH_2), 12.95 (s, 1H, COOH). ^{13}C NMR (101 MHz, DMSO-d6, δppm): 173.6, 56.7, 36.6, 31.8, 29.5, 29.4, 29.3, 29.2, 28.9, 28.6, 27.9, 25.5, 22.6, 14.4.

Synthesis of monomer 2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)ethyl acrylate (MAUPy)

6-Methylisocytosine (MIS, 3.0 g, 24.0 mmol) was added to 100 mL of DMSO and heated up to 170 °C under nitrogen atmosphere. Once the MIS dissolved, the oil bath was removed. 2-Isocyanatoethyl methacrylate (4.15 g, 26.6 mmol) was added immediately to the flask under vigorous stirring. The mixture was then quickly cooled to room temperature using a water bath. A fine white solid precipitated upon cooling. The precipitate was collected and washed with excess chilled acetone and dried under vacuum to obtain 5.7 g of a white solid (yield 86%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.95 (s, 3H, CH_3), 2.26 (s, 3H, ArCH_3), 3.58-3.62 (m, 2H, NHCH_2), 4.28-4.30 (t, 2H, OCH_2), 5.57 (s, 1H, C=CH_2), 5.81 (s, 1H, Ar-*H*), 6.20(s, 1H, C=CH_2), 10.50 (s, 1H, N*H*), 11.99 (s, 1H, N*H*), 13.01 (s, 1H, N*H*). ^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): 172.8, 167.3, 156.8, 154.5, 148.3, 136.1, 125.8, 106.8, 63.1, 38.8, 19.0, 18.3.

Synthesis of PHEA-UPy

HEA (2.0 g, 17.2 mmol), MAUPy (0.509 g, 2.0 mmol), N, N'-methylenediacrylamide (0.123g, 0.8 mmol), and RAFT agent C_{12}TTC (73 mg, 0.2 mmol) were added into a double-necked flask. AIBN (10 mg, 0.06 mmol) was used as free radical initiator and then added into the flask. 70 mL of DMSO was added to dissolve all the agents. Then the mixture was degased and fulfilled with nitrogen for three times and then stirred under 70 ℃ for three days. Most DMSO was removed by reduced pressure distillation. Then the remained mixture was dialyzed against deionized water for one day. After dried over 50 ℃, the cross-linked polymer **PHEA-UPy** was obtained.

Synthesis of $PPEG_{360}$-UPy

Poly(ethylene glycol) methacrylate (Mn = 360, PEG_{360}MA, 3.1 g, 8.6 mmol), MAUPy (0.254 g, 1 mmol), N, N'-methylenediacrylamide (62mg, 0.4 mmol), and RAFT agent C_{12}TTC(37 mg, 0.1 mmol) were added into a double-necked flask. AIBN (5 g, 0.03 mmol) was used as free radical initiator and then added into the flask. 80 mL of DMSO was added to dissolve all the agents. Then the mixture was degased and fulfilled with nitrogen for three times and then stirred under 70 ℃ for three days. Most DMSO was removed by reduced pressure distillation. Then the remained mixture was dialyzed against deionized water for one day. After dried under 50 ℃, the cross-linked polymer **$PPEG_{360}$-UPy** was obtained.

Synthesis of $PPEG_{500}$-UPy

Poly(ethylene glycol) methacrylate (Mn = 500, PEG_{500}MA, 4.3 g, 8.6 mmol), MAUPy (0.305 g,

1.0 mmol), N, N'-methylenediacrylamide (62 mg, 0.4 mmol), and RAFT agent C_{12}TTC (37 mg, 0.3 mmol) were added into a double-necked flask. AIBN (5 mg, 0.03 mmol) was used as free radical initiator and then added into the flask. 100 mL of DMSO was added to dissolve all the agents. Then the mixture was degased and fulfilled with nitrogen for three times and then stirred under 70 ℃ for three days. Most DMSO was removed by reduced pressure distillation. Then the remained mixture was dialyzed against deionized water for one day. After dried over 50 ℃, the cross-linked polymer **$PPEG_{500}$-UPy** was obtained.

