Supporting Information For

# **Self-Healable Gradient Copolymers**

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# Materials

All reagents used for synthesizing 3-bicyclo[2.2.1]hept-5-en-2-ylmethyl-1-decyl-3H imidazolium bis(trifluoromethylsulfonyl) amide (BDI) were obtained from Sigma-Aldrich Chemical Co. and used as received without further purification unless otherwise indicated. Dichloromethane was purified by the MBraun solvent purification system. Ethyl vinyl ether (stabilized with 0.1% N,N-diethyl aniline) was purchased from Alfa Aesar. The Grubbs third generation catalyst (**G3**) was synthesized according to the method reported previously.<sup>S1-S3</sup> *Exo*-1,4,4a,9,9a,10hexahydro-9,10(1',2')-benzeno-1,4-methanoanthracene (HBM) was synthesized according to previous report.<sup>S4-S6</sup> Artificial sweat solution is a potassium phosphate dibasic solution (1.0 M) purchased from Sigma-Aldrich (P8584).

# Methods

All manipulations of air- and/or moisture-sensitive compounds were carried out by using standard Schleck techniques or in an MBraun glovebox (MBraun, Germany) under a dry nitrogen atmosphere unless otherwise noted.

**The nuclear magnetic resonance (NMR) spectra:** The NMR spectra of monomers and polymers were recorded by a Bruker-400 MHz spectrometer (399.65 MHz for <sup>1</sup>H NMR and 125 MHz for <sup>13</sup>C NMR, respectively) at 25 °C.

**High-resolution mass spectra (HRMS):** HRMS measured by means of electron spray ionization (ESI) were recorded on a Bruker Daltonics mior OTOF-QII spectrometer.

Gel permeation chromatography (GPC) testing: Molecular weight and molecular weight distribution  $(M_w/M_n)$  values of polymer samples were determined by GPC. The GPC system used a Waters 515 HPLC pump and a Waters 2414 refractive index detector using two Visco GEL columns (I-MBHMW-3078 and I-MBLMW-3078, Viscotek) with dimethylformamide (DMF) containing 50 mM LiBr as the eluent at a flow rate of 1 mL/min at 40 °C.

**Thermogravimetric analysis (TGA):** TGA characterizations were performed from ambient temperature to 800 °C at the heating rate of 20 °C/min using the TA Instruments Q50 TGA.

**Dynamic mechanical analysis (DMA):** The DMA measurements were carried out on the rectangular samples  $(30 \times 5 \times 1 \text{ mm}^3)$  with TA Instruments Q800 in tension mode at a frequency of 1 Hz, an oscillatory amplitude of 15 µm, and a static force of 0.01 N. Samples were cooled to -60 °C and held for 2 min before being subsequently heated to 90 °C at a rate of 3 °C/min. Glass transition temperatures were determined from the peak values of tan $\delta$  vs. temperature curves.

**Transmission electron microscopy (TEM):** For TEM, ~100 nm thin cross-sections were sliced with the Leica EM FC7 cryo-ultramicrotome using a diamond knife at -120 °C, significantly below the glass transition temperature of all samples. High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images were obtained by a JEOL JEM-ARM200F microscope incorporated with a spherical aberration correction system for STEM.

**X-ray scattering measurements:** X-ray scattering for polymer films were performed on a Nano-inXider with Cu K $\alpha$  radiation ( $\lambda$ = 1.54 Å) at 25 °C. The generator was operated at 40 kV and 650 mA. The scattering intensity was collected with a twodimensional gas-filled wire detector (Bruker Hi-Star). The distance between the sample and detector was 938 mm (SAXS mode) or 79 mm (WAXS mode). 2D scattering patterns were analyzed using the Fit2D software. For each scattering frame, the exposure time was 300 s.

Atomic force microscopy (AFM): AFM images were recorded in tapping mode on a SPI3800N (Seiko Instruments Inc., Japan).

