Electronic Supplementary Information

Tough, Adhesive, Self-Healable poly(acrylic acid) hydrogel with Temperature sensibility as Epidermal Sensors

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Experimental Methods

Materials. N-isopropylacrylamide(NIPAAM), dopamine hydrochloride(DOPA), magnesium sulfate($MgSO_4$), sodium sulphate(Na_2SO_4), methacryloyl chloride, lithium chloride(LiCl) and triethylamine were purchased from TCI:Tokyo Chemical Industry Co. Ltd (Tokyo, Japan). Methanol, ethyl acetate, hydrochloric acid(HCl, 36 wt%), ethyl ether, acrylic acid(AA) and N,N-Dimethylformamide(DMF) were all purchased from Greagent. Photoinitiator 2-hydroxy-1-[4(-2-hydroxyethoxy)phenyl]-2-methyl-propanone (Irgacure 2959) was purchased from Acros. 2, 2'-azobisisobutyronitrile (AIBN) were purchased from Adamas.

Preparation of DMA. Fabrication of DMA is exhibited in Scheme S1. Firstly, DOPA(5.00 g) and triethylamine(3.58 ml) were added to 50mL DMF. After DOPA completely dissolved, the mixture solution of DMF (5.5 ml) containing triethylamine(5.5 ml) and methacryloyl chloride(3.0ml) were then added dropwise to the solution within 1h. Then, the mixed solution was in ice bath under stirring for another 1h. In order to remove a large amount of the solvent, the solution was concentrated under reduced pressure. The resulting white suspension was dissolved in ethyl acetate and then acidified to pH=2 using an aqueous 6 M HCl solution. After extraction for 3 times, the extracted brown organic layer was dried over $MgSO_4$ and Na_2SO_4, filtrated using filter paper, concentrated by rotary evaporation and washed with ethyl acetate again. Finally, DMA was obtained after drying the brown precipitate under vacuum overnight.

Preparation of NIPAAM-co-DMA. Fabrication of NIPAAM-co-DMA is exhibited in Scheme S1. The process was as the following. 1.13g NIPAAM(10.00 mmol), 0.22g DMA(1.00 mmol), 1ml HCl and 0.02g AIBN were dissolved in 20mL DMF in a round-bottom flask. Then, the mixture was immersed in a preheated oil bath at 65°C for 10 h. The reaction was cooled to room temperature and the mixture solution was added dropwise into cold ethyl ether (200 mL). The precipitate was separated via filtration and the resultant solid was dried in a vacuum oven at room

temperature for 2 days, yielding NIPAAM-co-DMA in the form of a clear white solid.

Preparation of Pristine PAA hydrogels. To prepare pristine PAA hydrogel, 2 g AA, 2 g H_2O and Irgacure 2959 (2.00×10^{-3}g) was mixed to a transparent solution under stirring. Then solution was added to a mold and irradiated from both sides of the mold for a total of 30 min using a UV with a wavelength 365 nm to obtain PAA hydrogel.

Preparation of PAA/NIPAAM-co-DMA hydrogels. To prepare the PAA/NIPAAM-co-DMA hydrogels, the definite amount of NIPAAM-co-DMA and Irgacure 2959 were dissolved in AA(Table S1)and then mixed with deionized water under stirring. The solution was then added to a mold and irradiated from both sides of the mold for a total of 30 min using a UV crosslinking chamber with a wavelength 365 nm to obtain a series of PAAxDNy hydrogels, in which x and y were stand the mass fraction of AA and NIPAAM-co-DMA in the mixture.

Preparation of PAA/NIPAAM-co-DMA-based sensors. To prepare the PAA/NIPAAM-co-DMA-based sensors, the 0.07g of NIPAAM-co-DMA 0.02g LiCl and 1mg Irgacure 2959 were dissolved in 1.8g AA and then mixed with 2.0g deionized water under stirring. The solution was then added to a mold and irradiated from both sides of the mold for a total of 30 min using a UV crosslinking chamber with a wavelength 365 nm.

Characterization

^{1}HNMR Spectrometer. ^{1}HNMR spectrometer was used to determine the structure of DMA and NIPAAM-co-DMA. The ^{1}HNMR spectra were recorded with an AVANCE 500 NMR spectrometer at 30 °C, and the chemical shifts were referenced to the solvent values. (δ= 2.49 ppm for DMSO).

Differential Scanning Calorimetry(DSC). The temperature sensitive point of the prepared hydrogel was measured using a second DSC experiment. For this test, swollen samples (3−5 mg) were weighed into aluminum Tzero hermetic pans and sealed. The samples were equilibrated at 25 °C under a constant nitrogen purge (50 mL/min) and then cooled to 10 °C at 10 °C/min and held for 2 min. The material was then heated to 60 °C at 10 °C/min and held for 2 min prior to cooling to 10 °C at 10°C/min. This thermal loop was completed twice, and the peak of the measured endotherm of the second cycle was reported as the the temperature sensitive point.