Synthesis of control polymer $PPEG_{500}$

Poly(ethylene glycol) methacrylate (Mn = 500, $PEG_{500}MA$, 4.3 g, 8.6 mmol), N, N'-methylenediacrylamide (62 mg, 0.4 mmol), and RAFT agent C_{12}TTC (37 mg, 0.3 mmol) were added into a double-necked flask. AIBN (5 mg, 0.03 mmol) was used as free radical initiator and then added into the flask. 100 mL of DMSO was added to dissolve all the agents. Then the mixture was degased and fulfilled with nitrogen for three times and then stirred under 70 ℃ for three days. Most DMSO was removed by reduced pressure distillation. Then the remained mixture was dialyzed against deionized water for one day. After dried over 50 ℃, the control polymer **$PPEG_{500}$** was obtained.

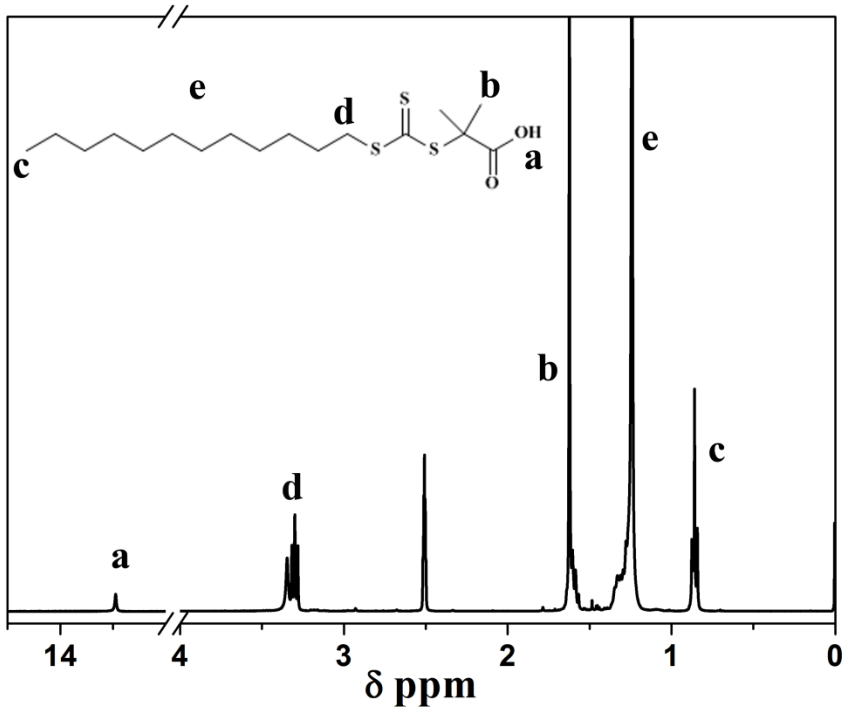

Figure S1. ^{1}H NMR spectra of RAFT agent C_{12}TTC.

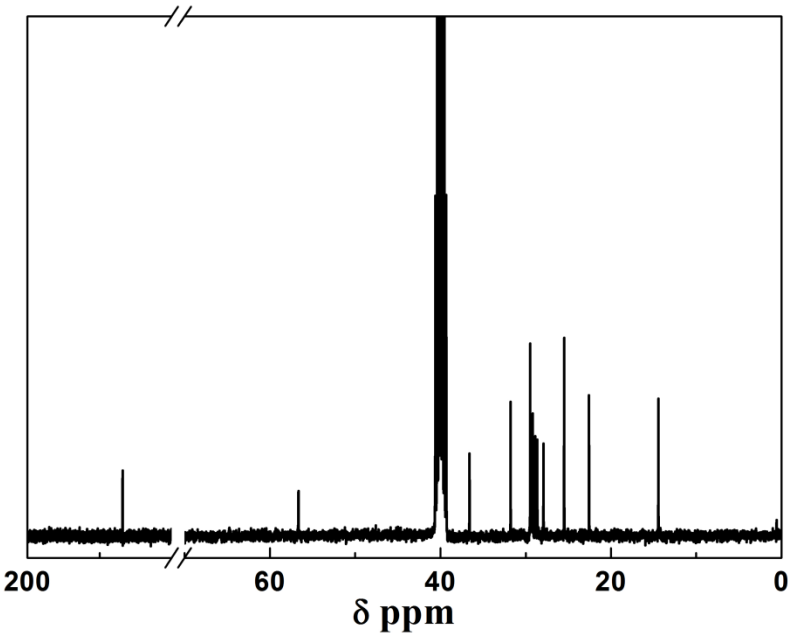

Figure S2. ^{13}C NMR spectrum of RAFT agent $C_{12}TTC$.