**Rheological testing:** Dynamic mechanical analyses were conducted using a discovery HR-2 rheometer. Polymer samples were placed under an 8-mm-diameter parallel plate with a gap of 0.8–2.0 mm. Storage moduli (G') and loss moduli (G") were measured in temperature dispersion tests in a range from 180 °C to 22 °C (5 °C/min) at a constant frequency of 10 rad/s with an applied strain ( $\gamma$ ) of 5.0–0.1%. Frequency sweep tests were conducted in a range from 628 rad/s to 6.28 × 10<sup>3</sup> rad/s at designated temperatures with an applied strain ( $\gamma$ ) of 0.05 or 0.1%.

**Mechanical property testing:** The tensile tests were performed with the Instron 5969 tensile testing machine. The synthesized polymer was compressed into the film with thickness of 1 mm and then cut into the dumbbell shape. Self-healing specimens were prepared by cutting the sample in two halves, gently pushing two interfaces together and letting the sample heal at the setting temperature for different durations. The original and healed samples were subjected to tensile measurement at the clamp speed of 100 mm/mm/min at room temperature (approximately 22 °C), where the initial sample length between clamps before stretching was 10 mm. Each measurement was repeated at least five times.

**Microwave radiation healing:** A microwave oven with an output of 1200W and a 220 V, 50 Hz power was used to impose microwave radiation to heal damaged polymer samples. This microwave oven could produce microwaves of up to 700 W, with a frequency of 2.45 GHz.

**Electrical testing:** The ionic conductivity of the material was measured using a BioLogic VMP3 with samples with an area of  $2.0 \text{ cm}^2$  and a thickness of 0.2 mm. The electrical current changes of the copolymer samples in a different state were obtained by B1500A semiconductor device analyzer (Keysight). The relative change of the

current is calculated:  $\Delta I/I_0 = (I - I_0)/I_0$ , where  $I_0$  and I are the current without and with applied strain, respectively. The gauge factor (GF) was calculated: GF = $\Delta I/I_0/\epsilon$ , where  $\epsilon$  was compressive strain.

#### Synthesis and polymerization

The synthesis of 3-bicyclo[2.2.1]hept-5-en-2-ylmethyl-1-decyl-3H-imidazolium bis(trifluoromethylsulfonyl)amide (endo:exo 80:20) (BDI): The synthesis of BDI was applied with a similar procedure according to previous report with some modifications.<sup>S7</sup> As shown in Scheme S1a, the synthetic procedure was described as below: 6.61 g (0.050 mol) of dicyclopentadiene and 21.63 g (0.200 mol) of 1-allylimidazole was charged into pressure flask. The mixture was stirred at 175 °C for 24 h. Excess 1-allylimidazole was removed under reduced pressure. Then the residual liquid was purified by silica gel chromatography with dichloromethane/methanol (100/1, v/v) as eluent. After spinning out solvent, brown oily liquid was obtained (7.66 g, 88% yield).

The brown oily liquid obtained as described above was dissolved in 100 mL of acetonitrile, and 19.46 g (0.088 mol) of 1-bromodecane was then added. After the reaction mixture was stirred and refluxed for 24 h, the solvent was removed. The residue was dissolved in water (200 mL) and extracted with diethyl ether (3×150 mL). The mixture was stirred overnight at room temperature after adding 1,1,1-trifluoro-n-[(trifluoromethyl)sulfonyl]-methane- sulfonamidlithiumsalt (LiTf<sub>2</sub>N) (13.90 g, 0.048 mol). Finally, the reaction solution was washed with dichloromethane (3×100 mL). The dichloromethane layer was then extracted with water (3×200 mL), dried with anhydrous magnesium sulfate, filtered, and concentrated to give monomer BDI as a brown yellow oil (yield: 22.22 g, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.83 (d, J = 23.9, 1H), 7.36 (ddd, J = 7.2, 4.0, 1.9, 2H), 6.47–5.87 (m, 2H), 4.46–3.73 (m, 4H), 3.07-2.42 (m, 3H), 2.09-1.72 (m, 3H), 1.61-0.52 (m, 20H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 8 139.3 137.5 135.9 135.6 135.2 130.9 124.6 122.6 122.4 121.4 118.2 115.1 55.0 54.1 50.2 49.6 44.9 44.1 42.5 42.0 39.9 31.8 30.7 30.1 29.9 29.4 29.3 29.2 28.8 26.1 22.6 14.1. HRMS (m/z): (posi.) found ( $M^+ = 315.2795$ ), calcd for  $C_{21}H_{35}N_2$ . ( $M^+$ = 315.2800). (nega.) Found (Tf<sub>2</sub>N<sup>-</sup> = 279.9174); calcd (Tf<sub>2</sub>N<sup>-</sup> = 279.9173).



