# Supporting Information

# Super tough and strong self-healing elastomers based on polyampholytes

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### **Supporting Information**

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#### **Experimental Section**

#### Material and methods

**Materials:** Butyl acrylate (BA, > 99.0%, TCI, stabilized with Hydroquinone monomethylether), acrylic acid (AA, > 99.0%, TCI, stabilized with Hydroquinone monomethylether), 2-(dimethyl amino)-ethyl methacrylate (DMAEMA, 99%, Adams, stabilized with Hydroquinone monomethylether), methyl benzoate (MB, 99% +, Adams), ethyl acetate, n-hexane , petroleum ether and methyl alcohol were purchased from Tansoole.com (China). 2, 2-azobisisobutyronitrile (AIBN) was obtained from Kermel (China). The reactants were used without further purification except BA, which was filtrated through a basic alumina column to remove the inhibitor. Carbon nanotube (CNT) (Nanocyl<sup>TM</sup> NC7000) was purchased from Nanocyl SA, Belgium.

**Synthesis**: The elastomers were synthesized by one-pot free-radical copolymerization of BA, AA and DMAEMA. In a typical process, 17.94 g (0.07 mol) of BA, 2.16 g (0.015 mol) of AA, 4.72 g (0.015 mol) of DMAEMA, a bit of AIBN and 2.04 g (0.015 mol) of methyl benzoate (as an internal standard for NMR tests) were firstly dissolved in 50 ml ethyl acetate then poured into a 250 ml there-neck round-bottom flask equipped with a magnetic stirrer and an economical allihn condenser. The mixture was bubbled with argon for at least 20 minutes to remove oxygen then stirred at 70 °C for 8 h under argon atmosphere to polymerize the monomers. After the polymerization, the product was precipitated in n-hexane or petroleum for at least three times. Finally, the product was dried at 40 °C in a vacuum oven to constant weight. The molecular weight was measured by gel permeation chromatography (GPC) with dimethylformamide (DMF) as the eluent. The synthetic scheme and results are shown in Scheme S1 and Table S1, respectively.

**Film preparation:** In a typical process, 4 g of HiSHE-27 was dissolved in 100 ml methanol, and then the solution was poured into a square Teflon mold. After the solvent was slowly evaporated at room temperature, the sample was put into a vacuum oven at 40 °C for 24 hours. The resulting transparent or slightly turbid film was shown in Fig. 1d.

**Fabricating strain sensor:** 0.02 g CNT was added into 5 ml methanol. The mixture was stirred for 1 hour and sonicated for 0.5 hour. At the same time, 1 g HiSHE-27 was dissolved in 20 ml methanol. After complete dissolution of HiSHE-27, the two objects were blended and sonicated for 1 hour to form a conductive ink, in which the CNT exhibited stable dispersion with the aid of HiSHE-27 molecules after 7 months (Fig. S15). Based on this fact, the inks with different CNT contents (the CNT content was defined as the mass of CNT divided by the mass of HiSHE-27) were made. Then the ink was sprayed onto a rectangular matrix (pure HiSHE-27) by a medicine spray bottle to form a thin conductive layer with 30  $\mu$ m in thickness. After drying in a vacuum oven for about 4 hours to remove the solvent, another rectangular matrix (pure HiSHE-27) was covered onto the conductive layer. Then a hot compression process was applied at 60 °C for 10 min to ensure a good connection between the layers. As a result, a sandwich shaped strain sensor with self-healing and shape-memory properties was fabricated (Fig. 4f and Fig. S14).

For monitoring human motions, the ink with 2 wt% CNT was sprayed onto a Teflon membrane by the medicine spray bottle. After drying in a vacuum oven for 4 hours to remove the solvent, the conductive layer was tailored and attached to a HiSHE-10 film to fabricate a flexible strain sensor for monitoring human motions.

We chose HiSHE-27 to fabricate the strain sensor based on two reasons: (1) CNTs can be distributed more homogenously in HiSHEs with high molar ratio of ionic monomers, and thus can construct a more stable conductive network; (2) the HiSHE-27 is more flexible than the HiSHE-37 and HiSHE-60, which is critical to fabricate strain sensor.

