

*Supporting Information*

**A strain-adaptive, self-healing, breathable and perceptive  
bottle-brush elastomer inspired by skin**

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**Supporting Information**

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Tables S1 and S2

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## Experimental Section

### Material and methods

**Materials:** Reagents were obtained from the indicated commercial suppliers and could be used without further purification unless otherwise specified: 2-Hydroxyethyl Methacrylate (HEMA, Adamas, 99%, safe dry), 2-Bromoisobutyryl bromide (BIB) (Adamas, 99%), triethylamine (TEA, Adamas, 99%), anhydrous dichloromethane (DCM, Adamas, 99%, safe dry), methyl methacrylate (MMA, Adamas, 99%), 2,2-Azobis(isobutyronitrile) (AIBN, TCI, 98.0%) was purified by recrystallization in ethanol before use. Toluene (Greagent, 99.5%), butyl acrylate (BA, TCI, 99.0% (GC)) was filtered through a plug of basic alumina oxide before use. N,N,N',N'',N''-pentamethyldiethylenetriamine (PMEDTA, TCI, 99.0% (GC)), copper (I) bromide (CuBr) was purified by stirring overnight in acetic acid glacial. Methanol (Adamas, 99.9%), tetrahydrofuran (THF, Greagent, 99.0%), ethyl acetate (Greagent, 99.5%), magnesium sulfate anhydrous (MgSO<sub>4</sub>, Adamas, 99%), sodium bicarbonate (NaHCO<sub>3</sub>, Adamas, 99%), hydrochloric acid (HCl, Greagent, 36-38%), alumina oxide (basic, Greagent), alumina oxide (neutral, Greagent), dichloromethane (DCM, Greagent, 99.5%), chloroform-d (CDCl<sub>3</sub>, Aldrich, 99.8atom% D). 4-4'-Bis(diethylamino) benzophenone (Adamas, 98+%), titanium(IV) chloride (TiCl<sub>4</sub>, Adamas, 99%), Zinc dust (Tianjin Bodi Chemical Co. LTD, 98.0%), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, Greagent, ≥99%), petroleum Ether (Greagent, the boiling range of 60-90 °C), silica gel (Greagent, 300-400 mesh).

**Synthesis of 2-(2-Bromoisobutyryloxy)ethyl methacrylate (BIEM).** BIEM was synthesized referring to literatures.<sup>1, 2</sup> HEMA (80 mmol), TEA (80 mmol), and anhydrous dichloromethane (60 ml) were added to a dry round-bottom flask, the mixture was cooled in an ice bath while stirring, and a solution of 2-BIB (88.0 mmol) in anhydrous dichloromethane (10 mL) was added dropwise through constant pressure funnel over 30 min under argon atmosphere. The mixed solution was kept cold and stirring overnight to complete the reaction. After at least 24 h, the white precipitate was filtered out and washed with DCM twice, the obtained organic phase was washed three times with 15 wt% HCl solution, 15 wt% NaHCO<sub>3</sub> solution and deionized water respectively and then dried with anhydrous MgSO<sub>4</sub>, and the solvent was removed through rotary evaporator to obtain a pale yellow liquid, which was defined by <sup>1</sup>H NMR (Figure S1).

**Synthesis of macroinitiators.** The macroinitiators were synthesized by free-radical copolymerization of MMA and

BIEM. MMA, BIEM and AIBN were dissolved in toluene in the specified proportion, the solution was bubbled with argon for 30 mins and then heated 70 °C for at least 12 h under argon atmosphere. The resulting solution was precipitated in methanol at least three times, and finally the precipitate was dried at 45 °C in a vacuum oven for at least 48 h. The actual ratio of MMA and BIEM in the copolymer was determined by <sup>1</sup>H NMR, and then the number of MMA (n) and BIEM (m) in the copolymer chain was calculated by combining the results of <sup>1</sup>H NMR (Figure S2) and GPC. The details of the four macroinitiators were shown in Table S1.

**Synthesis of bottlebrushes.** Bottlebrushes were prepared by atom transfer radical polymerization (ATRP) making use of macroinitiator as initiator. Typically for Brush-4-1, the Shrek reaction bottle was used as reaction vessel, macroinitiator-4-1(1 g, 1.05 mmol Br) was dissolved in 10 ml toluene first, and then BA (13.4579 g, 0.105 mol) and PMEDTA (0.3639 g, 2.10 mmol) were dissolved in another 10 ml toluene, the mixture was cooled in ice bath and bubble with argon for 2 h to remove oxygen in the solution as much as possible, afterwards, CuBr (0.1506 g, 1.05 mmol) was added in the reaction solution quickly and the reaction vessel was sealed, thereafter the mixture was heated 70 °C for 4 h under argon atmosphere. After the reaction, THF was added into the reaction solution to cool it down to room temperature rapidly, the product was filtered through a plug of neutral alumina oxide to remove most of Cu<sup>2+</sup> and Cu<sup>+</sup>, and THF was used as eluent. After filtering, THF was removed through rotary evaporator at 35 °C, then the resulting solution was precipitated in the mixed solvent of methanol and deionized water (3:1) at least three times. The precipitate was dried at 35 °C in a vacuum oven for at least 48 h finally.

**Synthesis of Tetra(4-(diethylamino)phenyl)ethene (TPE-4N).** TPE-4N was prepared from the reference.<sup>3</sup> 30 mmol of zinc dust and 10 mmol of 4-4'-Bis(diethylamino) benzophenone) were placed into 150 mL three-neck round-bottom flask with a reflux condenser. The flask was evacuated under vacuum and flushed with dry argon at least three time. Then 75 mL of THF was added. The mixture was cooled to -78 °C by liquid nitrogen and 10 mmol of TiCl<sub>4</sub> was added dropwise. The mixture was heated to room temperature slowly, stirred for 0.5 hours, then refluxed overnight. The reaction was quenched with 10 % aqueous K<sub>2</sub>CO<sub>3</sub> and then poured into water. The mixture was extracted tree times by CH<sub>2</sub>Cl<sub>2</sub>, the organic layers were washed twice with brine. After evaporation of the solvent, the crude products were purified on silica-gel column with petroleum ether as eluent. And a green-yellow solid was obtained.

**Fabrication of films.** The dilute solution was obtained by dissolving the bottle-brush elastomers and DP in ethyl acetate in a certain proportion, and then the solution was poured into a Teflon mold, after evaporating the solvent, the transparent film was positioned in the vacuum oven at 40 °C for 48 h to remove the solvent thoroughly, lastly, the film was put into the oven at 100 °C for 20 min to engender the dynamic cross-linking, the resulting films was ready for the further analysis.

**Fabrication of sensor.** CNTs and Brush-4-1 were dissolved in ethyl acetate to form a conductive solution, the conductive solution was sprayed on the rectangular matrix of Brush-4-1-DP- 1, the conductive layer was formed after the solvent evaporated, another rectangular Brush-4-1-DP-1 matrix was attached to the conductive layer, then the ends of the rectangular spline were coated with silver paint, then the sample was put in oven at 40 °C for 1 h to remove the solvent completely, the obtained device was used to detect its response to strain and pressure.