**Scheme S1.** Synthesis of monomers and copolymers. (a) Imidazolium-functionalized norbonene monomer BDI. (b) Gradient copolymers. (c) Block copolymers.

The synthesis of gradient copolymers: The gradient polymers were synthesized through ring-opening metathesis polymerization (ROMP). As shown in Scheme S1b, a typical synthesis process was conducted as follows: under nitrogen atmosphere, the certain proportion of mixed monomers was dissolved in dry, degassed dichloromethane (15 mL) in a 100 mL glass reactor equipped with a magnetic stirrer. An appropriate amount of G3 was dissolved in dry, degassed dichloromethane (5 mL), and injected into the reactor. The reaction was stirred at room temperature. After 12 h, the reaction mixture was quenched by addition of excess ethyl vinyl ether and stirred for another 30 min. The obtained copolymers were precipitated in methanol/hexane mixture, collected and then washed twice by methanol/hexane mixture and dried under reduced pressure for 24 h at 40 °C.

The synthesis of block copolymers: As shown in Scheme S1c, a typical synthesis process was conducted as follows: under nitrogen atmosphere, the certain proportion of HBM monomer was dissolved in dry, degassed dichloromethane (10 mL) in a 100 mL glass reactor equipped with a magnetic stirrer. An appropriate amount of G3, dissolved in dry, degassed dichloromethane (5 mL), was injected into the reactor. The

reaction was stirred at room temperature. After HBM monomer was polymerized completely, confirmed by <sup>1</sup>H NMR spectroscopy, 10 mL of dichloromethane solution of the BDI monomer was added to the reaction mixture. After 12 h, the copolymerizations were terminated by addition of a few drops of ethyl vinyl ether and stirred for another 30 min. The obtained copolymers were precipitated in methanol/hexane mixture, collected and then washed twice by methanol/hexane mixture and dried under reduced pressure for 24 h at 40 °C.

### Results

<sup>1</sup>H NMR spectra of copolymers and determination of copolymers composition: ROMP has been proven to be a powerful and broadly applicable method for synthesizing ionic polymer materials.<sup>S8-S10</sup> A series of ROMP at different BDI and HBM molar ratios was carried out using the **G3**, which exhibited very high catalytic activity to produce well-defined polymers. <sup>1</sup>H NMR spectra analyses showed that the molar ratios of BDI and HBM incorporated into polymers agreed well with the initial feed ratios, implying that the monomers could be quantitatively converted into copolymers (Table S1 and Fig. S1-S8).

