

Supplementary date

Damage Restoration in Rigid Materials via Keloid-inspired Growth Process

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Materials

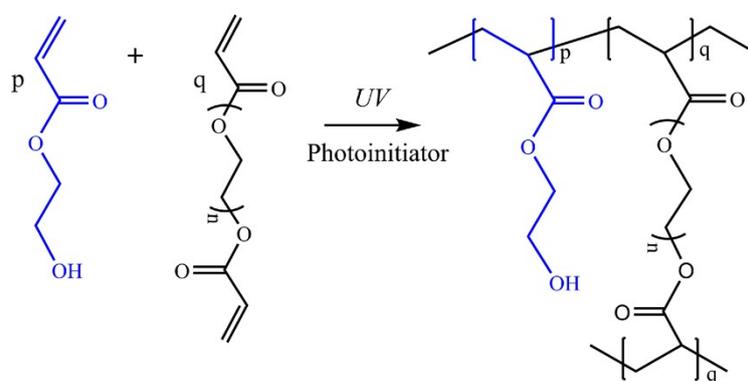
2-Hydroxyethyl methacrylate (HEMA), 2-hydroxyethyl acrylate (HEA), and 2-hydroxyethyl acetate (HEAt) were purchased from the Adamas Beta Chemical Reagent Co., Ltd (Shanghai, China). Photoinitiator of the phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide (I-819) and transesterification catalyst of the benzenesulfonic acid (BZSA) were supplied by the Meryer Chemical Technology Co., Ltd (Shanghai, China). Poly(ethylene glycol) diacrylate (A-PEG-A, 400 g mol⁻¹) was provided by the Adamas Beta Chemical Reagent Co., Ltd (Shanghai, China). Ethanol (EtOH), dimethylsulfoxide (DMSO) and tetrahydrofuran (THF) were obtained from Kelong Reagent Co., Ltd. (Chengdu, China).

Experimental Section

Synthesis of the PHEA with different crosslinking density

A series of crosslinked homopolymers of 2-hydroxyethyl acrylate (PHEA) were prepared via the route shown in Scheme S1. To identify the optimized crosslinking density, different

amounts of A-PEG-A crosslinking agents (0.5, 1, 2, and 5 mol%) were used. Here, the sample containing 2 mol% crosslinkers was selected to illustrate the synthesis. Accurately weighted HEA (6.00 g, 51.7 mmol), A-PEG-A (0.41 g, 1.03 mmol), and I-819 (0.11 g, 0.26 mmol) were mixed and stirred to achieve a transparent solution. The mixture was degassed under ultrasound for 30 min. After injected into a transparent container, the mixture was irradiated by UV light (10 mV cm^{-2}) for 5 h. The cured PHEA was washed with EtOH for 2 times (each time for 12 h), and then dried at $70 \text{ }^\circ\text{C}$ under vacuum to get the samples used for study. All samples were stored in a dryer before any characterizations.



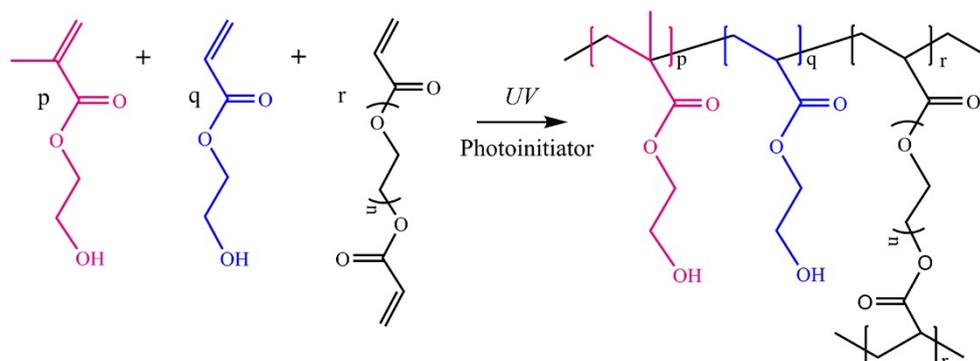
Scheme S1. The synthesis of the crosslinked PHEA.

