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Intrinsically Recyclable and Self-healable Conductive Supramolecular Polymer for Customizable Electronic Sensors

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1. Supplementary Methods

Materials. 2-ureido-4-[1H] pyrimidinone (Upy, 98%) and potassium acetate (99%) were purchased from Energy Chemical. Hexamethylene diisocyanate (HDI, 99%) and dibutyltin dilaurate (DBTDL) were provided by Aladdin Industrial Corporation. Ammonium persulfate(AR) and 2-hydroxy ethyl methacrylate (HEMA, 98%) were supplied by LYN (Beijing) technology Co. Ltd. 1-vinyl-3-thyl-imidazolium bromide ([VEIm][Br]) was obtained from Lanzhou Greenchem ILS, LIPC, CAS (Lanzhou, China). Sylgard-184 PDMS was purchased from Dow Corning Co. ABR ear impression silicone was commercially available on Taobao.com.

Synthesis of UPy-NCO. 2(6-Isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]-pyrimidinone (UPy-NCO) was synthesized as reported before[1] with the following procedure: 2-ureido-4-[1H]pyrimidinone (UPy, 1.0 equiv, 40 mmol, 5 g) was reacted with HDI (7.0 equiv, 280 mmol, 47 g) at 100 ^{o}C for 16 h under the protection of nitrogen. After hexane was added (100 mL), the resulting precipitate was filtered and washed with hexane (20 mL) for three times. The white powder was dried at 50 ^{o}C under vacuum. Yield: 92%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 13.14 (s, 1H), 11.89 (s, 1H), 10.21 (t, 1H), 5.84 (s, 1H), 3.29 (m, 4H), 2.25 (s, 3H), 1.65 (m, 4H), 1.43 (m, 4H).

Synthesis of UPy-HDI-HEMA. The synthesis of 2-(6-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl) ureido) hexylcarbamoyloxy) ethyl methacrylate (UPy-HDI-HEMA or UHH) was carried out according to a reported method.[2] UPy-NCO (5g, 17 mmol) and 2-hydroxy ethyl methacrylate (HEMA, 2.47g, 19 mmol) were dispersed in chloroform (50 mL). After stirring the mixture under nitrogen atmosphere for 5 min, a drop of DBTDL was added. The reaction was heated to 75 °C and stirred with reflux overnight. The cloudy suspension was precipitated into heptane and the resulting white powder was filtered and washed with hexane for three times. The product was dried at 50 °C under reduced pressure for 1 day. Yield: 89%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 13.15 (s, 1H), 11.88 (s, 1H), 10.15 (t, 1H), 6.15 (s, 1H), 5.86 (s, 1H), 5.60 (m, 1H), 5.0 (s, 1H), 4.34 (s, 4 H), 3.30-3.17 (m, 4H), 2.25 (s, 3H), 1.97 (t, 3H), 1.63 (m, 4H), 1.39 (m, 4H).

Synthesis of 1-vinyl-3-ethyl-imidazolium bromide ([VEIm][Ac]). [VEIm][Br] (24.36 g, 0.12 mol) and potassium acetate (11.76 g, 0.12 mol) were dissolved in 150 mL ethyl alcohol, respectively. One stock solution was dropwise added to the other and the mixture solution was stirred for 3 h. After cooling in -20 °C for 1 h, the mixture was filtered and the filtrate was rotary evaporated under low pressure. The crude product was cooled, filtered and rotary evaporated for several times, and a clear yellow liquid was obtained. Yield: 71%. ^{1}H NMR (DMSO, 400 MHz, ppm): δ 10.52(s, 1H), 8.32 (t, 1H), 8.02 (t, 1H), 7.49-7.43 (m, 1H), 6.08-6.03(m, 1H), 5.37-5.34(m, 1H), 4.27(m, 2H), 1.6(s, 3H), 1.44(t, 3H).

Synthesis of Poly(UHH-co-IL). 20% Poly(UHH-*co*-IL) was synthesized via copolymerization with the following procedure. UHH (4.23 g, 10 mmol) was added in [VEIm][Ac] (7.28 g, 40 mmol) and stirred in hot water bath until dissolving completely. Then, 0.5 wt.% ammonium persulfate (57.55 mg) was added and the mixture was subjected to polymerization at 75 °C under vacuum for 8h. Following the above procedure, Poly(UHH-*co*-IL) with different UHH molar ratio of 10%, 15% were obtained by changing the molar fraction of UHH.

Characterization. Thermogravimetric analysis (TGA) was measured on a TA INSTRUMENTS Q50. Samples were loaded on platinum pans and the temperature was ramped to 800 ^{o}C at a rate of 10 ^{o}C/min under nitrogen atmosphere. Five different samples include UPy-HDI-HEMA, [VEIm][Ac], 10%, 15% and 20% Poly(UHH-*co*-IL) were measured respectively according to above method. And the TGA results are shown on Fig. S5. TGA was also used to measure the dynamic solubility of Poly(UHH-*co*-IL) with 10%, 15% and 20% UHH in dimethylformamide (DMF) (Fig. S8). In detail, Poly(UHH-*co*-IL) samples with different UHH amounts were immersed in the same amount of DMF. Then, the DMF solution dissolving part of Poly(UHH-*co*-IL) at different soaking times was extracted for quantitative measurement of the polymer concentration.