For monitoring the neck motions, made use of paper cutting art, polyester (PET) film was cut out a specific shape, which was pasted on the Brush-4-1-DP-1 substrate, after spraying with the conduction solution, the film was put into oven at 40 °C for 1 h to remove the solvent, finally, the PET film was stripped to obtain a particular conductive pattern (Figure S13).

**Preparation of the sample for detecting acid gases.** 5 mg TPE-4N was dissolved in 20 ml THF. The TPE-4N solution was sprayed on the one of the surfaces of the Brush-4-1-DP-1 matrix with a length of 5 mm, a width of 5 mm and a thickness of 0.5 mm, then the film was placed in the oven at 40 °C for 1 h to remove the solvent completely, in the end, another Brush-4-1-DP-1 matrix with the similar size was tightly attached to the TPE-4N-sprayed surface, and the resulting sample was used for qualitative detection of the presence of the acid gas.

#### **Measurements and methods**

**Fourier transform infrared spectroscopy (FTIR):** On-line FTIR data was obtained by Thermo Scientific Nicolet iS50 FTIR on the transmission-mode at the temperature from 30 °C to 100 °C. Wavenumber scale was from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>.

**Proton nuclear magnetic resonance (<sup>1</sup>H NMR):** <sup>1</sup>H NMR were recorded by a Bruker AV III HD 400 MHz

spectrometer, and the solvent was  $\text{CDCl}_3$  ( $\delta$  (1H) = 7.26 ppm).

**Gel permeation chromatography (GPC):** The molecular weight was measured by a Tosoh HIC-8320GPC with tetrahydrofuran (THF) as the eluent.

**Differential scanning calorimetry (DSC):** The heat flow curves of brush-like elastomers were acquired on the Q2000 (TA instruments). The sample was firstly heated from 25 °C to 100 °C and then cooled from 100 °C to -70 °C with the rate of 20 °C/min to eliminate thermal history, and then the sample was heated from -70 °C to 100 °C with the rate of 10 °C/min to record the heat flow. The glass transition temperature ( $T_g$ ) of the samples were defined as the inflection point of the heating curves.

**Rheology:** The rheological measurements were carried out by the HAAKE MARS (Mars III). Temperature sweeping from 20 °C to 120 °C was performed with the strain of 1% and the constant frequency of 1 Hz under the heating/cooling rate of 10 °C/min.

Frequency sweeping from 0.01 Hz to 100 Hz was conducted at 298.15 K, 313.15 K, 328.15 K, 343.15 K, 358.15 K, 373.15 K, respectively, and with a strain of 1%. Master curves, were obtained by shifting the frequency sweeping curves at different temperatures to 298.15 K (25 °C). The samples were the disks with diameter 20 mm and thickness 0.5-1.0 mm and the tests were performed in torsion mode.

**Dynamic mechanical analysis (DMA):** Dynamic mechanical properties were measured on the Q800 (TA instruments) in the tension mode. The geometry rectangular samples with the sizes about 19 mm (length) \* 5 mm (width) \* 0.3 mm (thickness) were heated from -70 °C to 80 °C with the heating rate of 5 °C/min, the frequency of 1 Hz and the preload force of 0.01 N.

**Atomic force microscope (AFM):** AFM height diagrams were gotten by AIST-NT SPM smartSPMTM-1000 in the tapping (AC) mode with the spring constant of 70 N/m and the resonance frequency of 289 kHz. Sample preparation: Brush-4-1-DP-2 was dissolved in THF with the concentration of 0.1 mg/ml. Spin coated the solution on the silicon slice using the spin coater (KW-4A). Afterwards the silicon slice was placed in the vacuum oven at 100 °C for 30 mins.

**Tensile test:** Tensile experiments were performed on an Instron 5967 tensile tester. Samples were cut into the dumbbell shape by a normalized cutter with the gauge length of 20 mm, the width of 2 mm and the thickness of 0.5-1 mm. Uniaxial tensile measurements were performed at room temperature in the air with the strain rate of 80 mm/min. The Young's modulus was determined by the slope within the initial linear region of the stress-strain curves.

**Electro-mechanical measurements:** Electro-mechanical tensile measurements were carried out on the Keithley 6487 in a resistance mode with assistance of a tensile tester (SANS CMT 4503). The setting voltage and electric current were 1 V and 25 mA. The results of resistance versus time were recorded by the software of Keithley 6487 test system and the data of strain versus time were recorded by the SANS tester software.

For the electro-mechanical tensile tests, silver paint layers on the two sides of the sandwich-shaped strain sensor as the electrodes were clamped with two conductive clips and were attached to the Keithley 6487 via wire leads. the sensor was fixed between two clamps of the tensile tester with the initial distance of 15 mm, afterwards, the sample was stretched to strain of 100 % at the rate of 2 mm/min.

For the electro-mechanical cyclic tensile tests, the sandwich-shaped strain sensors were stretched by the loading cycle to the maximum strain of 5% or 10% with the speed of 100 mm/min, firstly, and then unload at the same rate.

## Theoretical calculation

**True stress:** The true stress can be calculated by the following equation:

$$\sigma_{true} = (1 + \epsilon)\sigma$$

Where  $\sigma$  refers to stress and  $\epsilon$  refers to strain.

**Stiffness:** The softness is quantified by the stiffness, the smaller value of stiffness, the softer the material is, and the stiffness is defined as:

$$Stiffness = \frac{\Delta \sigma_{true}}{\Delta \epsilon}$$

Where  $\Delta \epsilon$  represents the change of strain,  $\Delta \sigma_{true}$  represents for the change of the  $\sigma_{true}$  during the  $\Delta \epsilon$ .

**Self-healing efficiency:** The self-healing properties are quantified by comparing the true fracture stress of the

pristine sample with the restored sample:

$$\text{Healing efficiency} = \frac{\sigma_{cut}}{\sigma_{uncut}}$$

Where the  $\sigma_{cut}$  refers to the true fracture stress of the cut samples, and  $\sigma_{uncut}$  refers to the true fracture stress of the uncut samples.

**Gauge factor (GF):** The sensitivity of the sensor is determined by the GF which was shown as follows:

$$GF = \frac{\Delta R / R_0}{\Delta L / L_0}$$

Where  $\Delta R$  represents for the change of resistance at the process of deformation;  $R_0$  is the resistance of the original resistance.  $\Delta L$  represents for the change of length;  $L_0$  is the original length of the sample before deformation.