The tensile results (Fig. S1 and Table S1) indicate that the Young's modulus slightly climbed from 1.2 to 3.3 MPa but the elongation at break decreased from 450.4% to 146.1% when the molar ratio of A-PEG-A increased from 0.5 mol% to 5 mol% for PHEAs. Tensile strength reached the highest value of 5.2 MPa for 2 mol%, so all of the substrates were prepared with 2 mol% of A-PEG-A crosslinker for the self-healing study without special illustration.

Synthesis of copolymer P-HEA-co-HEMA

Different concentrations of HEMA monomer were used in the synthesis of the P-HEA-co-HEMA, and the molar ratios of HEA: HEMA were set in 80:20, 60:40, 40:60, and 20:80. Here,

the molar ratio of 40:60 was taken to show the preparation process. As portrayed in Scheme S2, HEA (2.50 g, 21.6 mmol), HEMA (4.21 g, 32.4 mmol), A-PEG-A (0.43 g, 1.08 mmol) and I-819 (0.11 g, 0.26 mmol) were mixed and treated by the protocol described above.



Scheme S2. The synthesis of the rigid P-HEA-co-HEMA self-healing substrates.

2-Hydroxyethyl methacrylate (HEMA) is a more rigid monomer than 2-hydroxyethyl acrylate (HEA) because of the steric hindrance of methyl. Therefore, partial HEA could be replaced by HEMA to prepare more rigid P-HEA-co-HEMA matrices. As shown in Fig. S2 and Table S2, as the molar ratios of HEA:HEMA decreased from 100:0 to 40: 60, the Young's modulus sharply boomed from 2.9 MPa to 1.0 GPa and the distinct yielding is observed when the contents of HEMA beyond 40 mol% over the total monomers. The tensile strength also increased from 5.2 MPa to 18.4 MPa when the molar ratio of HEMA increased from 0 to 60 mol%. However, 80 mol% (20: 80) sample is too fragile to get uniform P-HEA-co-HEMA for self-healing study (Fig. S3). Therefore, P-HEA-co-HEMA with 60 mol% (40: 60) HEMA monomers is chosen to investigate the growth-induced self-healing performances. Without a special illustration, P-HEA-co-HEMA represents the substrates with 60 mol% of HEMA monomers and 2 mol% of A-PEG-A cross-linker for the growth-induced self-healing study.

Preparation of the nutrients

The nutrient solutions were prepared via mixing. Taking the PTS nutrients as an example, HEA

(7.50 g, 64.8 mmol), HEMA (12.63 g, 97.2 mmol), A-PEG-A (1.29 g, 3.24 mmol), I-819 (0.33 g, 0.78 mmol), and BZSA (0.26 g, 1.6 mmol) were mixed within a mouth packer to get a clear and free-flowing nutrient. The components of the PTS nutrient are the same as the formulation for the synthesis of rigid P-HEA-co-HEMA substrates except for the additional BZSA transesterification catalyst (1 mol%). Then, the nutrients were degassed under ultrasound. The nutrients were stored in a light-free condition. Other control nutrients of PS, NPTS, and TS were prepared by the same procedures.

The swelling process of P-HEA-co-HEMA

The P-HEA-co-HEMA splices were immersed in the nutrients and then weighted at different time intervals. The swelling ratios were calculated from the following Equation (1).

$$\text{Swelling ratio} = (m_t - m_0) / m_0 \quad \text{Equation (1)}$$

In the equation, m_0 is the initial weight of the species before swelling and the m_t is the weight after being swelled for time t .