#### **Measurements and methods**

**Fourier transform infrared spectroscopy (FTIR):** FTIR spectra were recorded using Thermo Scientific Nicolet iS50 FTIR by an attenuated total reflection mode at room temperature. The on-line tracing of ionic bonds is conducted through the transmission mode at room temperature. The wavenumber scale was from 4000 cm<sup>-1</sup> to 650 cm<sup>-1</sup>

Nuclear Magnetic Resonance (NMR): <sup>1</sup>H NMR spectra were measured on an Advance III

HD 400 MHz spectrometer (Bruker).  $CDCl_3$  ( $\delta$  (<sup>1</sup>H) = 7.27 ppm),  $CD_3OD$  ( $\delta$  (<sup>1</sup>H) = 3.11ppm and 4.87 ppm) and DMSO ( $\delta$  (<sup>1</sup>H) = 2.5 ppm) were used as the solvents.

The molar fractions of BA, AA and DMAEMA in the final products were obtained by calculating the difference of monomer contents before and after the polymerization with MB as the internal standard. The results were shown in Fig. S1.

**Differential scanning calorimeter (DSC):** Heat flow curves of HiSHEs were obtained on Q2000 (TA instrument) with the mass of all samples ranging from 3 mg to 8 mg. The sample was firstly heated from 25 °C to 170 °C and then cooled from 170 °C to -70 °C at a cooling rate of 20 °C/min to eliminate the thermal history. Afterwards, the heat flow was recorded from -70 °C to 150 °C at a heating rate of 10 °C/min. The glass transition temperature (Tg) of the sample was defined as the inflection point of the heating curve, and the results were shown in Fig. S7 and Table S1.

**Dynamic mechanical analysis (DMA):** Dynamic mechanical and shape-memory properties were measured on Q800 (TA Instrument) in a tension mode. The rectangle samples with 20 mm in length, 7 mm in width, about 1 mm in thickness were heated from -60 °C to 170 °C at a heating rate of 3 °C/min. Dynamic mechanical properties were acquired using a frequency of 1 Hz and a preload force of 0.01 N.

The shape memory behavior was examined by a controlled force mode. For all the samples, the thermal history was removed at 90 °C for 10 min. Both the heating and cooling rates were 3 °C/min.

To test the dual-shape memory behavior, a typical procedure was set as follows: Step 1: the sample of HiSHE-60 was heated to 90 °C and kept isothermally for 5 min, and then it is stretched to a set stress of 0.08 MPa in 2 min; step 2: the sample was cooled to 25 °C followed by unloading and isothermal treatment for 10 min to fix the temporary shape; step 3: the sample was heated to 90 °C and kept isothermally for 30 min for the recovery. This process was carried out for 3 times with different set stresses, including 0.08 MPa for the first cycle, 0.12 MPa for the second cycle and 0.14 MPa for the third cycle.

To test the multi-shape memory behavior, the procedure was set as follows: Step 1: the sample of HiSHE-37 was kept at 90 °C isothermally for 5 min; step 2: the sample was stretched to a set stress of 0.027 MPa in 1 min followed by cooling to 0 °C and held under this stress for 10 min; step 3: the sample was unloaded in 1 min and kept isothermally for 10 min to fix the temporary shape; step 4: the sample was heated to 90 °C in a step-wise manner with a step interval of 15 °C. During each step interval, the sample was isothermally held for 30 min to allow shape recovery.

**Atomic force microscopy (AFM):** Sample preparation: In a typical procedure, HiSHE-27 was dissolved in methanol with a concentration of 0.2 mg/ml. The solution was spin-coated on a silicon slice using a spin coater (KW-4A). The silicon slice was then placed in a vacuum oven at 40 °C for 5 hours to completely dry the sample.

AFM phase maps and force mapping were carried out on an AIST-NT SPM SmartSPMTM-1000 in a tapping (AC) mode with a spring constant of 70 N/m and a resonance frequency of 289.09 kHz. DMT Modulus maps were measured in (QNM) mode. The samples were probed and their force curves were acquired. Yong's modulus was derived from these force curves according Derjaguin, Muller Toropov. (DMT) model.