## Figures and Tables

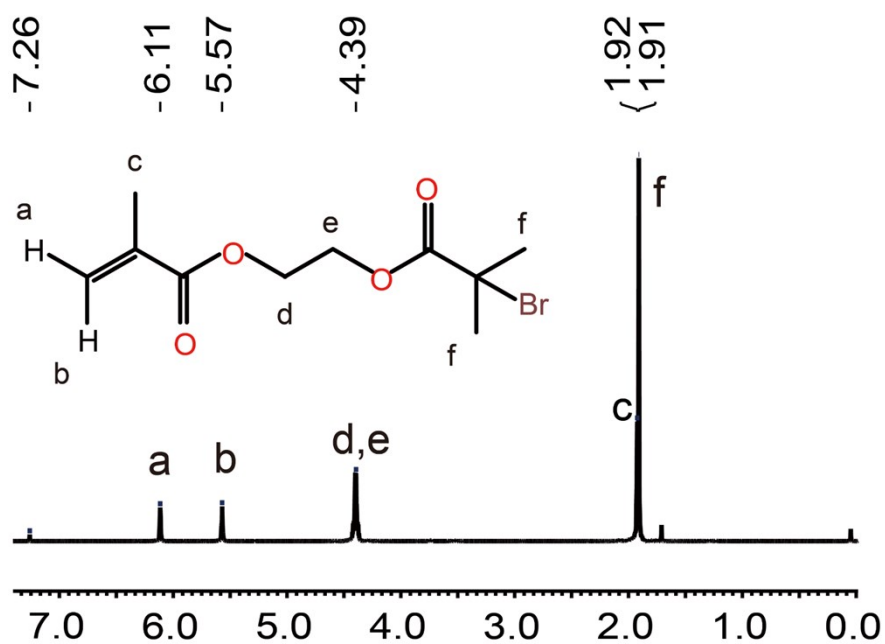


Figure S1. The  $^1\text{H}$  NMR spectra of BIEM (400 MHz,  $\text{CDCl}_3$ ).

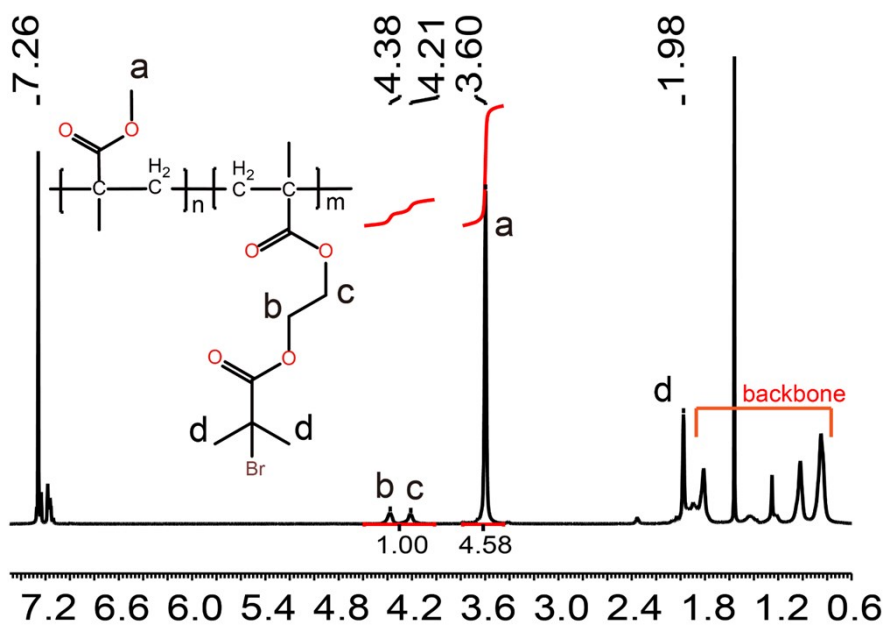
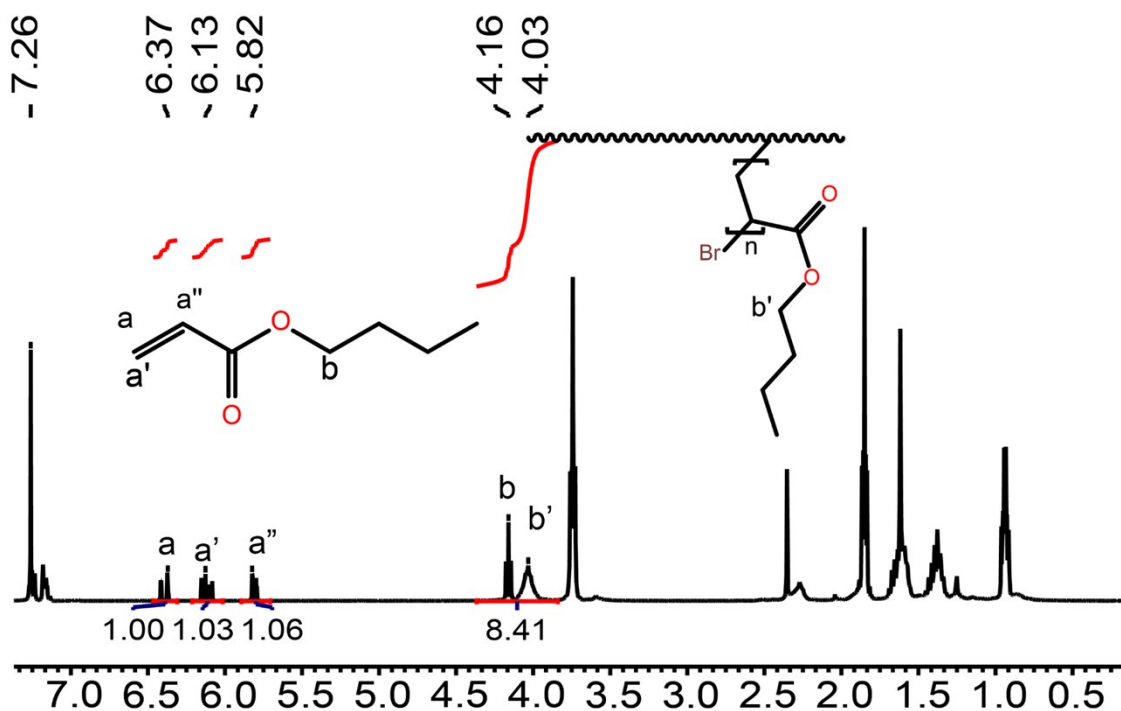


Figure S2. The  $^1\text{H}$  NMR spectra of microinitiator-4-1 (400 MHz,  $\text{CDCl}_3$ ):

$$m(\text{BIEM})/n(\text{MMA}) = (\text{area}(b+c)/4) / (\text{area}(a)/3) = 1:6.1$$





**Figure S3.** The  $^1\text{H}$  NMR spectra of Brush-4-1 reaction mixture at 70% conversion (400 MHz,  $\text{CDCl}_3$ ):

$$\text{conversion} = (\text{area}(b+b')/2 - \text{area}(a+a'+a'')/3) / (\text{area}(b+b')/2) = 75\%.$$