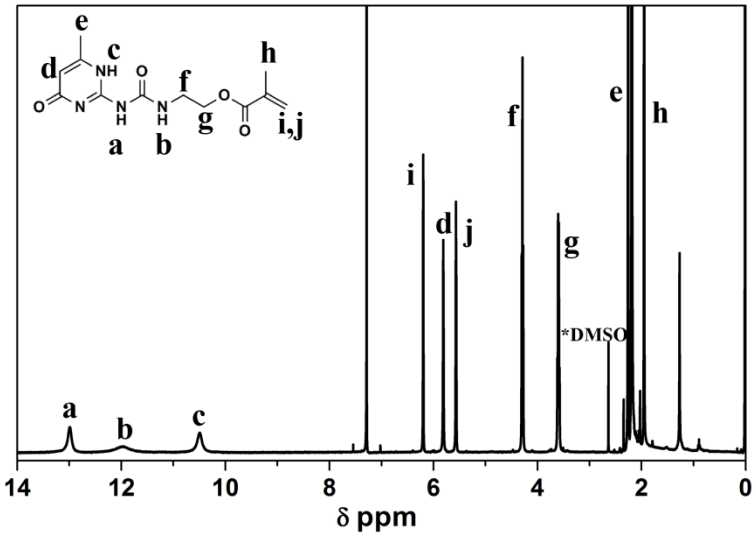

Figure S3. ^{1}H NMR spectrum of monomer MAUPy.

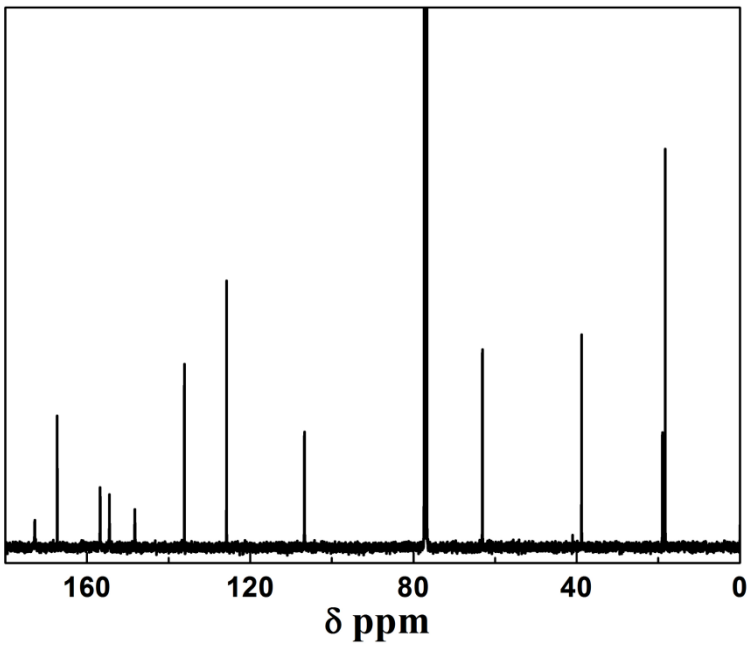

Figure S4. ^{13}C NMR spectra of monomer MAUPy.