The copolymer compositions were determined by comparing the integrating of sterically hindered HBM and imidazolium BDI through <sup>1</sup>H NMR analysis. The resonances at  $\delta$  8.3-9.0 ppm (resonance a in Fig. S1-S8) were assigned to the proton of imidazolium in BDI, and protons of benzene ring in HBM were detected at  $\delta$  6.5-7.2 ppm (resonance b in Fig. S1-S8). The peak of unstrained double bonds in main chain appeared at  $\delta$  5.0-5.7 ppm (resonance c in Fig. S1-S8). The signals between  $\delta$  3.75-4.50 ppm were ascribed to the protons benzal directly connected norbornene skeleton and the protons adjacent to the imidazolium ring (signal d in Fig. S1-S8). There were 2 protons of double bonds per BDI repeat unit (m) and 2 protons of double bonds per HBM repeat unit (n) (see equation (S1)). There were 4 methylene protons peaks adjacent to norbornene skeleton and N of imidazolium (m) and 2 benzal directly connected norbornene skeleton (n), respectively (see equation (S2)).

The BDI:HBM composition ratios of polymers were calculated from the relative intensities of the specific protons using equations as below:

$$2m+2n = c_{1H \text{ NMR Integation}}$$
(S1)

 $4m+2n = d_{1H \text{ NMR Integation}}$ (S2)

Using the above two equations could calculate m and n, the BDI:HBM block composition ratios (m, n) were quantified for each sample as below:

(1) BDI:HBM composition ratio for GCP-1 (Fig. S1):

2m + 2n = 1.544m + 2n = 3.01





**Fig. S1** <sup>1</sup>H NMR spectrum of GCP-1 and corresponding protons integrated for calculating BDI:HBM ratio.

(2) BDI:HBM composition ratio for GCP-2 (Fig. S2):



**Fig. S2** <sup>1</sup>H NMR spectrum of GCP-2 and corresponding protons integrated for calculating BDI:HBM ratio.





**Fig. S3** <sup>1</sup>H NMR spectrum of GCP-3 and corresponding protons integrated for calculating BDI:HBM ratio.

(4) BDI:HBM composition ratio for GCP-4 (Fig. S4):

2m + 2n = 2.76 4m + 2n = 4.89 $m : n_{calc.} = 3.38 : 1$ 



**Fig. S4** <sup>1</sup>H NMR spectrum of GCP-4 and corresponding protons integrated for calculating BDI:HBM ratio.

(5) BDI:HBM composition ratio for BCP-1 (Fig. S5):

2m + 2n = 1.324m + 2n = 2.58

 $m : n_{calc.} = 21 : 1$ 



**Fig. S5** <sup>1</sup>H NMR spectrum of BCP-1 and corresponding protons integrated for calculating BDI:HBM ratio.

(6) BDI:HBM composition ratio for BCP-2 (Fig. S6):

2m + 2n = 1.76 4m + 2n = 3.33 $m : n_{calc.} = 8.2 : 1$ 



**Fig. S6** <sup>1</sup>H NMR spectrum of BCP-2 and corresponding protons integrated for calculating BDI:HBM ratio.

(7) BDI:HBM composition ratio for BCP-3 (Fig. S7):





**Fig. S7** <sup>1</sup>H NMR spectrum of BCP-3 and corresponding protons integrated for calculating BDI:HBM ratio.

(8) BDI:HBM composition ratio for BCP-4 (Fig. S8):

$$2m + 2n = 2.69$$
  
 $4m + 2n = 4.74$   
 $m : n_{calc.} = 3.33 : 1$ 



**Fig. S8** <sup>1</sup>H NMR spectrum of BCP-4 and corresponding protons integrated for calculating BDI:HBM ratio.



**Fig. S9** Two-dimensional nuclear Overhauser effect spectroscopy (NOESY) spectra of (a) gradient GCP-4 copolymer and (b) block BCP-4 copolymer.