**Table S1.** Characterization of macroinitiators

	Feed mole ratio	Actual mole ratio of	Mn	PDI	BIEM (Br)/chain (m)
	MMA: BIEM	MMA: BIEM	g/mol		
Macroinitiator-1- 6	1:6	1:5.77	38286	2.51	129
Macroinitiator-1- 1	1:1	1:1.02	32217	2.94	85
Macroinitiator-2- 1	2:1	1.72:1	28601	2.72	60
Macroinitiator-4- 1	4:1	6.1:1	64795	2.89	68

**Table S2.** Characterization of bottlebrushes.

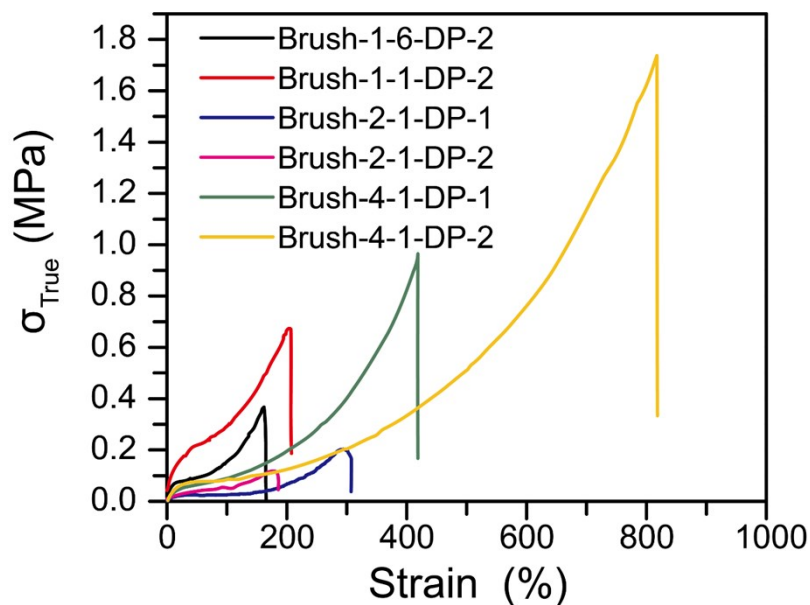
sample	the theoretical grafting density (MMA: BIEM) <sup>a</sup>	Actual grafting density (MMA: BIEM) <sup>b</sup>	BA: BIEM (Feed mole ratio) <sup>c</sup>	Actual length of side chain <sup>d</sup>	DP: Br (mole ratio)
Brush-1-6-DP-1	1:6	1:5.77	100:1	About 75	1:1
Brush-1-6-DP-2	1:6	1:5.77	100:1	About 75	2:1
Brush-1-1-DP-1	1:1	1:1.02	100:1	About 75	1:1
Brush-1-1-DP-2	1:1	1:1.02	100:1	About 75	2:1
Brush-2-1-DP-1	2:1	1.72:1	100:1	About 75	1:1
Brush-2-1-DP-2	2:1	1.72:1	100:1	About 75	2:1
Brush-4-1-DP-1	4:1	6.7:1	100:1	About 75	1:1
Brush-4-1-DP-2	4:1	6.7:1	100:1	About 75	2:1

<sup>a</sup> The feed ratio of MMA and BIEM when the main chains were synthesized;

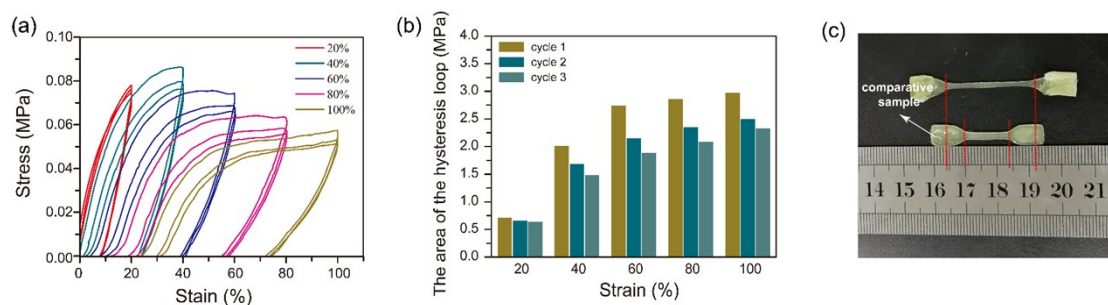
<sup>b</sup> The actual molar ratio of MMA and BIEM in the backbones;

<sup>c</sup> The mole ratio of initiator group and monomer during the grafting reaction;

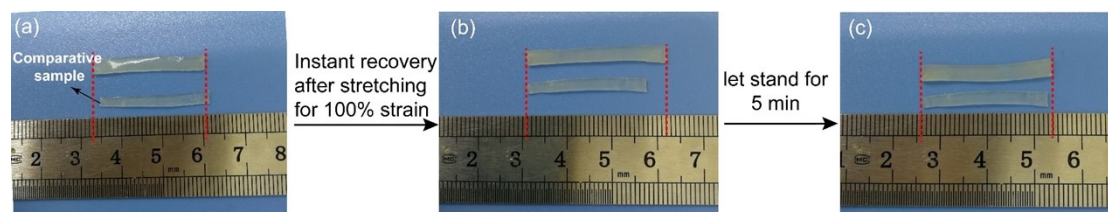
<sup>d</sup> The degree of polymerization of the side chains.



**Figure S4.** Representative stress-strain curves of Brush-1-6-DP-2, Brush-1-1-DP-2, Brush-2-1-DP-1, Brush-2-1-DP-2, Brush-4-1-DP-1 and Brush-2-1-DP-2 at the tensile rate of 80 mm/min.

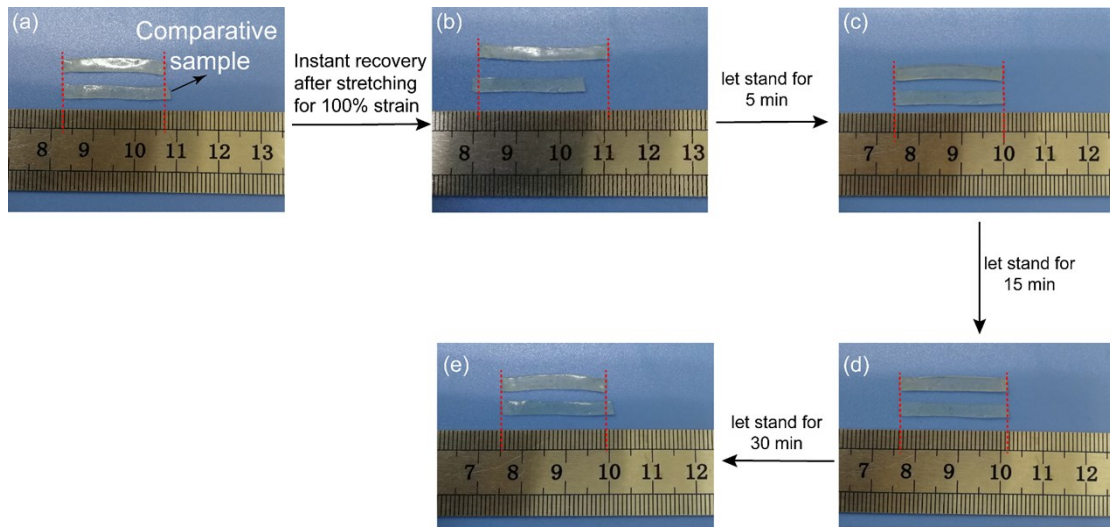


**Figure S5.** (a) The loading-unloading curves of Brush-4-1-DP-2 under the strain of 20%, 40%, 60%, 80% and 100%; (b) The area of the hysteresis loop of each cycle under the strain of 20%, 40%, 60%, 80% and 100%; (c) The length of Brush-4-1-DP-2 recovered after tension failure (strain at break is 815%), after being broken, the length of Brush-4-1-DP-2 cannot be completely restored, the residual strain is 100%.