Self-healing program of the high Young's modulus P-HEA-co-HEMA

P-HEA-co-HEMA with 60% rigid HEMA monomer was used to be investigated the self-growth self-healing behavior. The virgin P-HEA-co-HEMA films were knifed with surgical blades, and the P-HEA-co-HEMA almost be separated into two parts (Fig. S10). Nutrients were provided to the injured samples by immersing the sample into the nutrients. After swelling, the swollen and cracked samples were covered with photomasks, and the injured areas were exposed to the UV irradiation (10 mV cm^{-2}) for 2 h. After the polymerization at crack surroundings, the repaired samples were washed with EtOH for 2 times to remove any unpolymerized nutrients, and then the repaired P-HEA-co-HEMAs were dried at $70 \text{ }^\circ\text{C}$ under

vacuum for 24 h to get the healed P-HEA-co-HEMAs.

Characterization

Tensile mechanical properties were researched by the Instron universal testing machine (model 5943, USA). The size of the splices is $20 \times 4 \times 0.5$ mm, and the crosshead speed is 20 mm min^{-1} . More than 8 independent specimens were implemented for collecting reliable data. For cyclic loading / unloading tensile fatigue resistance measurements, 5% maximum tensile strain and 1000 cycles were selected with a crosshead speed of 20 mm min^{-1} .

The micrograph was recorded by the optical microscope (Nexcope, model NM910-TR, China) equipped with Industrial Digital Camera (model NEXCam-T20).

The temperature variation during the in-situ polymerization of the nutrients was monitored by the infrared imaging devices (Fortric, model 226s, China).

DMA tester (Q850 DMA, TA Instruments) was conducted to characterize the thermomechanical properties in a stretching mode. Samples with the dimension of $20 \text{ mm} \times 5.0 \text{ mm} \times 0.5 \text{ mm}$ were tested at a frequency of 1 Hz and an amplitude of $15 \mu\text{m}$. The temperature was first equilibrated at $-100 \text{ }^\circ\text{C}$ for 5 min, and then increased with a heating rate of $3 \text{ }^\circ\text{C min}^{-1}$.

The macrograph was taken by the digital camera (Nikon D7100).

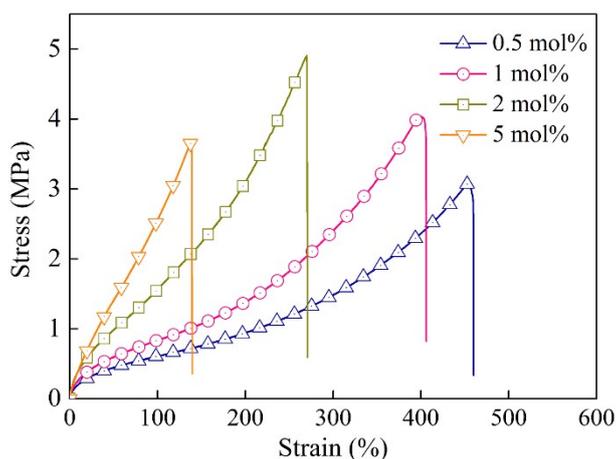


Fig. S1. Tensile stress-strain curves of the PHEA with different crosslinking densities.

Table S1. The tensile mechanical results of PHEA with different crosslinking densities.

Samples	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
0.5 mol%	1.2±0.15	2.7±0.32	450.4±25.2
1 mol%	1.7±0.24	3.8±0.46	403.9±11.4
2 mol%	2.9±0.18	5.2±0.53	274.6±14.4
5 mol%	3.3±0.19	3.5±0.15	146.1±4.9

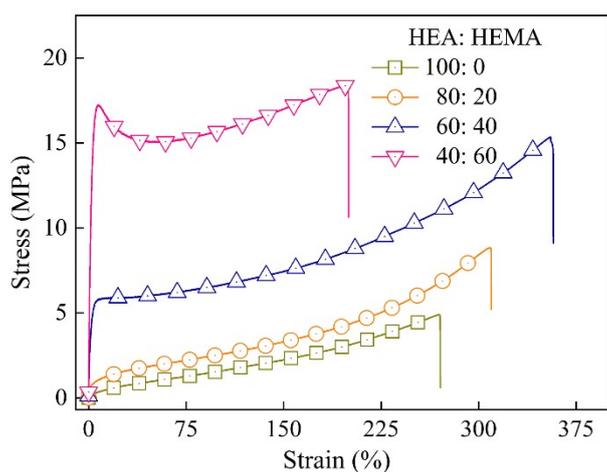


Fig. S2. The tensile stress-strain curves of P-HEA-co-HEMA with different molar ratios of the hard HEMA monomer.