| nomopolym            |                                 |                                   |                       |                             |   |                 |
|----------------------|---------------------------------|-----------------------------------|-----------------------|-----------------------------|---|-----------------|
| sample <sup>a)</sup> | [BDI]:[HBM]:[ <b>G3</b> ]<br>b) | [BDI]/[HBM] <sub>nmr</sub><br>c)) | $M_{\rm n,theor.}$ d) | $M_{n,GPC} e^{)}$ (cal. PS) | $M_{ m w}/M_{ m n}$ <sup>e)</sup> (cal. PS) | <i>T</i> g (°C) |
| HP                   | 200:/:1                         | -                                 | 119000                | 82000                       | 1.36  | 20.6            |
| GCP-1                | 200:10:1                        | 21.00                             | 122000                | 89000                       | 1.26  | 27.9            |
| GCP-2                | 200:25:1                        | 8.11                              | 125000                | 92000                       | 1.25  | 37.7            |
| GCP-3                | 200:50:1                        | 3.98                              | 132000                | 97000                       | 1.29  | 52.5            |
| GCP-4                | 200:60:1                        | 3.38                              | 135000                | 98000                       | 1.29  | 63.0            |
| BCP-1                | 200:10:1                        | 21.00                             | 122000                | 90000                       | 1.37  | 26.2            |
| BCP-2                | 200:25:1                        | 8.20                              | 125000                | 95000                       | 1.33  | 27.7            |
| BCP-3                | 200:50:1                        | 4.07                              | 132000                | 99000                       | 1.40  | 28.0            |
| BCP-4                | 200:60:1                        | 3.33                              | 135000                | 100000                      | 1.42  | 36.7            |

**Table S1.** Results of ring-opening metathesis polymerization (ROMP) for homopolymer and copolymers.

<sup>a)</sup> Ring-opening metathesis polymerization (ROMP) to give copolymers with different HBM contents; <sup>b)</sup> the feed molar ratio of BDI, HBM and **G3**; <sup>c)</sup> molar ratio of BDI and HBM in polymers through <sup>1</sup>H NMR spectra; <sup>d)</sup> the  $M_{n,theor.}$  was calculated from the <sup>1</sup>H NMR based BDI:HBM molar ratios and the polymerization monomer-to-catalyst ratios; <sup>e)</sup> the measured  $M_n$  and  $M_w/M_n$  of polymer samples with linear PS standards by GPC using N,N-dimethylformamide containing 50 mM of LiBr as the eluent; <sup>f)</sup>  $T_g$  was determined according to the peak values in tan $\delta$  curves *via* DMA tests.

#### **Reactivity ratios of copolymerization**

Copolymerization of BDI and HBM using the **G3** was performed in dichloromethane at room temperature with various monomer feed compositions (<10% conversion). The reactivity ratios could be obtained by using Equation (S3) (the Fineman–Ross method), for which the reactivity ratio of HBM ( $r_{\rm HBM}$ ) was the negative value of the slope and reactivity ratio of BDI ( $r_{\rm BDI}$ ) was the intercept.

$$(f-1)/F = -r_{\text{HBM}} \times f/F^2 + r_{\text{BDI}} \tag{S3}$$

here *f* refers to the ratio of HBM and BDI compositions in polymers, respectively; *F* refer to the ratio of the feed compositions of HBM and BDI monomers. The values of various parameters for calculating reactivity ratios of HBM and BDI were summarized in Table S2. Fig. S10 showed the plots of (f-1)/F versus  $f/F^2$ . From data fitting by the least-squares regression, the obtained reactivity ratios of BDI  $(r_{BDI})$  and HBM  $(r_{HBM})$  were 0.11 and 1.50, respectively. The value  $r_{BDI} \times r_{HBM} = 0.16$ , being less than 1, indicating that the copolymers synthesized using G3 have gradient composition distributions