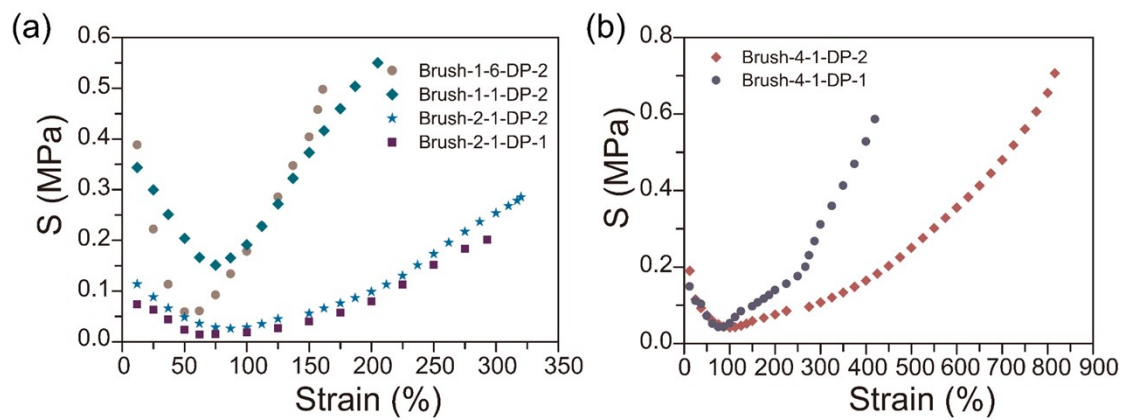


**Figure S6.** The length recovery process of Brush-4-1-DP-2 after stretching the sample to 100% strain. (a) The original state of Brush-4-1-DP-2; (b) The strain of the sample was restored to 11% in an instant; (c) After 5 min,

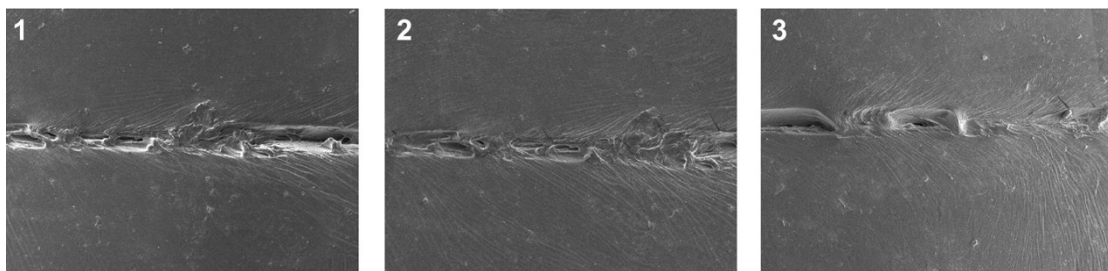
the length was completely restored.



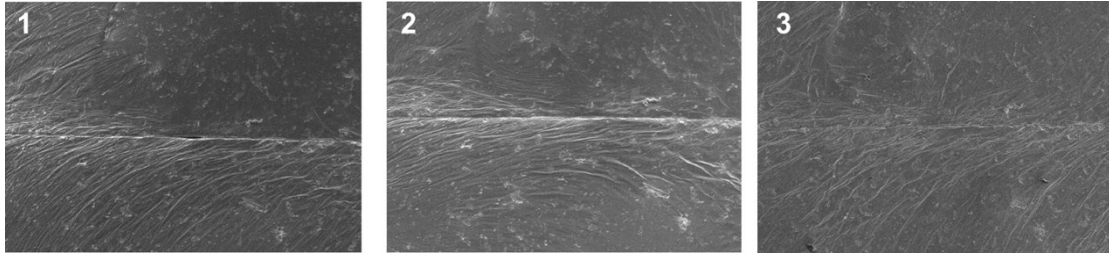
**Figure S7.** The length recovery process of Brush-4-1-DP-1 after stretching the sample to 100% strain. (a) The original state of Brush-4-1-DP-1; (b) The strain of the sample was restored to 25% in an instant; (b) After 5 min, the residual strain is 8%; (c) After 15 min, the residual strain is 4%; (d) After 30 min, the length was completely restored.



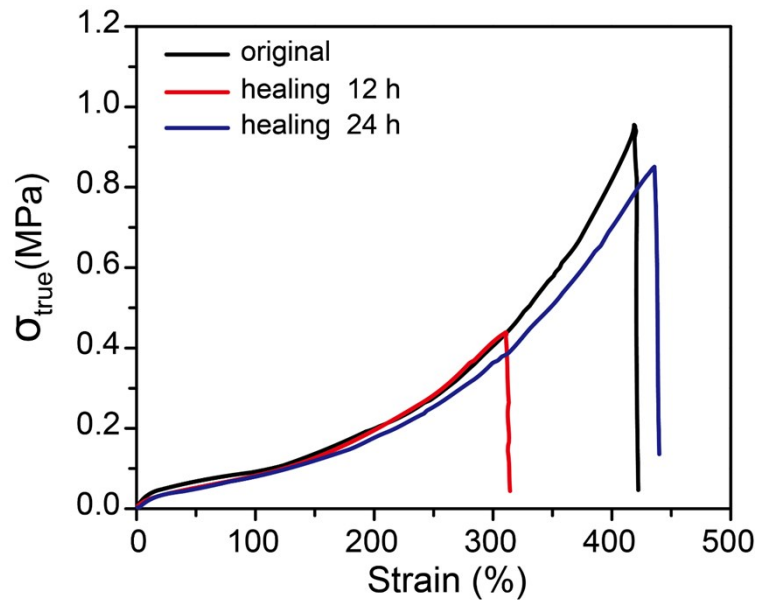
**Figure S8.** (a) The stiffness ( $S$ ) of Brush-1-6-DP-2, Brush-1-1-DP-2, Brush-2-1-DP-2, Brush-2-1-DP-1 as a function of strain; (b) The stiffness ( $S$ ) of Brush-4-1-DP-2, Brush-4-1-DP-1.