Table S2. The tensile mechanical results of P-HEA-co-HEMA with different molar ratios of the soft HEA to hard HEMA monomers.

Samples	Young's Modulus (GPa)	Tensile Strength (MPa)	Yield stress (MPa)	Elongation at Break (%)
100: 0	0.003±0.0002	5.2±0.53	--	274.6±14.4
80: 20	0.006±0.0001	9.8±1.6	--	310.7±19.9
60: 40	0.6±0.1	15.4±2.9	7.5±1.4	368.5±22.9
40: 60	1.0±0.1	18.4±2.1	17.2±3.1	198.2±13.8



Fig. S3. The extremely fragile sample of P-HEA-co-HEMA with 80 mol% of hard HEMA monomer (scale bar, 1 cm).

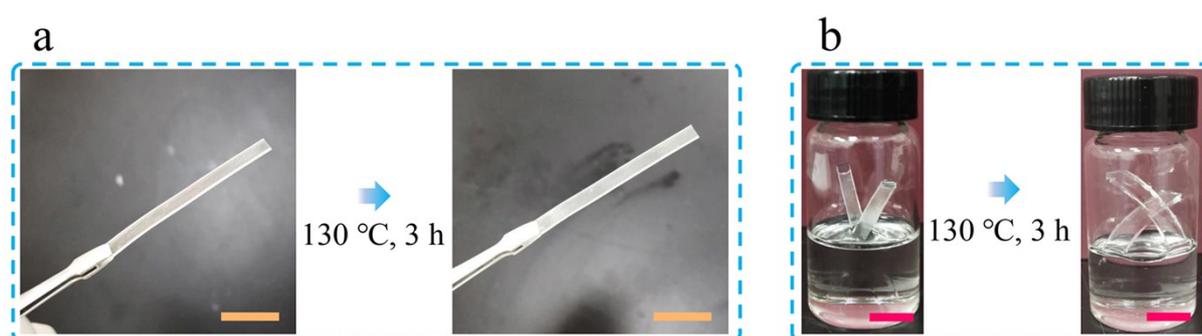


Fig. S4. (a) The P-HEA-co-HEMA specimen could withstand the 130 °C high temperature without melting (scale bar, 1 cm). (b) The P-HEA-co-HEMA specimens could not dissolve into DMSO even being heated at 130 °C for 3 h (scale bar, 1 cm).



Fig. S5. The clear nutrients PTS are stable after being stored in a light-free condition (testing time: 90 days, scale bar, 1 cm).

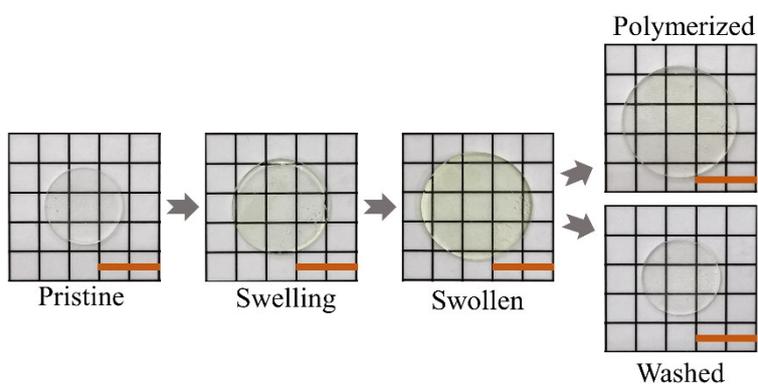


Fig. S6. Graphs of the swelling and polymerization of the nutrients within P-HEA-co-HEMAs (scale bar is 1 cm).