Gel permeation chromatography (GPC) measurements were recorded on the breeze system (styragel columns), Waters Corporation (Milford, MA) with polystyrene as standard and dimethylformamide (DMF) as eluent. GPC results are supplied in Fig. S6.

Dynamic mechanical analysis (DMA) characterizations of Poly(UHH-*co*-IL) was conducted on a TA Q800 apparatus with a film tension clamp. The stress-strain curves were recorded at a strain rate of 0.1 N/min. And the temperature-sweeping modulus curves (Fig. 2c) were obtained at a constant frequency of 1 Hz and a temperature ramping rate of 2 ^{o}C/min from -20 to 80 ^{o}C.

ARES-G2 Rheometer (TA Instruments) was used to measure the viscosity of 10%, 15% and 20% Poly(UHH-*co*-IL) at different temperatures ranging from 30 ^{o}C to 60 ^{o}C. Measurements were performed with a gap spacing about 1 mm. And the procedure was Oscillation Temperature Sweep with fixed parameter including 1% strain and 10 rad/s angular shear frequency.

Temperature sensing tests of Poly(UHH-*co*-IL) sensor at a serials of fixed temperatures. Poly(UHH-*co*-IL) temperature sensor was fabricated as the following procedure. A thin polyethylene terephthalate (PET) film was served as the substrate on which two electrodes attached with 1 cm spacing. Then, 2mm thickness Poly(UHH-*co*-IL) slice with rectangular shape was put onto the PET substrate and connected with the two electrodes. The sensor was connected with CHI660e electrochemical workstation (Shanghai CH instrument Co. Ltd, China) and all electrical signals were measured via the impedance-time method. The thermal response of Poly(UHH-*co*-IL) sensor was monitored by alternatively switching it between two constant heating stages with testing temperature and room temperature. The interval of switching time was 2 minutes.

Fabrication and measurement of Poly(UHH-*co*-IL) thermal-sensing earplug. The detailed fabrication process of Poly(UHH-*co*-IL) thermal-sensing earplug includes the following steps:

i) Before taking an impression, the auditory canal and the eardrum have to be examined. The auditory canal has to be depilated and any wax or cerumen should be cleaned. After being protected with a cotton plug placed at the end of the external auditory canal in front of the eardrum, inject the ABR ear impression silicone slowly into the ear canal until the concha is filled completely. This step should be operated by professional technicians.

ii) After silicone curing, remove the impression carefully from the ear and cut the edge of the silicone impression in order to get a desired shape.

iii) Mixture of polydimethylsilioxane (PDMS) prepolymer and curing agent was prepared and poured into a pastic box. Then the silicone ear impression was immersed in PDMS mixture just below the liquid surface. After curing for 5h in 60 ^{o}C, the impression was carefully removed from PDMS.

iv) The Poly(UHH-*co*-IL) sample was cut into small pieces, and they were stuffed into PDMS mold followed with thermal treatment at 90 ^{o}C for 2h. After cooling, a Poly(UHH-*co*-IL) sample was obtained which matches the external auditory canal completely.

v) The prepared Poly(UHH-*co*-IL) sample have to be insulated with ear by coating two thin layers of polyethylene membrane (0.01 mm) between which two stripes of conductive tape was adhered for connecting the two end of this earplug thermometer. Then, the earplug thermometer was used to measure the ear canal temperature similarly following the method mentioned above.

Derivation of the relationship between thermal response and the viscosity change along with temperature change. In order to theoretically evaluate the thermal response of Poly(UHH-*co*-IL) as function of temperature change, a free-volume model was applied to clarify the sensing mechanism. According to the definition of thermal response based on the relative change of conductance, thermal response could be calculated as the function of the relative change of conductivity as well.

$$\frac{\Delta G_T}{G_{T_r}} = \frac{\sigma_T}{\sigma_{T_r}} - 1 \tag{1}$$

Where G_{T_r} and σ_{T_r} are the initial electrical conductance and conductivity at room temperature, respectively, and σ_T is the conductivity at a certain temperature.