**Tensile test:** Tensile experiments were performed on an Instron 5967 tensile tester. Uniaxial tensile measurements were carried out in air at room temperature with a strain rate of  $0.067 \text{ s}^{-1}$ . The dumbbell shaped samples were cut using a normalized cutter. The dumbbell shaped samples have a central part of 20mm in length, 4 mm in width and 0.3-1 mm in thickness.

Cyclic tensile tests were also performed on the same machine at the strain rate of 0.067 s<sup>-1</sup>. For each sample, three incremental maximum strains were selected. Stress-strain curves during the loading and unloading processes to each maximum strain were recorded for three times.

Fracture tests were also measured on the same machine with the method of single edge notch test. A rectangular sample of HiSHEs (30 mm in length, 5mm in width and 0.3-1 mm in thickness) was cut with a razor blade to make a notch of 1 mm length in the middle of the

sample. The sample was fixed on the two clamps of tensile tester with a pre-set distance of 20 mm, and then subjected to uniaxial tension with a strain rate of 0.005 s<sup>-1</sup>. Another un-notched sample with the same dimensions was also tested under the same conditions.

**Polarizing optical microscopy (POM):** The cross-section of sandwich shaped sensor was observed using a polarizing optical microscopy (Olympus BX-51) in air. A slice of specimen was obtained by a razor blade and placed on the glass slide; then photographs of the cross-section were acquired with the aid of a digital camera Olympus DP-27.

**Electro-mechanical measurements:** Electro-mechanical tensile measurements were performed on a Keithyley 6487 in a resistance mode assisted with a tensile tester (SANS CMT 4503). The set voltage and electric current were 1V and 25 mA, respectively. The data of resistance versus time were recorded by the software of Keithyley 6487 test system and meanwhile the data of strain versus time were recorded by the SANS tester software.

For the electro-mechanical tensile tests, a sandwich shaped sensor with 50 mm in length, 5 mm in width and 1.5 mm in thickness was painted with conductive silver paint on both ends to form electrodes of 5 mm in length. After 10 min evaporation of the solvent, the electrodes were clamped with two conductive clips. The conductive clips were used as electrical contacts and attached to the Keithyley 6487 via wire leads. Then, the conductive clips were fixed between two clamps of the tensile tester with an initial distance of 25 mm. Subsequently, the sample was stretched at a rate of 2 mm/min until mechanical failure.

The electro-mechanical cyclic tensile tests were carried out at the tensile rate of 2 mm/min. Two sandwich shaped strain sensors were prepared. One of them was stretched to 150% of the original length at 90 °C and then fixed at the temporary shape at 20 °C for 1 h. Both the original sample and the temporally fixed sample were clamped onto the tensile tester and stretched from 0% to 8% for 200 circles.

#### **Theoretical calculation**

Strain energy density  $(U_T)$ : The strain energy density upon failure  $(U_T)$  was calculated by the integrated area below the stress-strain curves as illustrated by the following equation:

$$U\mathbf{T} = \int_{0}^{\sigma_{h}} \sigma \, d\varepsilon$$

where the  $\sigma$  stands for the stress;  $\varepsilon$  stands for the strain.  $\sigma_b$  is the fracture stress.

**Fracture energy (Gc):** The fracture energy of elastomers was calculated using the classic equation developed by Greensmith,<sup>[1]</sup> as follows:

$$Gc = \frac{6WC}{\sqrt{\lambda c}}$$

where the W stands for the strain energy density integrated from the stress-strain curve of unnotched sample before the  $\lambda c$  ( $\lambda c = \varepsilon + 1$ ); C stands for the length of the notch of the notched sample;  $\varepsilon$  stands for fracture strain of notched sample.

**Energy dissipation efficiency:** The cyclic tension was carried out to study the energy dissipation of HiSHEs. The energy dissipation efficiency was defined as the ratio between the integrated area in the hysteresis loop and that under the loading curve, as illustrated by the following equation:

$$Energy \ dissipation \ efficiency = \frac{\int_{0}^{\sigma_{max}} \sigma d\varepsilon - \int_{0}^{\sigma_{max}} \sigma d\varepsilon}{\int_{0}^{\sigma_{max}} \sigma d\varepsilon}$$
$$\int_{0}^{\sigma_{max}} \sigma d\varepsilon \\ loading \\ loading$$

where the  $\sigma$  stands for the stress;  $\varepsilon$  stands for the strain;  $\sigma_{max}$  is the stress at the maximum strain.