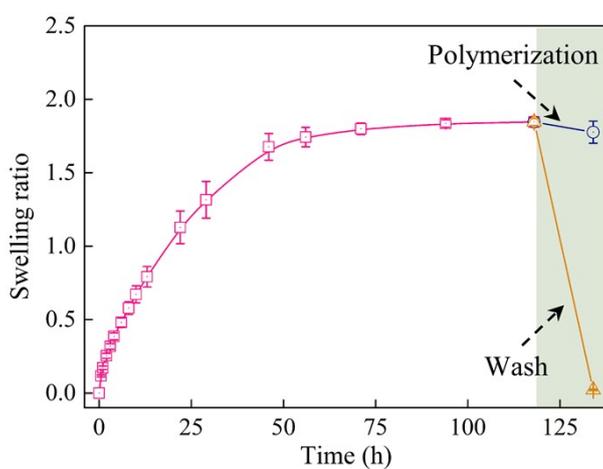


Fig. S7. Weight variation during the swelling and in-situ polymerization of the P-HEA-co-HEMAs.

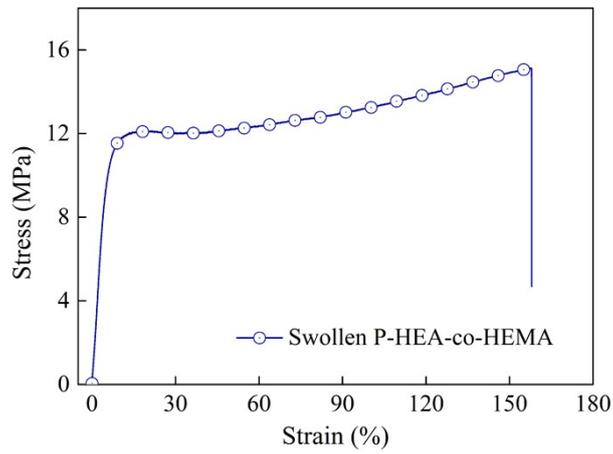


Fig. S8. Stress-strain curve of the lightly swollen P-HEA-co-HEMA (about 5 wt.% swelling ratio).

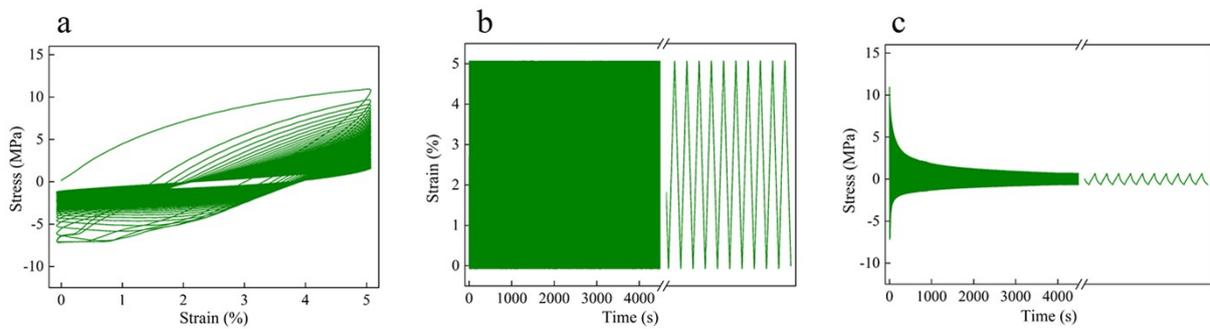


Fig. S9. Cyclic loading/unloading tensile deformation for fatigue test for 1000 cycles. (a) The stress-strain curves, (b) the strain-time curves, and (c) the stress-time curves for the swollen P-HEA-co-HEMA, respectively.