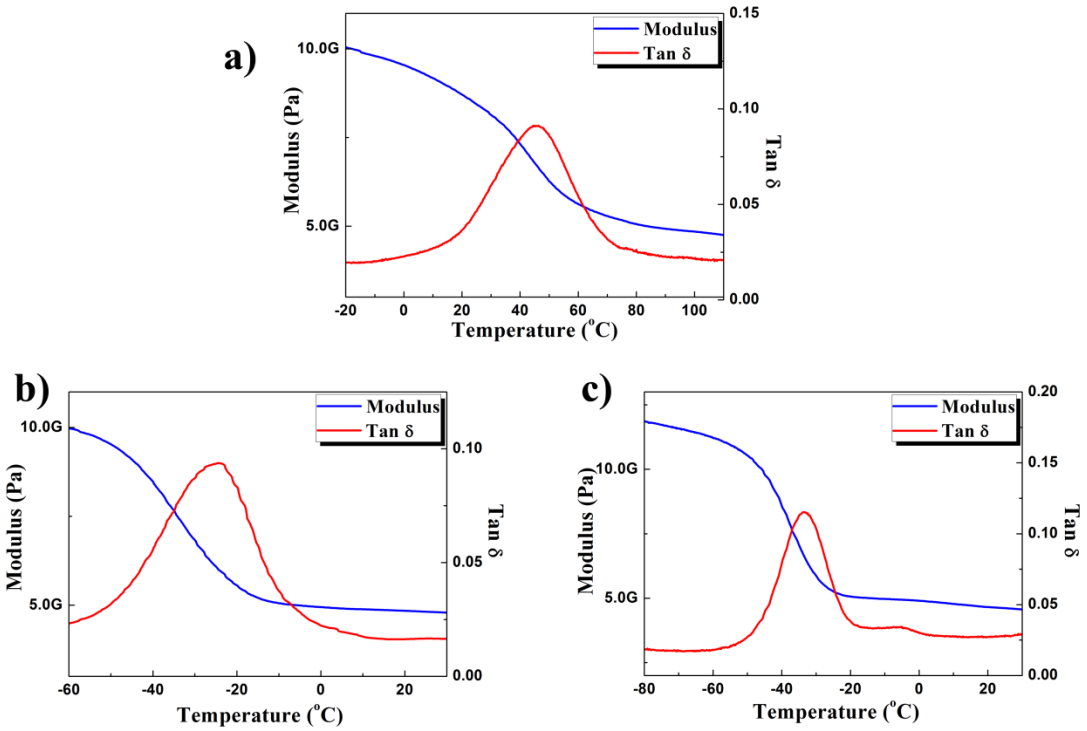

Figure S5. DMA results of polymer a) PHEA-UPy, b) $PPEG_{360}$-UPy and c) $PPEG_{500}$-UPy.

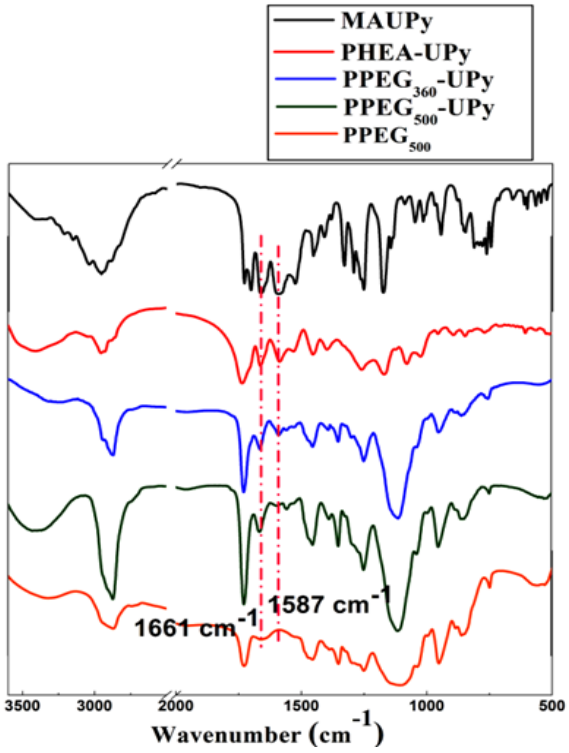

Figure S6. FTIR spectra of monomer MAUPy, copolymers PHEA-UPy, $PPEG_{360}$-UPyM, $PPEG_{500}$-UPy and the control polymer $PPEG_{500}$.