Mechanical property measurements. The tensile tests were performed using a universal testing machine (UTM2203, Shenzhen Suns Technology Stock Co.Ltd., China). Cylindrical hydrogels with a diameter of 4.5mm and a height of 8mm were cut and analyzed with a rate of 50.0 mm/min. During tensile tests, the toughness was estimated by area below the stress-strain curves, the original cross section (15.89 mm^2) was used to calculate the tensile stress, and the tensile strain (λ) was defined as the length (l) relative to the initial gauge length (l_0) of the specimen using Eq.(1)

$$\lambda = (l - l_0) / l_0 \tag{1}$$

For cyclic tensile tests, gel specimens were first stretched to an extension ratio $\lambda = 6$ and then unloaded. The dissipated energy was estimated by area below the stress-strain curves or between the loading-unloading curves.

For fracture propagation resistance experiment, samples with a cut notch(radius≈ 2 mm) was performed with a rate of 50.0 mm/min.

For mechanical property measurements under different temperatures, the tensile tests were performed at 15℃ 25℃ 35℃ especially using a universal testing machine (UTM2203, Shenzhen Suns Technology Stock Co.Ltd., China). Cylindrical hydrogels with a diameter of 4.5mm and a height of 8mm were cut and analyzed with a rate of 50.0 mm/min.

Self-Healing. Cylinder shaped samples, of which both added with different dyestuff respectively, were cut into two pieces. The two pieces were then brought together slightly to ensure the two surfaces were fully contacted, and sealed (prevent water from evaporating). After a specific healing time, the tensile test was conducted at the same crosshead speed of 50 mm/min. The efficiency of self-healing (E_H)was defined as the tensile strain(λ_1) of the healed samples relative to the tensile strain(λ_2) of unbroken samples using Eq.2.

$$E_H = \lambda_1 / \lambda_2 \times 100\% \tag{2}$$

Rheology. *measurements.* The rheology test of the hydrogel samples (cylinders, 20mm in diameter and 2mm in height) were measured on Anton Paar MCR320. The strain(γ) amplitude sweep was conducted to demonstrate elastic response of the hydrogels with a constant frequency (1 rad/s)of 1 Hz. The frequency(f) sweep was performed over the angular frequency range of 0.001–100 rad/s at a constant strain of 1%. The temperature sweep was peoformed with a constant frequnency (1 rad/s) at a constant strain of 1%.

Lap Shear Adhesion Testing. The adhesive properties of hydrogels were analyzed using an ASTM standard lap shear test (F2255-05) with modifications. Briefly, 20 μL of the prepolymer solution was applied to a glass slide pretreated with 3-(trimethoxysilyl)propyl methacrylate (TMSPMA). A Ti slide or a second TMSPMA-treated glass slide was put into contact with the hydrogel to result in an overlapping (adhesive bonded) area of around 2.0×2.0 cm^2. After UV light irradiation for 10 mins, the samples were tested until failure in a lap shear setup using an Instron 5542 mechanical tester equipped at a cross-head speed of 1.3 mm/min. The adhesion strength(A) was defined as the maximum of stress(F) divided by the area(S) of hydrogels sample using Eq.3.

$$A = F / S \tag{3}$$

Measurement of Electrical Properties. The electrochemical impedance tests were performed by using a Solartron 1470E multi-channel potentiostat electrochemical workstation (Solartron Public Corp.,Ltd). The impedance data were analyzed by using the ZView software according to the Randles equivalent circuit. The resistance changes of the PAA/NIPAAM-co-DMA-based sensors were obtained by using an electrochemical analyzer/workstation (CHI600E, China). The gauge factor is defined as Eq.4 , where R and R_0 are

the resistances of the bending hydrogels and the original hydrogels, respectively.