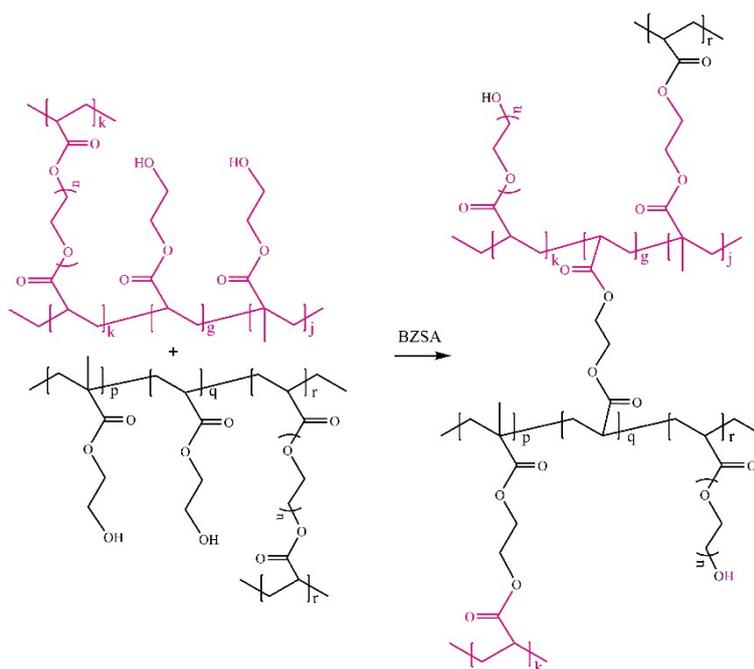


Fig. S10. Transesterification scheme between the P-HEA-co-HEMA chains catalyzed by BZSA.

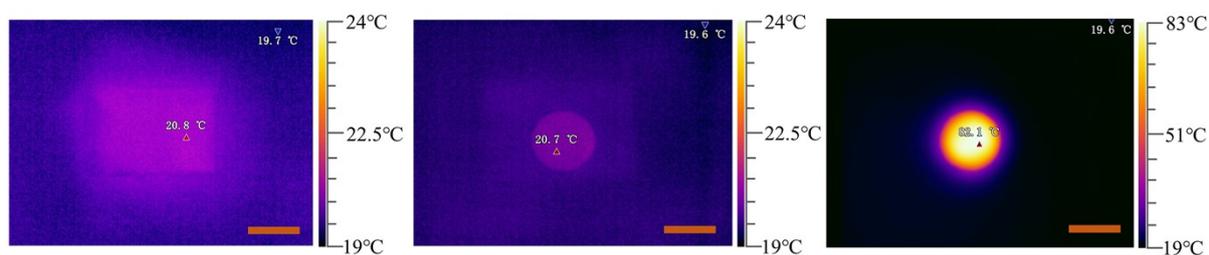


Fig. S11. Infrared photos and temperature distributions of the swollen P-HEA-co-HEMA before and during the UV irradiation. The nutrients (PTS) contained polymerizable HEMA and HEA monomers.

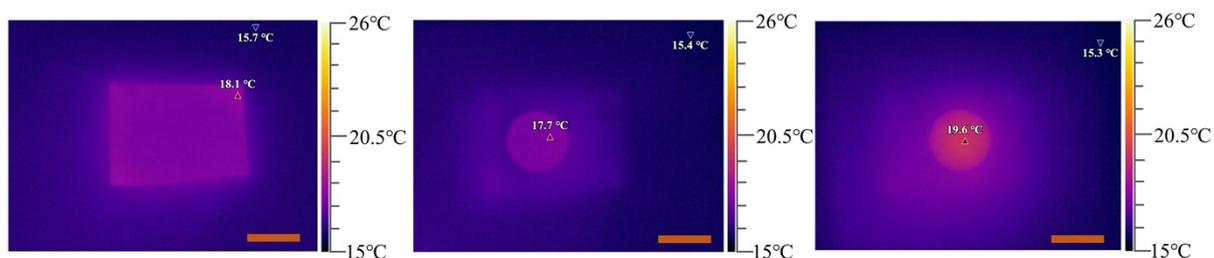


Fig. S12. Infrared photos and temperature distributions of the swollen P-HEA-co-HEMA before and during UV irradiation. The nutrients (NPTS) contained non-polymerizable HEA

monomers.