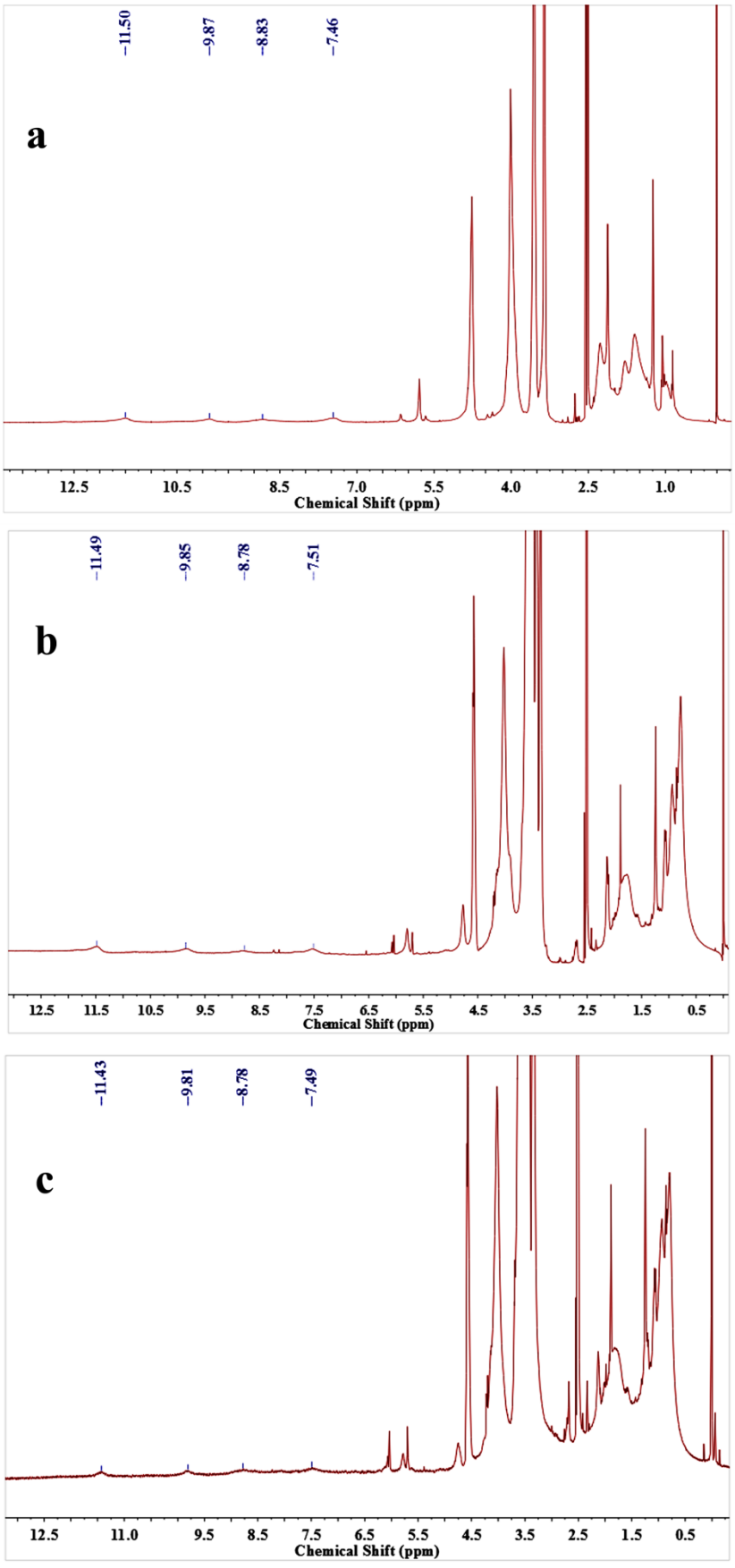

Figure S7. ^{1}H NMR spectra of copolymers PHEA-UPy (a), $PPEG_{360}$-UPy (b), $PPEG_{500}$-UPy (c) The peaks of

protons that correspond to the protons of UPy groups were clearly observed at high chemical shift region (δ>7 ppm).

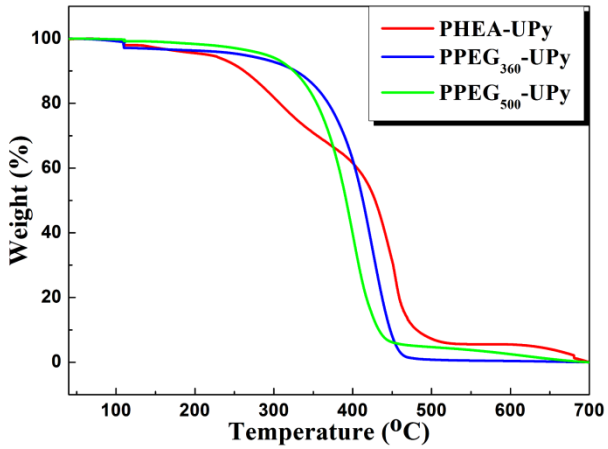

Figure S8. Thermalgravimeric analysis (TGA) for the polymers.