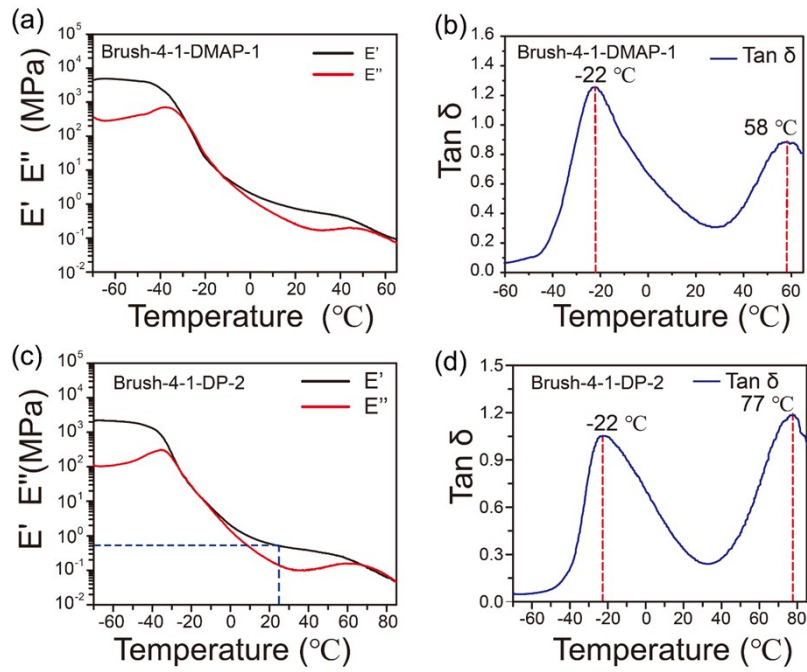
**Figure S9.** SEM images of healing process of Brush-4-1-DP-1 after fracture at room temperature: (1) the original state after scratching; (2) the state after healing for 4 h; (3) the state after healing for 24 h.



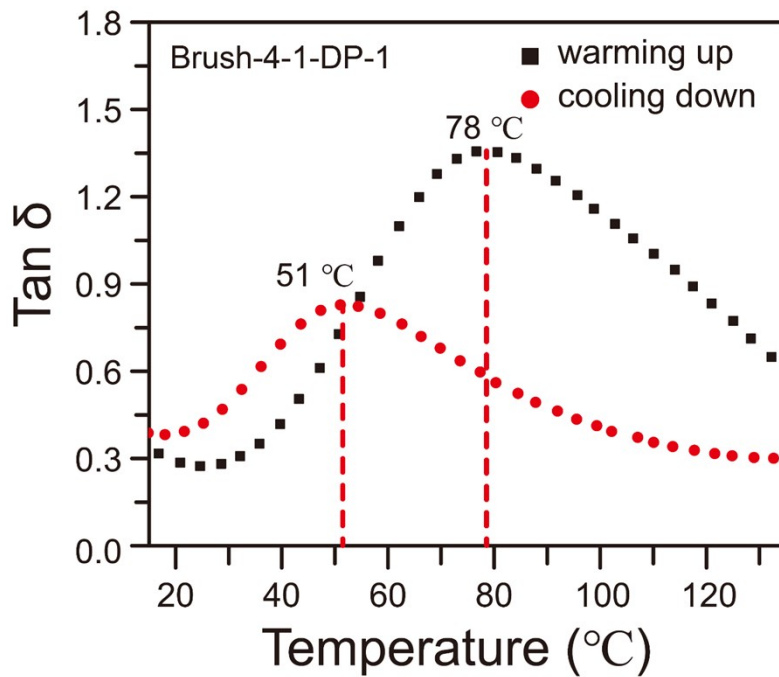
**Figure S10.** SEM images of healing process of Brush-4-1-DP-2 after fracture: (1) the original state after scratching; (2) the state after healing for 4 h; (3) the state after healing for 24 h.



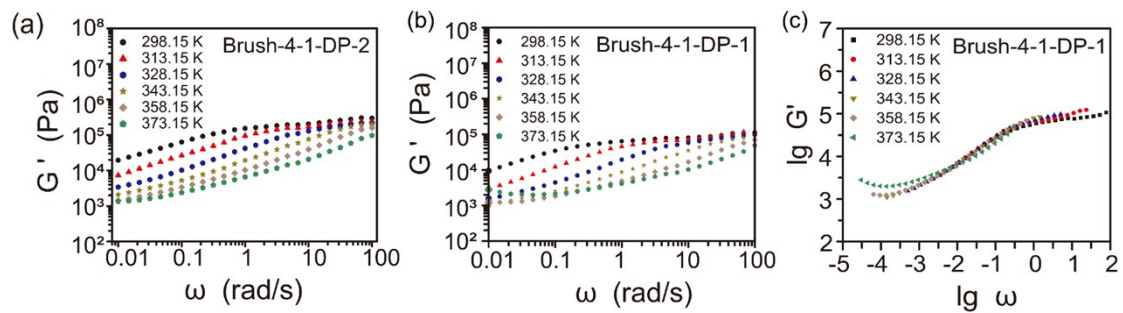
**Figure S11.** Representative stress-strain curves of the Brush-4-1-DP-1 uncut sample, and cut samples healed at room temperature for 12 h and 24 h.



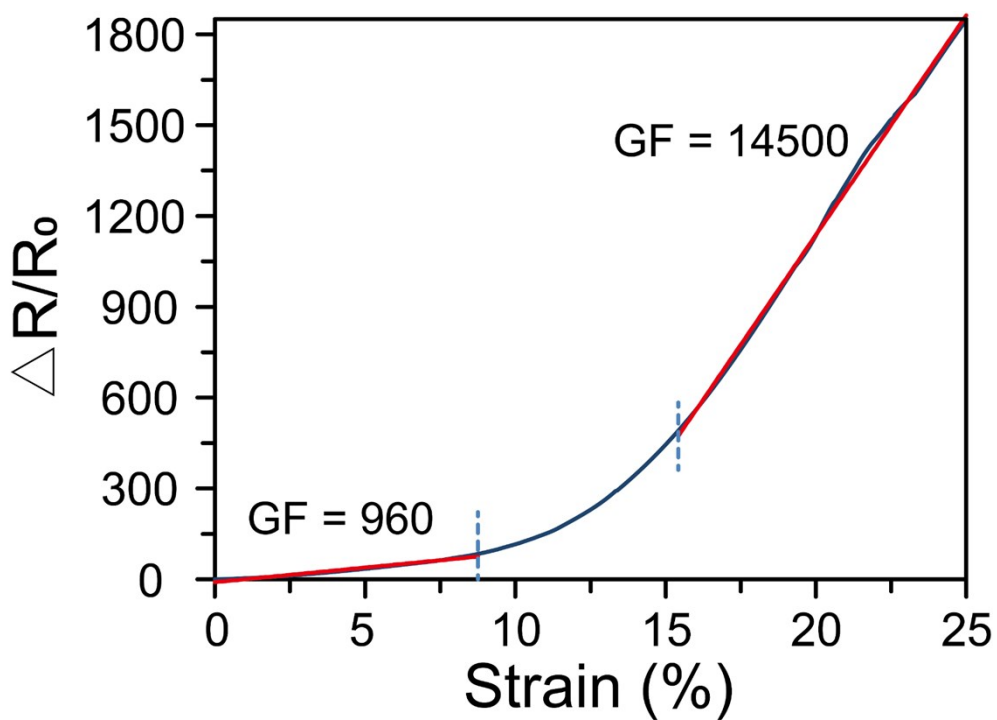
**Figure S12.** The results of DMA in the stretching mode at the heating rate of 5 °C/min: (a) the storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of Brush-4-1-DP-1 and (b) the  $\tan \delta$  of Brush-4-1-DP-1; (c) the storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of Brush-4-1-DP-2 and (d) the  $\tan \delta$  of Brush-4-1-DP-2.