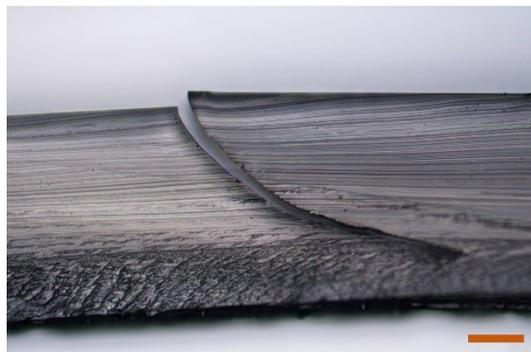


Fig. S13. The side view of the cracked P-HEA-co-HEMA film (scale bar is 50 μm).

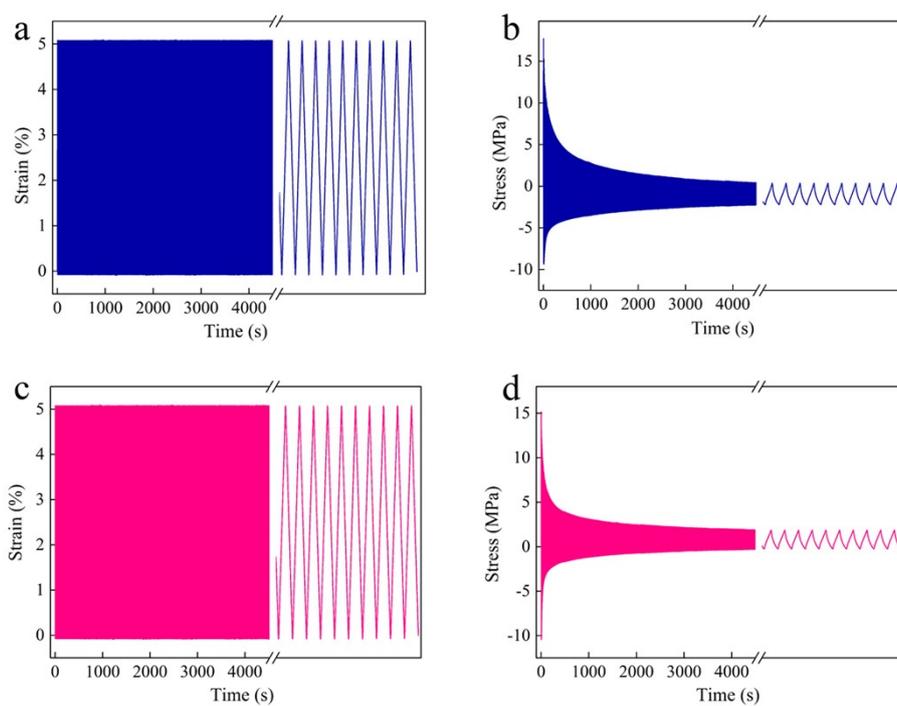


Fig. S14. Cyclic loading/unloading tensile deformation for fatigue test for 1000 cycles. (a) and (c) are the strain-time curves for the virgin and the repaired (PTS nutrient) P-HEA-co-HEMA, respectively. (b) and (d) The stress-time curves for the virgin and the repaired (PTS nutrient) P-HEA-co-HEMA, respectively.