Ionic conductivity in polymers could be considered as the transition of ions from one equilibrium position to another. Cohen and Turnbull have conceived a general theory for ionic transport phenomena. This theory suggests that statistical redistribution of the free volume opens up voids for diffusive displacement.[3, 4] Transport or diffusive occurs by the movement of an ion into a hole with a size greater than some critical value V^* which could be regarded as the volume of this ion. And then Miyamoto and Shibayama derived a simplified electrical conductivity equation which takes free volume into consideration and has been adopted generally to describe the conduction phenomena in polyelectrolyte.[5] The electrical conductivity σ_T is comprehensively expressed by Supplementary eq. 2:

$$\sigma_T = \sigma_0 exp\left[\frac{-rV^*}{V_f} + \frac{E_f + \frac{W'}{2\varepsilon}}{kT}\right] \tag{2}$$

Upon combining Supplementary eq. 1 with Supplementary eq. 2, Supplementary eq. 3 is obtained as below:

$$\frac{\Delta G_T}{G_{T_r}} = exp\left[rV^*\left(\frac{1}{V_{f,T_r}} - \frac{1}{V_{f,T}}\right) + \frac{E_f + \frac{W'}{2\varepsilon}}{k}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right] - 1 \tag{3}$$

Here, r is the numerical factor to correct the overlap of the free volume; V^* is a critical value similar to the volume of the ion; E_f means the energy barrier of ion transition; W' represents the ionic dissociation energy; ε is the dielectric constant and k is

Boltzmann's constant. V_{f,T_r} and $V_{f,T}$ are the free volume at room temperature and test temperature, respectively. Since the first six factors are constants in a certain systems or not sensitive within a narrow temperature region, it can be inferred that the thermal-sensing ability is only attributed to the free volume change under different temperature.

Owing to the difficulty of measuring free volume, viscosity was commonly tested for the determination of free volume. Doolittle developed an accurate equation for entangled polymer systems that defines viscosity as a simple function of relative free volume: [6]

$$ln\eta = B\left(\frac{V_0}{V_f}\right) + lnA \tag{4}$$

Combining Supplementary eq. 3 with Supplementary eq. 4, we can get the Supplementary eq. 5:

$$\frac{1}{V_{f,T_r}} - \frac{1}{V_{f,T}} = \frac{ln\eta_{T_r} - ln\eta_T}{BV_0} = \frac{1}{BV_0} ln\frac{\eta_{T_r}}{\eta_T} \tag{5}$$

where η is viscosity, V_0 is the total volume extrapolated to zero without change of phase, A and B are constants. η_{T_r} and η_T are the viscosity at room temperature and the test temperature, respectively. From Supplementary eq. 5, we find $\frac{1}{V_{f,T_r}} - \frac{1}{V_{f,T}}$ and $ln\frac{\eta_{T_r}}{\eta_T}$ has a positive relationship because $\frac{1}{BV_0}$ is a positive constant.

At last, viscosity-temperature behavior could be described via Arrhenius equation: [7]

$$\eta = \eta_0 exp\left(\frac{E^*}{RT}\right) \; or \; ln\eta = ln\eta_0 + \frac{E^*}{RT} \tag{6}$$

Combining Supplementary eq. 5 with Supplementary eq. 6, we can get the Supplementary eq. 7:

$$ln\frac{\eta_{T_r}}{\eta_T}=\frac{E^*}{R}\left(\frac{1}{T_r}-\frac{1}{T}\right) \tag{7}$$

Where η_0 is a constant; R is the gas constant; E^* is the flow activation energy. Since $\frac{1}{T_r}-\frac{1}{T}$ is invariable at certain temperature difference, $ln\frac{\eta_{T_r}}{\eta_T}$ and $\frac{1}{T_r}-\frac{1}{T}$ built a positive relationship:

$$\frac{\Delta G_T}{G_{T_r}}\propto\frac{E^*}{R}\left(\frac{1}{T}-\frac{1}{T_r}\right) \tag{8}$$

According these positive relationships, we draw a conclution that thermal response value are determined by the value of the $\frac{E^*}{R}$ which is the slope of viscosity change along with temperature change and a larger slope value can lead to better thermal sensitivity.

Calculation of independent-samples t-test. Independent-samples t-test was applied to check if a significant difference exists between the results measured by Poly(UHH-*co*-IL) sensor and IR thermal camera. At first, F-test should be required to check whether the two distributions have the same variance and the F value could be calculated as follows:

$$F=\frac{s_1^2}{s_2^2} \tag{9}$$

Where s_1 and s_2 are the standard deviation of two groups detected by IR thermal camera and Poly(UHH-*co*-IL) sensor, respectively. As calculated, the F value equals to

1.725 less than the critical value $F_{0.05}(4{,}4) = 6.39$, which means no significant difference between the two standard deviation.

After that, t-test could be operated as follows. It can be assumed that the two methods of temperature measuring have same accuracy. And t value could be figured out:

$$t = \frac{(\bar{x}_2 - \bar{x}_1)\sqrt{\frac{n_1 + n_2}{n_1 n_2}}}{\sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}}} \tag{10}$$