**Self-healing efficiency:** The self-healing efficiency was calculated by the ratio between fracture stress of cut sample and that of uncut sample, as follows:

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

where the  $\sigma_{cut}$  stands for the fracture stress of cut sample and  $\sigma_{uncut}$  is the fracture stress of uncut sample

The shape fixity (Rf) and recovery (Rr): The shape fixity ratio and shape recovery ratio were defined as follows

$$Rf(N) = \frac{\varepsilon_{ul}(N) - \varepsilon_{ul}(N-1)}{\varepsilon_l(N) - \varepsilon_{ul}(N-1)}$$
$$Rr(N) = \frac{\varepsilon_{ul}(N) - \varepsilon_r(N)}{\varepsilon_{ul}(N) - \varepsilon_r(N-1)}$$

where the N is the serial number of the shape;  $\varepsilon_{ul}$  stands for the fixing strain after cooling and unloading;  $\varepsilon_l$  is the strain after loading.  $\varepsilon_r$  stands for the recovery strain after heating;

**Gauge factor (GF):** The sensitivity of the electrical property was determined by the gauge factor and shown as follows:

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

where  $\Delta R$  stands for the change in resistance when deformed.  $R_0$  is the resistance of original sample.  $\Delta L$  stands for the change in length;  $L_0$  is the original length of the sample before stretching.

#### Discussions

The strain dependency of HiSHE-23 is demonstrated in Fig. S16. The samples are stretched at different strain rate respectively at 400 mm/min, 100 mm/min and 50mm/min. Since the HiSHEs have multi-strength ionic aggregates, the stress-strain curves show obvious strain rate dependency. The higher of the strain rate, the stiffer samples show. Which indicate the highly viscoelastic of HiSHEs.

The single-edge notch test is carried out to detect the toughness of HiSHEs. During the process of stretching, the sample changes from transparent to white when the deformation comes near the breaking strain. After the breaking, the phenomena of white disappears. This is the same to "macro-craze" found in Wu's research.<sup>[2]</sup> The "macro-craze" is observed in the samples when the molar fraction of ionic monomers is equal to or higher than 23% when

stretched; indicating a good energy dissipation.

## References

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## Supplementary figures



Scheme 1. The synthesis of HiSHEs.

Sample	Content of ionic monomers in HiSHEs	Mn (g/mol)	PDI	<i>Tg</i> ⁰C
	$(\frac{n_{anion} + n_{cation}}{n_{total}})$			
PBA	0/100	348160	2.07	-46.78
BA-AA-DM-10	10.2/100	86235	2.73	-29.63
BA-AA-DM-14	14.0/100	23557	3.32	-23.48
BA-AA-DM-19	19.0/100	72784	2.27	-14.64
BA-AA-DM-23	22.8/100	45950	2.52	-0.41
BA-AA-DM-27	27.0/100	63281	2.35	10.76
BA-AA-DM-37	37.0/100	44700	2.21	11.76 (96.16)
BA-AA-DM-60	59.4/100	20648	1.66	15.04 (98.47)

Table 1. The formula for HiSHEs



Figure S1. (a) <sup>1</sup>H NMR spectra of monomers before (red line) and after (black line) copolymerization. MB is an internal standard. (b) <sup>1</sup>H NMR spectrum of HiSHE-19.



Figure S2. a) Photographs of the mixture of AA and DMAEMA with different molar ratios taken after 3 months in the air. As shown in the picture, salt is formed in the mixture, indicating ionic bonds are formed between AA and DMAEMA. The quantity of the salt reaches a maximum when the AA/DMAEMA molar ratio is 1:1. b) The tensile stress versus the molar ratio of AA to DMAEMA for HiSHEs with the molar fraction of BA fixed at 70% (the samples are stored in desiccator for 1 month). It is shown that the tensile stress of the sample with a AA/DMAEMA molar ratio of 1:1 is the highest, indicating that this molar ratio is the best ratio for the mechanical properties.