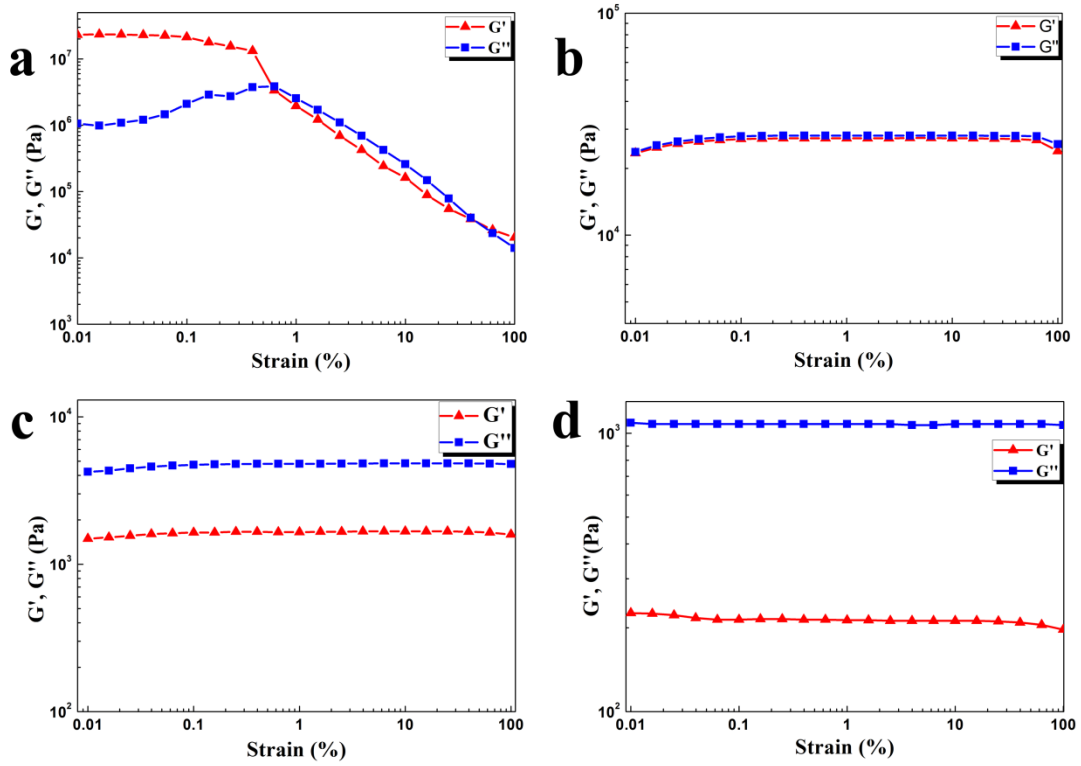

Figure S9. The dynamic strain sweep spectra of a) PHEA-UPy, b) $PPEG_{360}$-UPy, c) $PPEG_{500}$-UPy and d) control polymer $PPEG_{500}$.