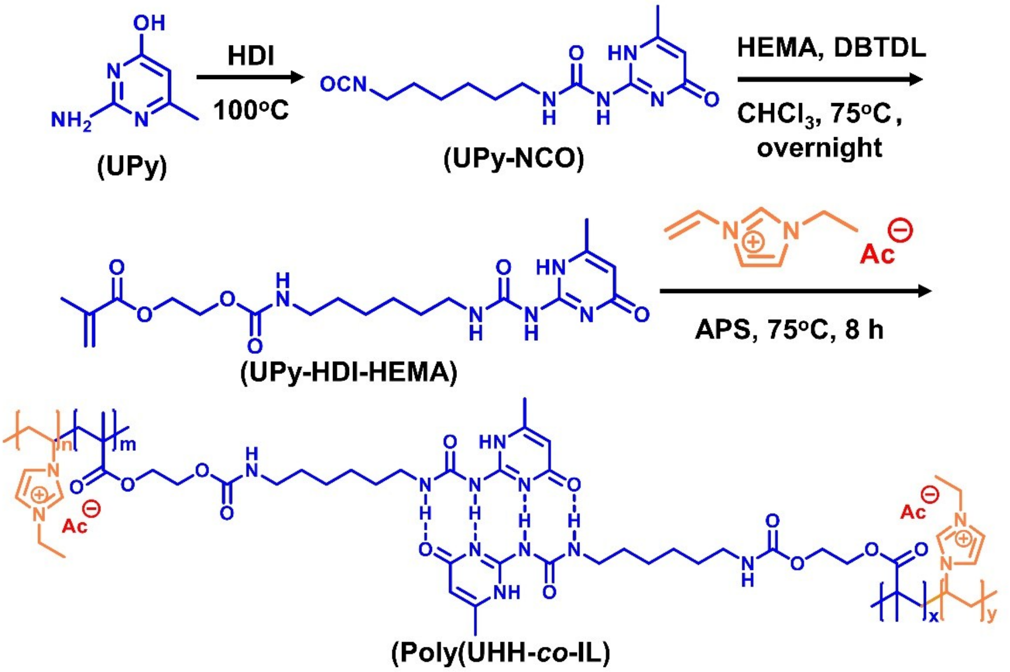
Where $\bar{x}_1$ and $\bar{x}_2$ are the mean value of temperatures detected by IR thermal camera and Poly(UHH-*co*-IL) sensor; n is the time of the measurement ($n_1 = n_2 = 5$). As calculated, t value as well as the *t*-test result equals to 0.218, less than the critical value $t_{0.05}(8) = 2.776$. Above result means that the significant value is larger than 0.05 which indicates the assumption could be accepted and no significant difference exists between two measuring methods. What' more, this calculation result is consistent with results analyzed by Statistical Product and Service Solutions (SPSS, International Business Machines Corporation) which figures out that the significant value equals to 0.833 larger than 0.05 (Table S1).

Table S1: The result of independent-samples test operated by SPSS

		Levene's Test for Equality of Variances		t-test for Equality of Means						
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
									Lower	Upper
Temp.	Equal variances assumed	0.579	0.469	0.218	8	0.833	0.04000	0.18385	-0.38395	0.46395

	Equal variances not assumed			0.218	7.470	0.834	0.04000	0.18385	-0.38924	0.46924

2. Supplementary Figures



Scheme S1. The synthetic route of Poly(UHH-*co*-IL).

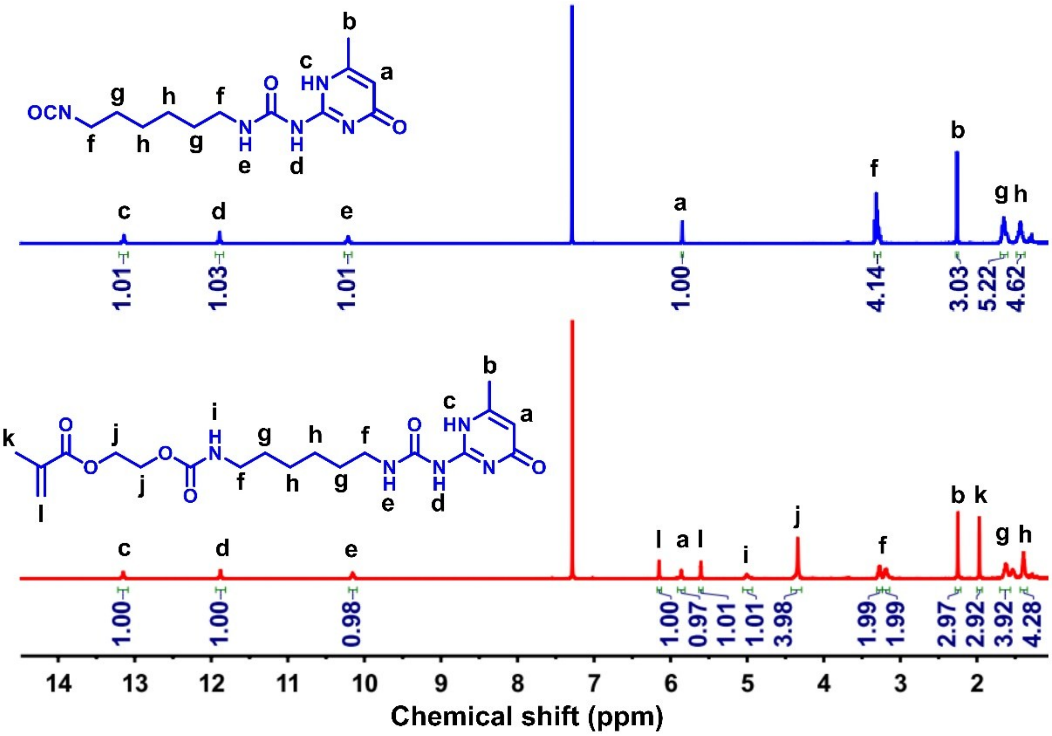


Fig. S1. ^{1}H-NMR spectra of UPy-NCO and UPy-HDI-HEMA.