| Entry <sup>a)</sup> | $M_{\rm BDI}$ | $M_{\rm HBM}$ | $M_{\rm BDI}$ | $m_{\rm HBM}$ | $F^{\mathfrak{b})}$ | <i>F</i> <sup>c)</sup> | $f/F^2$ | (f-1)/F |
|---------------------|---------------|---------------|---------------|---------------|---------------------|------------------------|---------|---------|
| 1                   | 0.200         | 0.800         | 0.515         | 3.555         | 0.250               | 0.145                  | 2.316   | -3.419  |
| 2                   | 0.299         | 0.701         | 0.380         | 1.595         | 0.426               | 0.238                  | 1.311   | -1.787  |
| 3                   | 0.498         | 0.502         | 0.395         | 0.870         | 0.990               | 0.454                  | 0.463   | -0.551  |
| 4                   | 0.703         | 0.297         | 0.570         | 0.780         | 2.366               | 0.731                  | 0.131   | -0.114  |
| 5                   | 0.201         | 0.799         | 0.730         | 0.755         | 3.961               | 0.967                  | 0.062   | -0.008  |

Table S2. Various parameters for calculating reactivity ratios of HBM and BDI.

<sup>a)</sup> Copolymers obtained at low conversion (<10%) from different monomer feed compositions; <sup>b)</sup> F,  $M_{BDI}/M_{HBM}$ ,  $M_{BDI}$  and  $M_{HBM}$  refer to the feed compositions of BDI and HBM monomers, respectively; <sup>c)</sup> f,  $m_{BDI}/m_{HBM}$ , and  $m_{BDI}$  and  $m_{HBM}$  refer to BDI and HBM compositions in polymers, respectively.



**Fig. S10** Plots of (f-1)/F versus  $f/F^2$  with least-squares regression line for BDI and HBM copolymerization.

# Dynamic mechanical analysis (DMA)



**Fig. S11** DMA traces of (co)polymers. (a) HP. (b) GCP-1. (c) GCP-2. (d) GCP-3. (e) GCP-4. (f) BCP-1. (g) BCP-2. (h) BCP-3. (i) BCP-4.

#### Thermogravimetric analyses (TGA)



**Fig. S12** TGA curves of (co)polymers in nitrogen. (a) HP. (b) GCP-1. (c) GCP-2. (d) GCP-3. (e) GCP-4. (f) BCP-1. (g) BCP-2. (h) BCP-3. (i) BCP-4.

The TGA results of Fig. S12 showed that the (co)polymers exhibit rather good thermal stability below 300 °C in nitrogen atmosphere.<sup>S11, S12</sup> Two decomposition stages were observed as further increasing the temperature. The first decomposition stage (320-370 °C) was attributed to decomposition of HBM units and the second one (370-470 °C) was corresponding to degradation of the remained segments in polymers.



**Fig. S13** AFM images. (a) height and (b) phase image for GCP-3 film surface; (c) height and (d) phase image for BCP-3 film surface.

#### X-ray scattering testing



**Fig. S14** (a) Small angle X-ray scattering intensity as a function of scattering wave vector q for the gradient copolymers, block copolymers and HP at room temperature; X-ray scattering intensity as a function of scattering wave vector q for (b) block copolymers and (c) gradient copolymers and homopolymer.

For block copolymers, diffraction peak was also not detected at the low content of HBM unit (< 11.1 mol%). However, by increasing the weight fraction of HBM unit, mcirophase separation was observed.