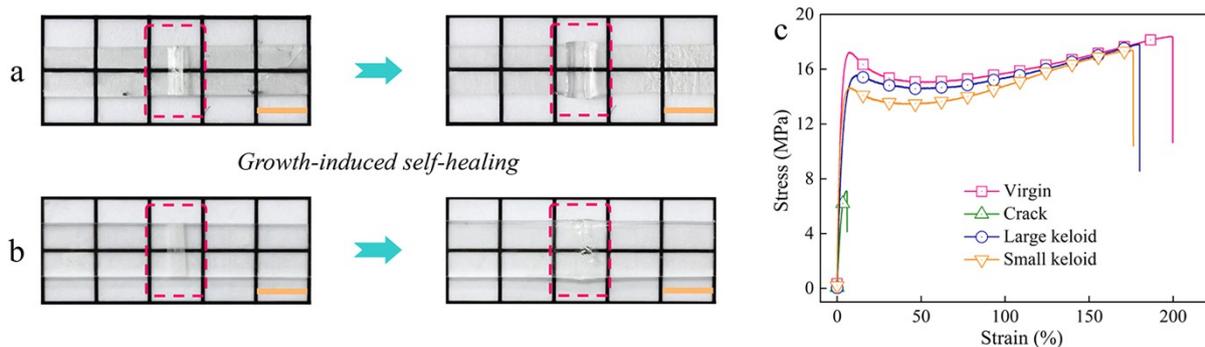


Fig. S15. (a) Large keloid from the high swelling ratio of PTS nutrient (scale bar, 0.5 cm). (b) Small keloid from the low swelling ratio of PTS nutrient (scale bar, 0.5 cm). (c) Tensile stress-strain curves of the virgin, cracked, and the healed (large and small keloid) P-HEA-co-HEMAs.

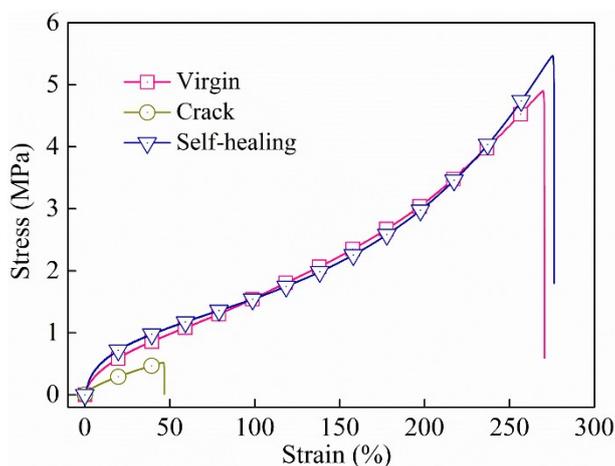


Fig. S16. Tensile stress-strain curves for the virgin, cracked, and growth-induced self-healing PHEA (molar ratio 100:0 of HEA: HEMA).

Table S3. Tensile test results and self-healing efficiency of the virgin and repaired P-HEA-co-HEMA samples.

Sample	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Toughness (MJ m ⁻³)	Self-healing efficiency (%)
Virgin	2.9±0.18	5.2±0.53	275±14	6.01	--
Crack	2.3±0.21	0.5±0.10	48±7	0.15	--
Self-healing	3.1±0.28	5.8±0.62	271±18	6.38	106.2

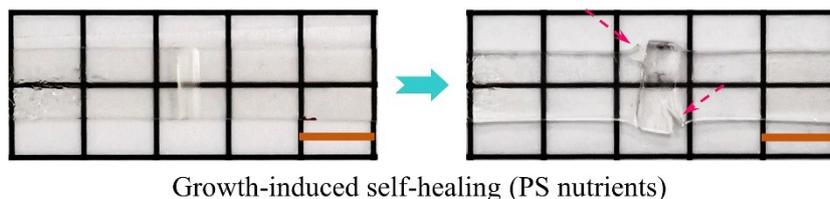


Fig. S17. Graphs of the cracked P-HEA-co-HEMA (left) and growth-induced self-healing P-HEA-co-HEMA (right) based on PS nutrients. Because no transesterification occurred, new cracks emerged between the interfaces of the keloid and the substrates. (Scale bar, 0.5 cm).

Table S4. Tensile test results and self-healing efficiencies of the growth-induced self-healing P-HEA-co-HEMA samples based on PTS, soft PTS, and hard PTS nutrients, respectively.

Sample	Young's Modulus (GPa)	Tensile Strength (MPa)	Yield Stress (MPa)	Elongation at Break (%)	Toughness (MJ m ⁻³)	Self-healing Efficiencies (%)
PTS	0.9±0.1	18.1±1.0	16.1±1.4	175.9±16.5	27.81	86.1
Soft PTS	0.07±0.01	7.2±0.8	--	50.8±6.7	2.57	7.9
Hard PTS	1.0±0.1	20.1±2.3	15.0±1.5	160.4±23.1	26.19	81.1