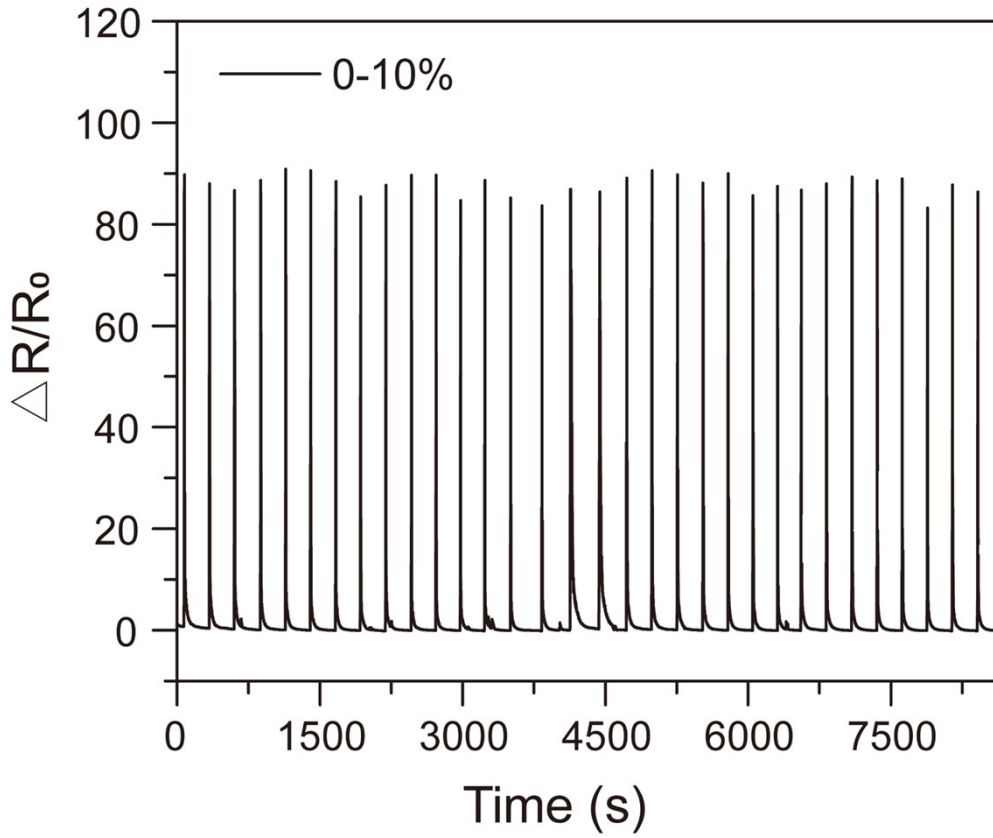
**Figure S13.** The result of rheological test at the temperature-scanning mode from 20 °C to 120 °C, the  $\tan \delta$  of Brush-4-1-DP-1 during the process of warming up and cooling down.



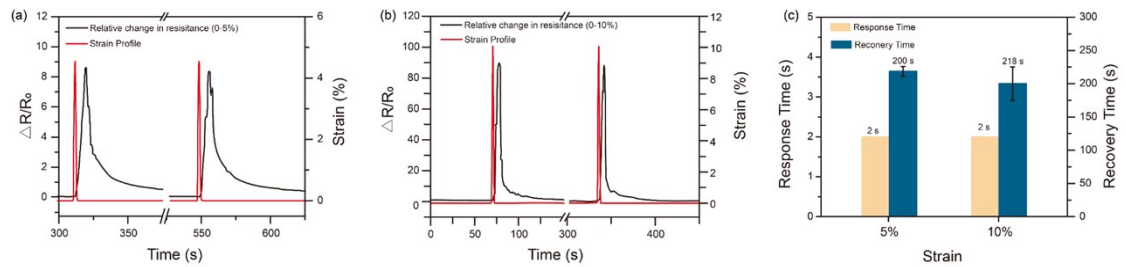
**Figure S14.** The storage modulus ( $G'$ ) of (a) Brush-4-1-DP-2 and (b) Brush-4-1-DP-1 as a function of frequency in a temperature range from 298.15 K to 373.15 K; (c) The master curves of  $\lg G'$  as a function of the logarithm of angular frequency ( $\lg \omega$ ) at 295.15 K.