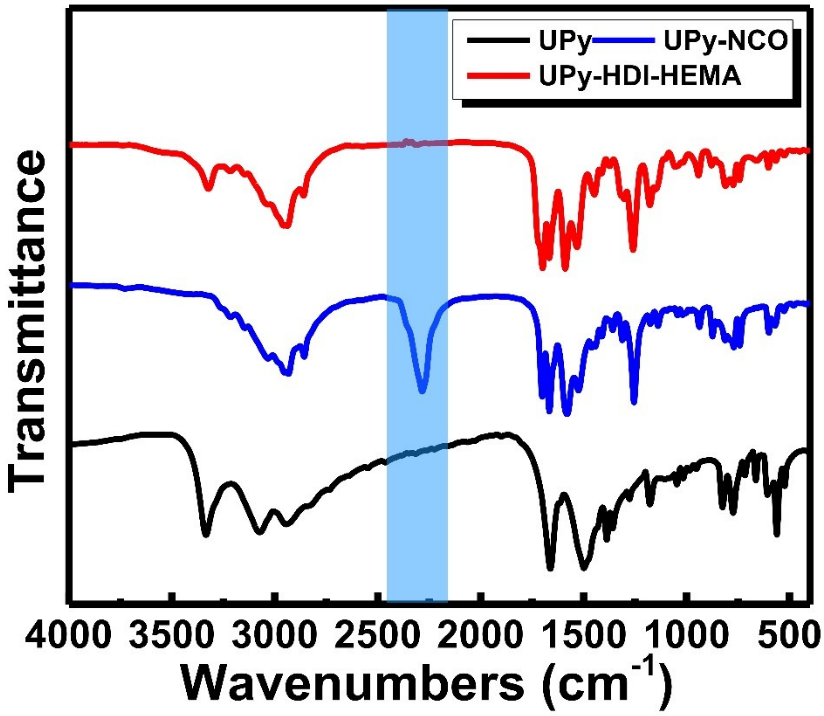


Fig. S2. FTIR spectra of UPy, UPy-NCO and UPy-HDI-HEMA. The main absorption peaks at ca. 2280 cm^{-1} suggest the existence or disappearance of –NCO group.

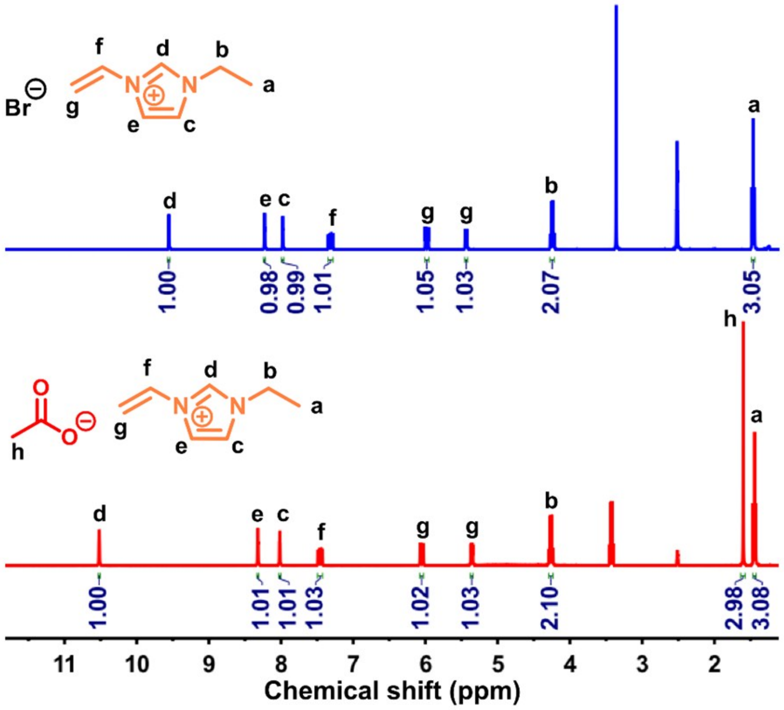


Fig. S3. ^{1}H NMR spectra of [VEIm][Br] and [VEIm][Ac].