Figure S3. Ionic bond in HiSHEs a) FTIR spectra of HiSHE-60, PBA, poly(BA-AA) and poly(BA-DMAEMA). Compared with PBA, poly(BA-AA) and poly(BA-DMAEMA), a transmission peak at 1580cm<sup>-1</sup> appears in HiSHE-60, which is the COO<sup>-</sup> antisymmetric stretching vibration of ionized COOH due to the ionic interaction between AA and DMAEMA.<sup>[3]</sup> (the position of ionic peak in HiSHEs (1580cm<sup>-1</sup>) is different from that in monomers mixtures (1594cm<sup>-1</sup>) because the test modes are different. The former is attenuated total reflection mode and the latter is transmission mode). b): FTIR spectra of HiSHEs with different molar fractions of ionic monomers. The intensity of transmission peak at 1580cm<sup>-1</sup> increases with the increase of molar fraction of ionic monomers.



Figure S4. (a) Height map and (b) the corresponding modulus map of HiSHE-27. (c) The corresponding modulus value at the points of A, B and C. The point of A represents the biggest aggregate, B is smaller and C is smallest. As shown in (b) and (c), the results indicate that the bigger aggregates tend to be stiffer (A, B), while the smaller ones are softer (C).



Figure S5. Storage modulus (a) and loss modulus (b) of HiSHEs and pure PBA. Compared with pure PBA, HiSHEs have much wider glass transition region.



Figure S6. (a) Width of glass transition (W`) of HiSHEs and PBA determined from DSC curves. Inset shows the definition of W. (b) Tg of PBA and HiSHEs. The Tg value increases with the increase of molar ratio of ionic monomer, indicating that more ionic interactions lead to stronger depression of molecular mobility. In addition, a new Tg manifests around 98 °C in HiSHEs with the molar fraction of ionic monomers higher than 27%, corresponding to the glass transition of the stiffest ionic aggregates in the samples.



Figure S7. AFM phase images of HiSHEs with different molar fraction of ionic monomers. With increasing molar fraction of the ionic monomers, the total number of ionic aggregates increases, also the big and stiff aggregates become more prevalent than the small and soft ones



Figure S8. The recovery ability of HiSHEs after deformation or fracture. (a) The relative length change versus time of HiSHEs after fracture. L0 is original length of sample, L is the length after fracture. (b) Photographs of recovery process of HiSHE-23 after the fracture, which shows that the sample can nearly recover to its original length after 60 min from its fracture length. (c) The recovery of mechanical property of HiSHE-23. The sample is stretched to 400 % and put in atmosphere. After 24 hours waiting, the sample is stretched to 400 % again. Because of the slightly hygroscopicity of ionic bonds, the tensile strength can not recover to the original at room temperature.



Figure S9. Photographs of single-edge notch tension process of HiSHE-37, which shows a crack blunting behavior under stretching.



Figure S10. Efficiency of energy dissipation of HiSHEs under various strains.



Figure S11. (a) Stress-strain curves of HiSHE-23 healed at 25 °C for different time. (b) The healing efficiency of HiSHE-23 healed at 25 °C for different time.



Figure S12. The strain versus temperature map of multiple shape memory of HiSHE-37. As we can see, the recovery process of multi-shape memory starts from 30 °C and these recovery stages demonstrate the multi-shape behavior exists in HiSHE-37.



Figure S13. Photos displaying the quadruple-shape memory process of HI-SHE-37 at different temperatures.



Figure S14. Polarizing microscope map of the sandwich shaped strain sensor. A is the layer of the pure HiSHE-27 and B is the layer of the CNT/HiSHE-27. The thickness of the CNT/HiSHE-27 layer is about 30µm.



Figure S15. CNT/HiSHE-27 ink stored for 7 months at room temperature; indicating a good distribution of CNTs in HiSHEs.



Figure S16. The strain-rate dependency of HiSHE-23. The samples are stretched with different strain rate.



Figure S17. The sample of HiSHE-23 before (a) and after (b) fracture when stretched, the "macro-craze" is observed in the samples when the molar fraction of ionic monomers is equal to or higher than 23% when stretched; indicating a good energy dissipation.