| _ |                      |              |   |                          |                          |                        |  |
|---|----------------------|--------------|---|--------------------------|--------------------------|------------------------|--|
|   | Sample <sup>a)</sup> | HBM<br>(wt%) | Young's<br>modulus<br>(MPa) <sup>b)</sup> | Yield<br>stress<br>(MPa) | Breaking<br>stress (MPa) | Breaking<br>strain (%) | Toughness<br>(MJ m <sup>-3</sup> ) <sup>c)</sup> |
|   | HP                   | 0            | 7.53±0.73                                 | -                        | $1.80{\pm}0.02$          | 1909±37                | 12.7   |
|   | GCP-1                | 2.2          | 22.00±1.14                                | $0.66 \pm 0.04$          | 2.80±0.15                | 1402±34                | 25.0   |
|   | GCP-2                | 5.4          | 67.68±4.61                                | 2.01±0.05                | 4.65±0.32                | 1087±26                | 29.8   |
|   | GCP-3                | 10.2         | 176.64±7.54                               | 7.39±0.50                | $6.67 \pm 0.05$          | 637±12                 | 33.2   |
|   | GCP-4                | 12.0         | 285.97±5.67                               | 16.24±0.43               | 6.19±0.12                | 400±18                 | 29.9   |
|   | BCP-1                | 2.2          | 15.38±1.02                                | -                        | 4.50±0.14                | 1430±29                | 21.4   |
|   | BCP-2                | 5.4          | 27.04±2.04                                | -                        | 4.79±0.13                | 1120±9                 | 25.3   |
|   | BCP-3                | 10.2         | 81.10±5.50                                | -                        | 5.54±0.18                | 976±27                 | 27.1   |
|   | BCP-4                | 12.0         | 135.20±5.74                               | -                        | 4.81±0.11                | 835±20                 | 26.2   |

### Mechanical properties

**Table S3.** Mechanical properties of homopolymer and copolymers.

<sup>a)</sup> Strain rate = 100 mm min<sup>-1</sup>, room temperature; <sup>b)</sup> Young's modulus, calculated from the initial slope of stress-strain curves (strain < 5%); <sup>c)</sup> Toughness was calculated from the area of the curve of stress *vs* strain.



**Fig. S15** Stress-strain curves of the virgin and recovery GCP-1 sample undergoing large strain of 1000%. The recovery is at 25 °C for 24 h.



**Fig. S16** Plots of *G*', *G*", and tan  $\delta$  (*G*"/*G*') values. (a) HP. (b) GCP-1. (c) GCP-2. (d) BCP-1 recorded during the temperature dispersion tests in a range from 180 to 25 °C (5 °C/min) at a constant frequency ( $\omega$ ) of 6.28 rad/s and an applied strain ( $\gamma$ ) of 5.0%.

The temperature-dependent viscoelastic modulus of GCP-1 was performed at 180-25 °C (5 °C/min) at a constant frequency ( $\omega$ ) of 6.28 rad/s. Despite the fact that molecular weight of GCP-1 is less than 10<sup>5</sup> Da, a wide rubber plateau region, typical of long polymer chains upon being entangled, at around 50-80 °C was observed due to

the presence of ionic aggregates in addition to polymer entanglement.

## **Self-healing properties**

| Self-healing motifs           | Young's<br>Modulus (MPa) | Toughness<br>(MJ m <sup>-3</sup> ) | Repair condition            | Healing<br>efficiency of<br>elongation at<br>break (%) | Reference  |
|-------------------------------|--------------------------|------------------------------------|-----------------------------|--|------------|
| imidazoliums                  | 7.5                      | 12.7                               | 3 h at r.t.                 | 100  |            |
|                               | 22                       | 25                                 | 6 h at r.t.                 | 100  |            |
|                               | 67.7                     | 29.8                               | 50 h at r.t.                | 60   | This study |
|                               | 176.6                    | 33.2                               | 40 h at 50 °C               | 86   |            |
|                               | 286                      | 29.9                               | 18 h at 70 °C               | 100  |            |
| hydrogen bond                 | 26                       | 12.6                               | Overnight at 70<br>°C       | 100  | S13        |
|                               | 37.6                     | -                                  | 18 h at 45 °C               | 45   | S14        |
|                               | 35.7                     | -                                  | 24 h at r.t.                | 75   | S15        |
| olefin cross-metathesis       | 2.34                     | 11.1                               | 3 h at 50 °C                | >90  | S16        |
| Disulfides                    | 1.45                     | 26.9                               | 2 h at r.t.                 | 88.2   | S17        |
| Agar/HPAAm DN gels            | 0.1                      | 9.4                                | 24 h at r.t.                | 40   | S18        |
| polyelectrolytes<br>hydrogels | 5.4                      | 14.8                               | 12 h at r.t. <sup>1)</sup>  | 66   | S19        |
| boroxines                     | 182                      | -                                  | 12 h at 70 °C <sup>2)</sup> | 100  | S20        |
|                               | 112                      | -                                  | 18 h at r.t.                | 85   | S21        |
| Zn(OTf) <sub>2</sub> -PDMS    | 1.1                      | -                                  | 48 h at r.t.                | 76   | S22        |
| zinc-imidazole                | 41                       | 5.5                                | $2h_{ot} \pi t$             | > 05   | 522        |
| interactions                  | 30.7                     | 10.4                               | 5 fl at 1.t.                | 293  | 525        |
| acylhydrazone                 | 0.027                    | 14.1                               | 24 h at r.t.                | 85   | S24        |
| diselenide                    | 2.4                      | -                                  | 48 h at r.t. <sup>3)</sup>  | 72   | S25        |