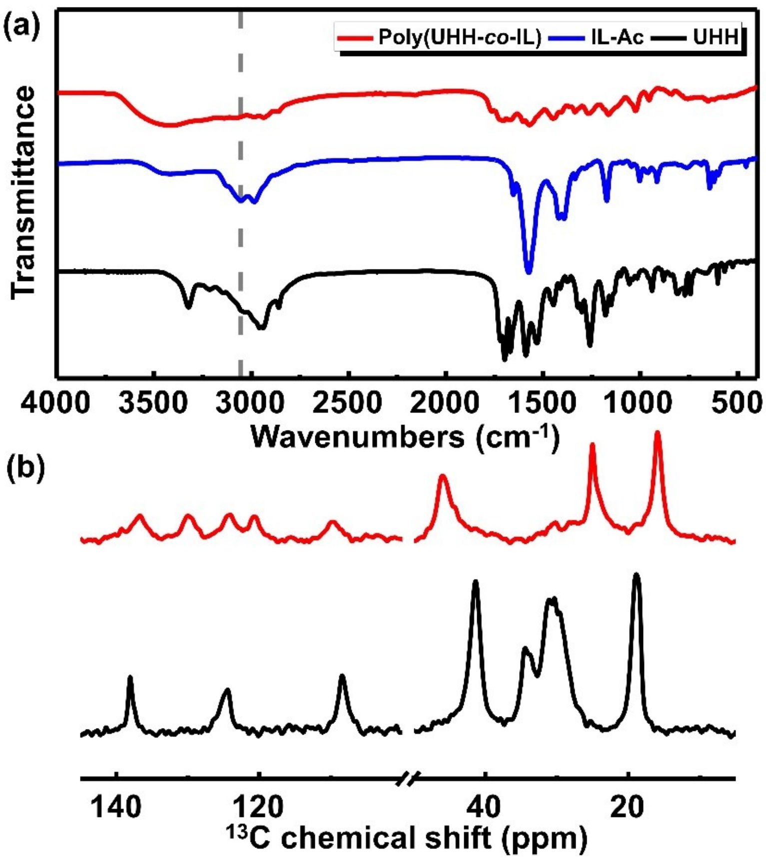


Fig. S4. (a) FTIR spectra of Poly(UHH-co-IL), [VEIm][Ac] and UHH. The absorption peak at ca. 3050 cm^{-1} disappears after copolymerization which means the stretching vibrations of =C-H decreased largely even disappeared. (b) Solid ^{13}C NMR spectra of Poly(UHH-co-IL) (red) and UHH (black). The intensities of carbon-carbon double bond signal at 125 and 136 ppm become weak after copolymerization.

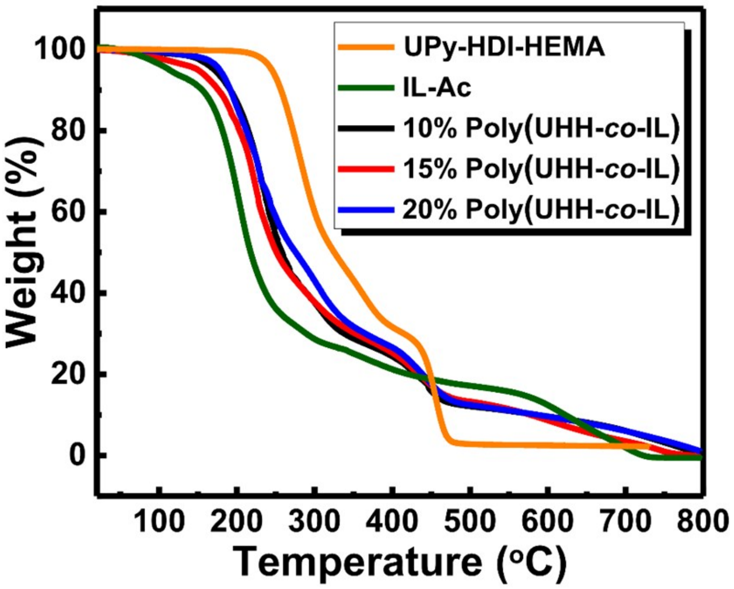


Fig. S5. TGA curves of UPy-HDI-HEMA, [VEIm][Ac], Poly(UHH-*co*-IL) with different molar fractions of UHH.

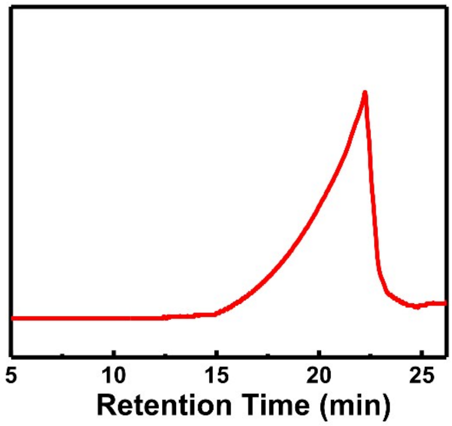


Fig. S6. GPC curve (DMF as eluent) of Poly(UHH-*co*-IL) with UHH molar fraction of 20%. Average M_n=35, 000 Da.