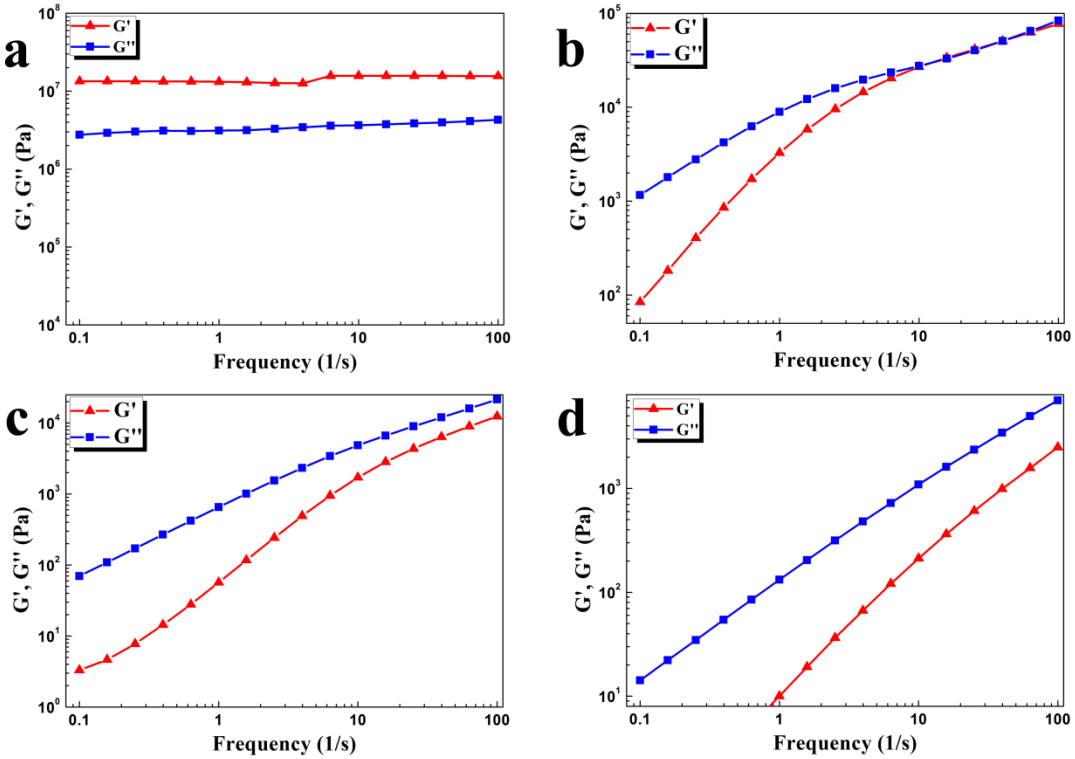

Figure S10. Storage modulus (G') and loss modulus (G'') versus scanning frequency for the polymers a) PHEA-UPy, b) $PPEG_{360}$-UPy, c)$PPEG_{500}$-UPy and d) control polymer $PPEG_{500}$.

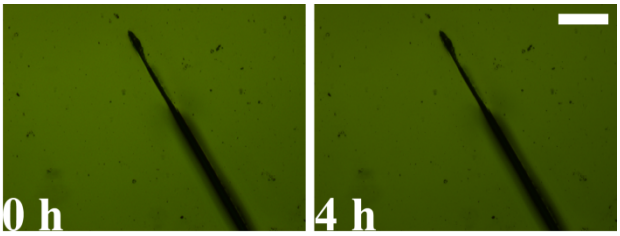

Figure S11. Images of the crack on PHEA-UPy film at ambient temperature without any extra treatment: a) 0 h, b) 4 h after crack generation (scale bar: 400 μm).