**Table S4.** Comparisons of mechanical properties and repair capability of our ionic copolymers and previously reported materials.

<sup>1)</sup> with aid of saline solution, <sup>2)</sup> water-assisted self-healing, <sup>3)</sup> visible-light-induced self-healing.



**Fig.S17** Stress-strain curves of gradient copolymers with the same composition ratio (HBM = 20 mol%) but different molecular weight (Strain rate = 100 mm/mm/min).



**Fig. S18** Stress-strain curves of the original and healed polymer samples at different healing temperatures. (a) HP at room temperature. (b) GCP-1 at room temperature and 50 °C. (c) BCP-1 at room temperature. (d) GCP-2 at room temperature and 50 °C. (e) GCP-3 at 50 °C. (f) GCP-3 at 60 °C. (g) GCP-3 at 70 °C. (h) GCP-4 at 70 and 90 °C.



**Fig. S19** The stress-strain curves of gradient copolymer samples healed for different durations with microwave irradiation. (a) GCP-1. (b) GCP-2. (c) GCP-3. (d) GCP-4.



**Fig. S20** The relative current–time curve of GCP-1 polymer film for detecting stability in electric circuit (Voltage = 20V).



**Fig. S21** Temperature dependence of the ionic conductivities of ionic copolymers and homopolymer in the temperature range from 20 to 80 °C.

| Strain senser                     | Repair condition | response    | gauge factor  | cyclical   | Reference     |
|-----------------------------------|------------------|-------------|---|------------|---------------|
| Strain Senser                     | Repair condition | time        | gauge lactor  | stretching |               |
| Ionic copolymer                   | 6 h at r.t.      | 114 ms      | 3.0 within 5%<br>compressive<br>strain              | 7000       | This<br>study |
| Soft and hard<br>network hydrogel | 5 min at r.t.    | -           | 0.478 in a<br>amplitude<br>deformation of<br>0-200% | 200        | S26           |
| ternary polymer composite         | 24 h at r.t.     | 50 ms       | 11.6 within<br>100% strain                          | 1500       | S27           |
| MWCNT/TPE smart coating           | no healing       | 8 ms        | 15.6 within 6%<br>strain                            | 5000       | S28           |
| carbonized silk<br>fabric         | no healing       | 70 ms       | 9.6 within 250% strain                              | 10000      | S29           |
| SWCNT/hydrogel                    | 60 s at r.t.     | -           | 0.24 within 100% strain                             | 700        | S30           |
| Carbon nanotube<br>fiber          | no healing       | 10-12<br>ms | 0.56 within 200% strain                             | 10000      | <b>S</b> 31   |

Table S5. Summary of performance parameter of current strain sensors reported.

### **Illustration of Supporting Movies**

Movie S1. Repeated jabbing of GCP-1 samples.

*Movie S2.* large stretchability of the notched GCP-1 sample at a deformation rate of 100 mm/mm/min.

*Movie S3.* Repeated mending ability of the GCP-1 sample under the water.

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