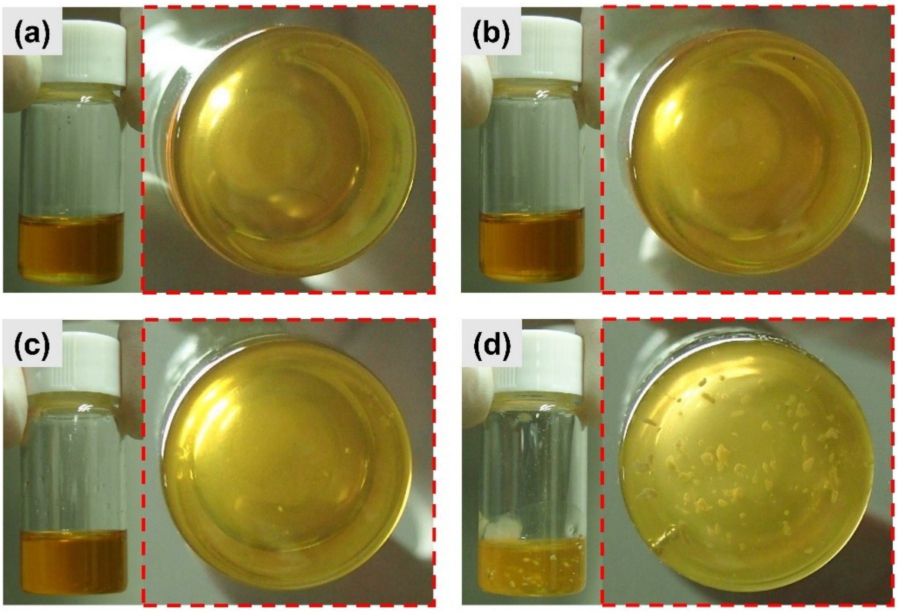


Fig. S7. Optical images of the mixture solution of UHH and [VEIm][Ac] before copolymerization. The molar fraction of UHH is: (a) 10%, (b) 15%, (c) 20% and (d) 25%. We found UHH become really difficult to be fully dissolved in [VEIm][Ac] when the molar fraction of UHH exceeds 20 %, and when increasing to 25 %, a lot of white powder still existed even if stirring in hot water bath (60 oC) for 1 hour.

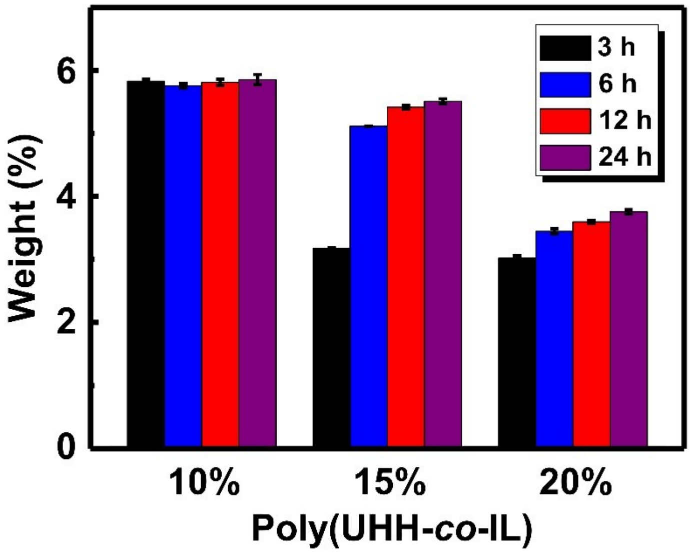


Fig. S8. The dynamic solubility of Poly(UHH-co-IL) with 10%, 15% and 20% UHH in DMF.

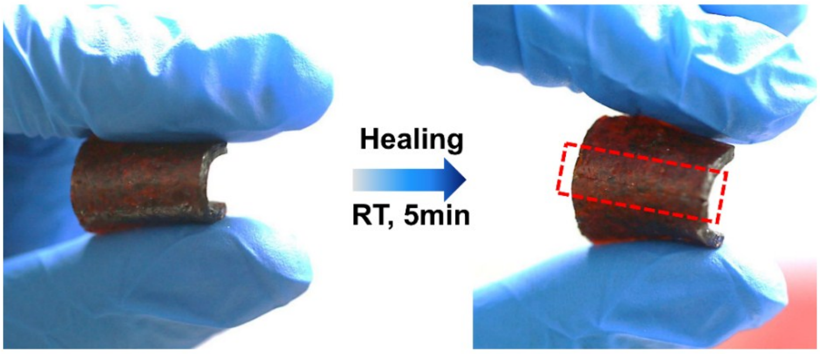


Fig. S9. Photographs of Poly(UHH-*co*-IL) with UHH molar fraction of 20% healed at room temperature after the broken parts were put together for 5 min.