**Figure S15.** Relative resistance as a function of strain.

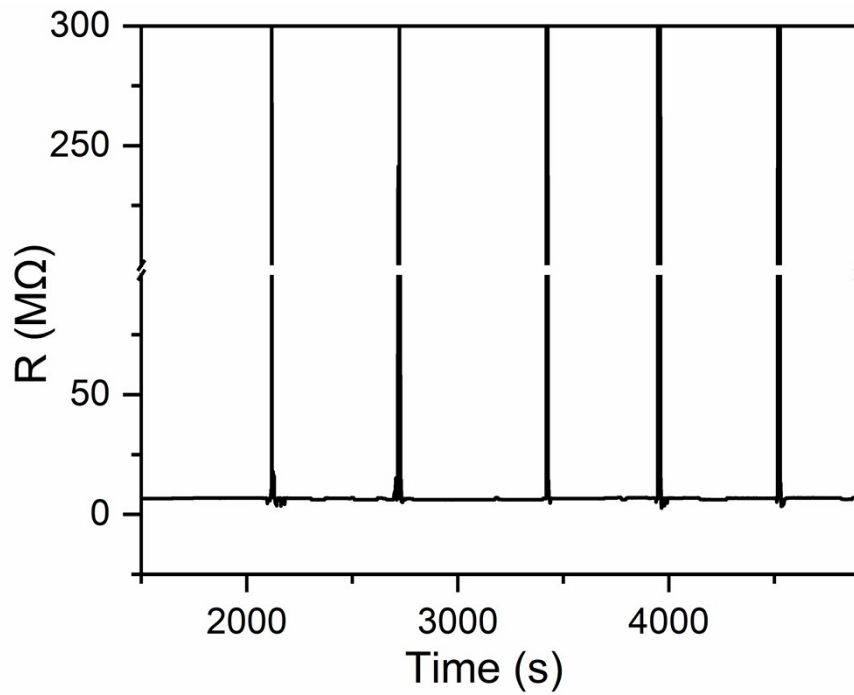


**Figure S16.** Relative resistance versus time for stretching the sensor cyclically at the strain of 0-10%.

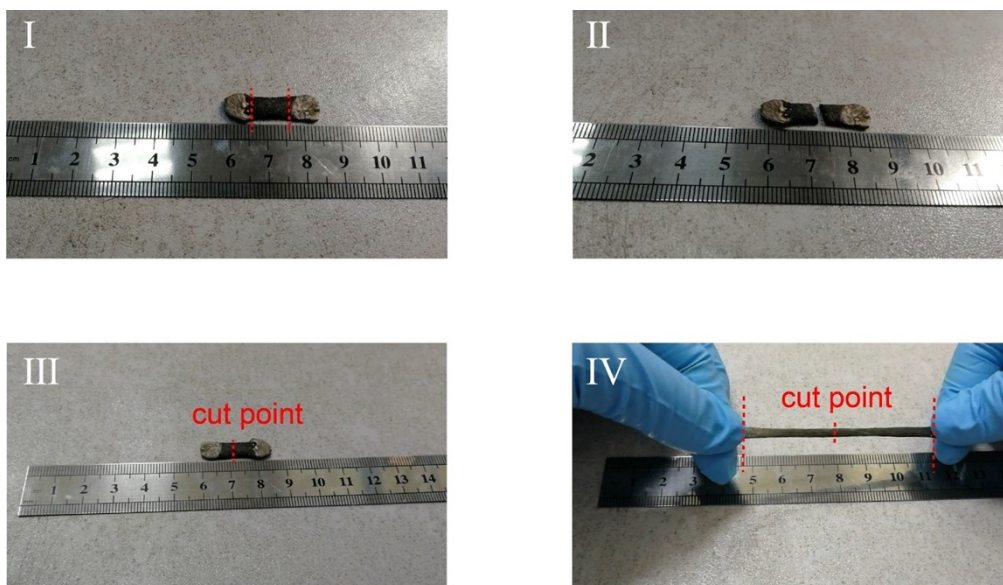


**Figure S17.** (a) Relative change in resistance response to the cyclic strain of 5%; (b) Relative change in resistance response to the cyclic strain of 10% (c) Response and recovery times of the sensor at the strain of 5% and 10%.

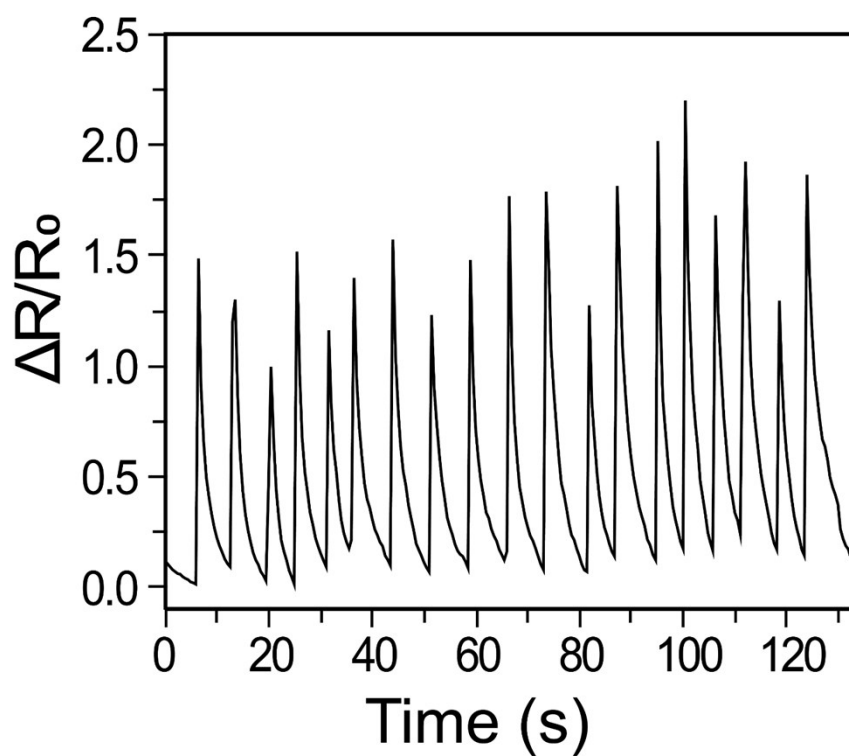




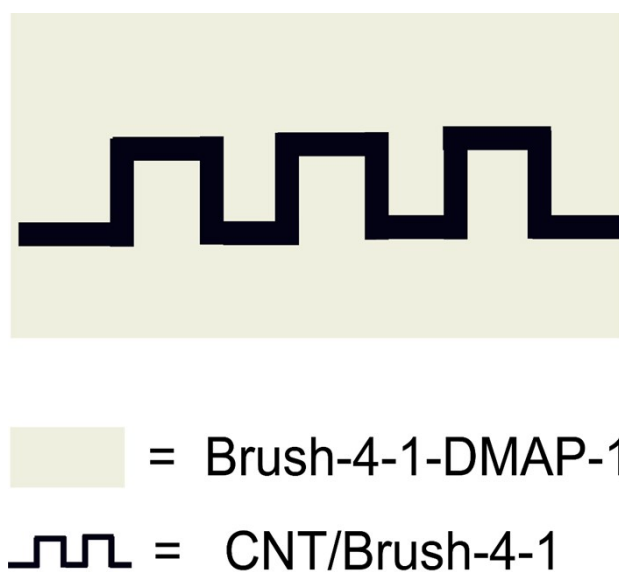
**Figure S18.** The cycles of the cutting– healing process of the strain sensor’s resistance.



**Figure S19.** The self-healed strain sensor could sustain more than six times stretching. I ) The original strain sensor; II ) cut off the strain sensor; III) The self-healed strain sensor after healing at room temperature for 24h; IV) Stretch the self-healed strain sensor.



**Figure S20.** Relative resistance versus time for tapping the sensor cyclically attached to the keyboard.



**Figure S21.** Schematic diagram of a sensor with a special pattern.

### Supplementary References

1. A. M. Hanlon, R. Chen, K. J. Rodriguez, C. Willis, J. G. Dickinson, M. Cashman and E. B. Berda, *Macromolecules*, 2017, **50**, 2996-3003.

2. G. Liu, Z. Liu, N. Li, X. Wang, F. Zhou and W. Liu, *ACS Appl Mater Interfaces*, 2014, **6**, 20452-20463.
3. Z. M. Wang, H. Nie, Z. Q. Yu, A. J. Qin, Z. J. Zhao and B. Z. Tang, *J Mater Chem C*, 2015, **3**, 9103-9111.