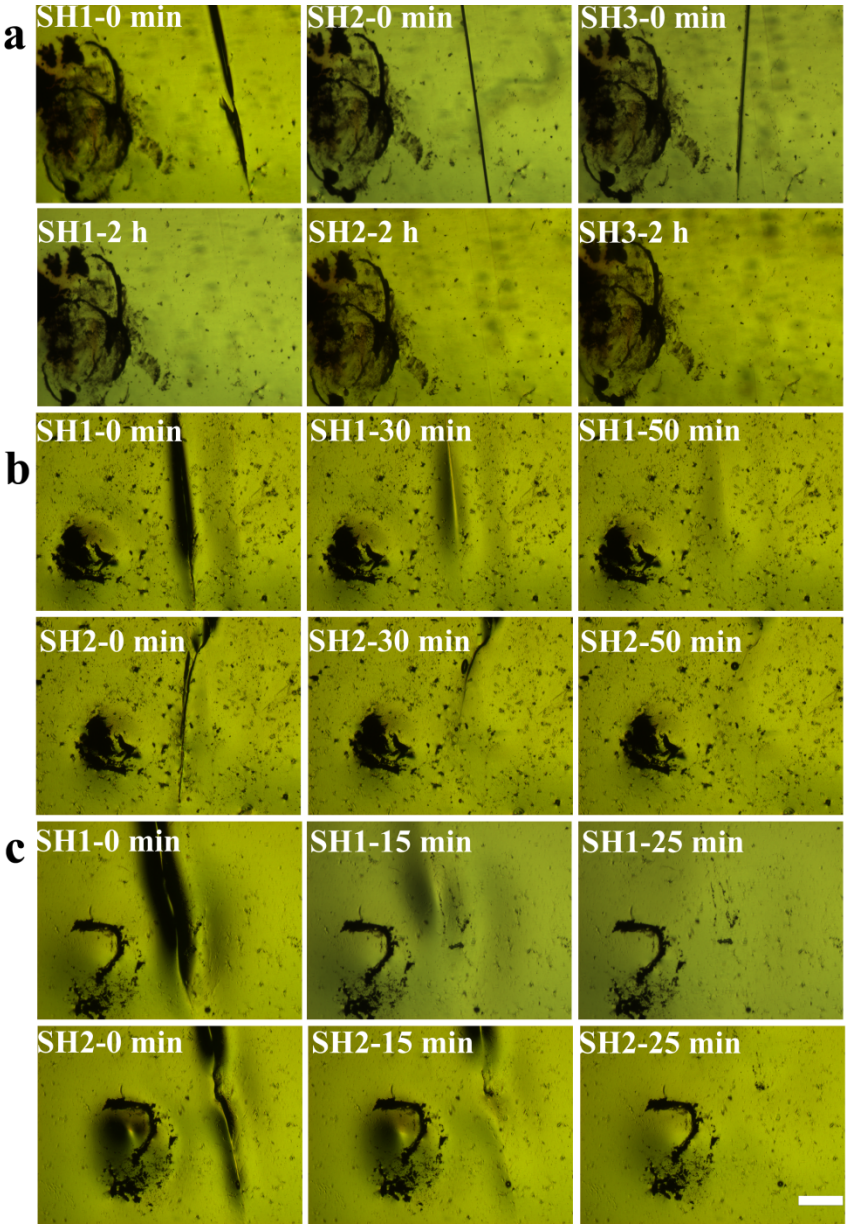

Figure S12. Repeatable healing ability of PHEA-UPy in relative humidity of 50% (a), $PPEG_{360}$-UPy (b) and $PPEG_{500}$-UPy (c) films without any special treatment. Scale bar: 400 μm.

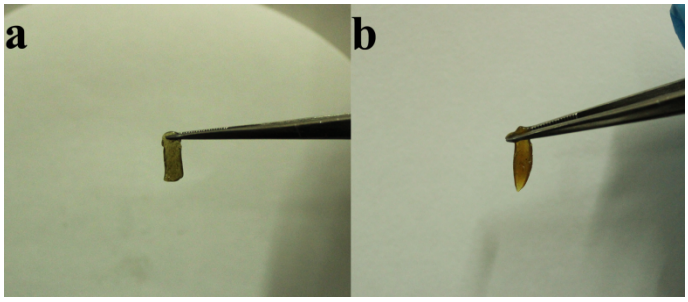

Figure S13. Images of $PPEG_{360}$-UPy (a) and $PPEG_{500}$-UPy (b) copolymers.

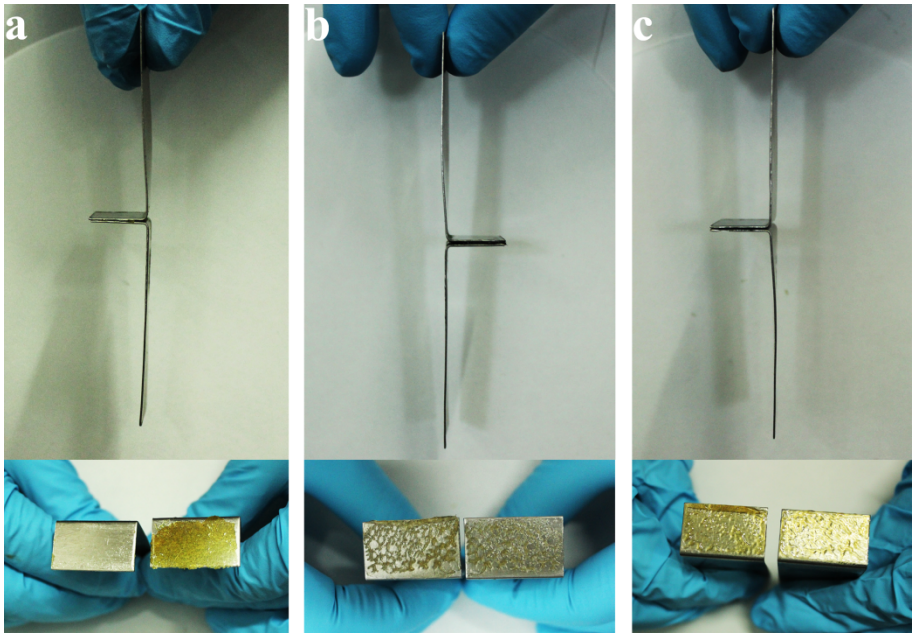

Figure S14. The images of the adhesion test samples and the interfaces after tensile tests: a) PHEA-UPy, b) $PPEG_{360}$-UPy and c) $PPEG_{500}$-UPy copolymers.

Table S1. Summary of polar and dispersion components of SEs of the prepared copolymers.

Polymer	**PHEA-UPy**	**$PPEG_{360}$-UPy**	**$PPEG_{500}$-UPy**
SE	38	81	63
Polar component	19	80	56
Dispersion component	19	1	8

Note and reference

1. W. M. Gramlich, G. Theryo and M. A. Hillmyer, *Polym. Chem.*, 2012, **3**, 1510-1516.