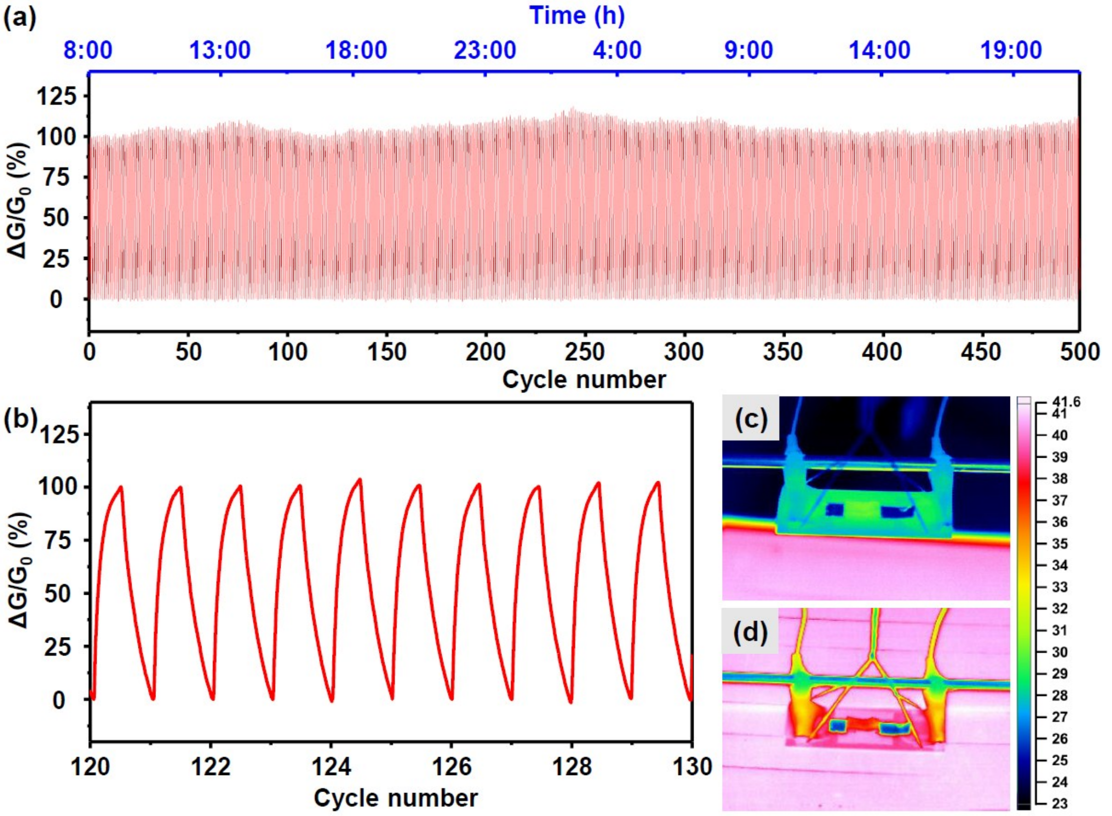


Fig. S10. The 500 cycles of thermal sensing test. (a) Thermal response of Poly(UHH-co-IL) thermometer among 500 on-off cycles; (b) Magnified curve of (a); (c, d) Infrared thermal images of cooling (up) and heating (down) state of the sensor and ΔT was detected about 9 ^oC. As calculated, the average response value is 105.9% and the standard deviation is only 3.74%.

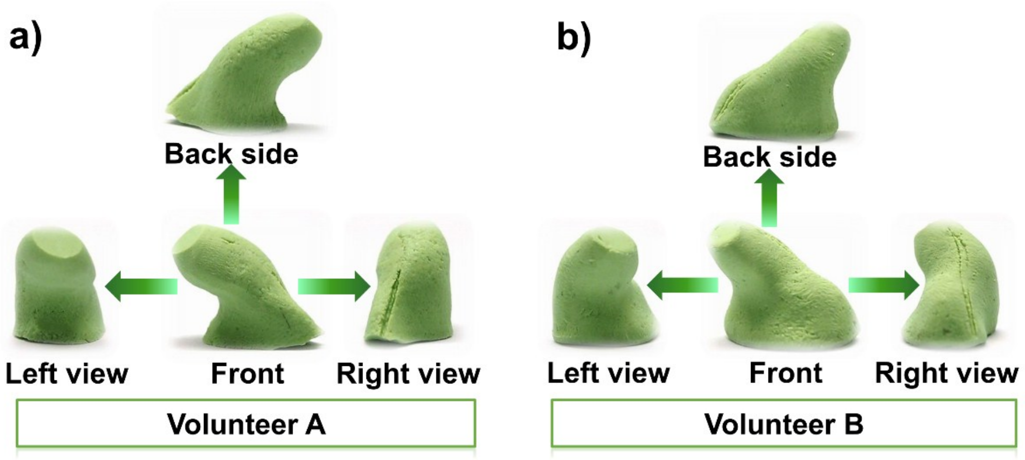


Fig. S11. Solidified silicone ear impressions replicated by a) Volunteer A and b) volunteer B's external auditory canal.

3. References for the Supporting Information

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