$$GF = R/R_0 \times 100\% \qquad (4)$$
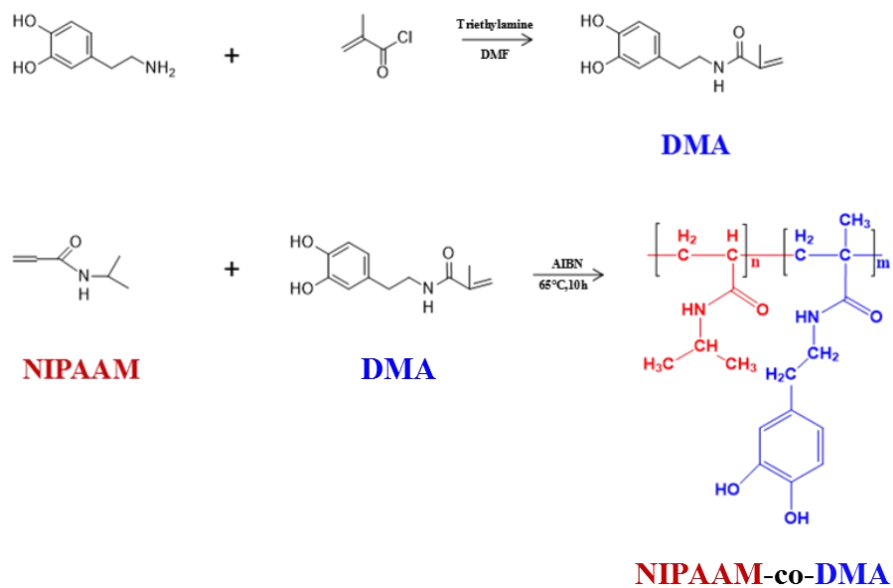
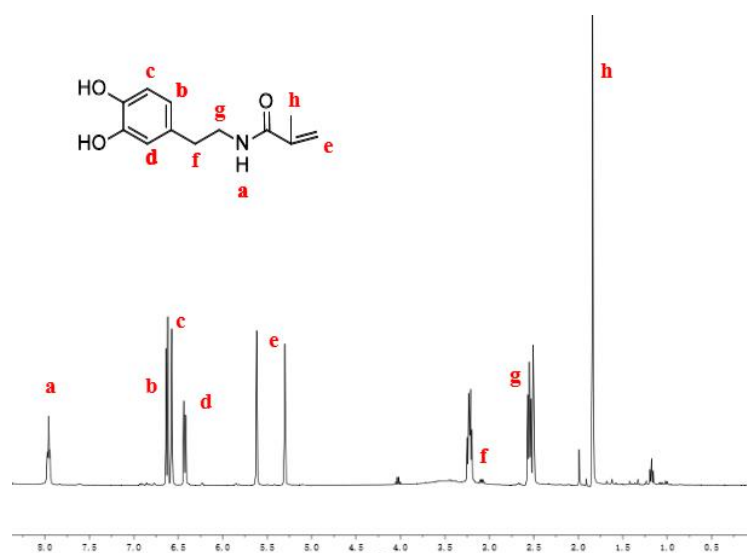**Scheme S1** Synthetic route to the DMA and copolymer NIPAAM-co-DMA

Fig S1. ^{1}H NMR Spectra of DMA.
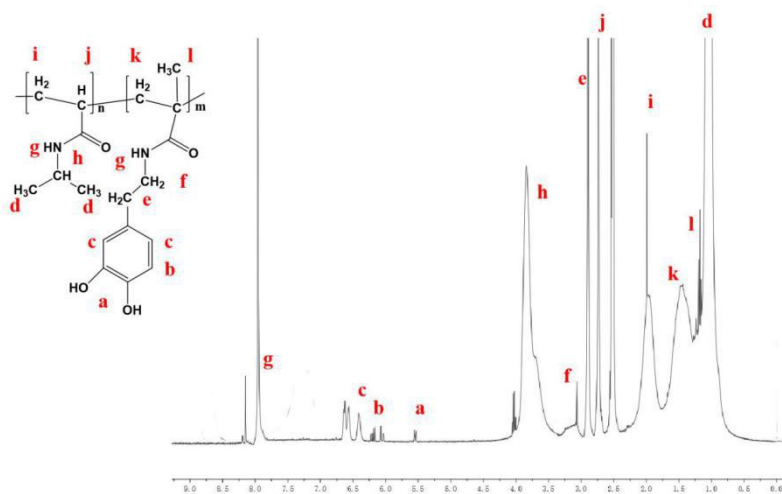
Fig S2. ^{1}H NMR Spectra of NIPAAM-co-DMA.

Table S1 Composition of nine samples of PAA/NIPAAM-co-DMA hydrogels

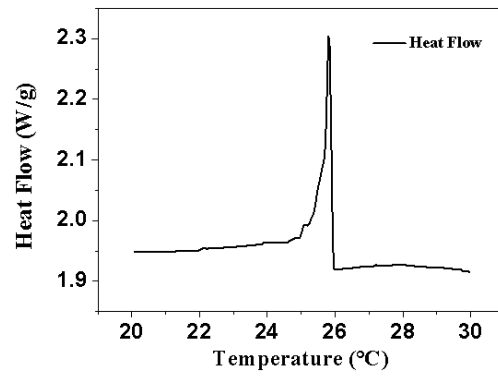| Samples	NIPAAM-co-DMA/g	AA monomer/g	H_2O/g	Irgacure 2959/mg
$PAA_{0.5}DN_{0.012}$	0.05	2	2	1
$PAA_{0.5}DN_{0.015}$	0.06	2	2	1
$PAA_{0.5}DN_{0.017}$	0.07	2	2	1
$PAA_{0.5}DN_{0.020}$	0.08	2	2	1
$PAA_{0.5}DN_{0.022}$	0.09	2	2	1
$PAA_{0.4}DN_{0.017}$	0.07	1.6	2.4	0.8
$PAA_{0.6}DN_{0.017}$	0.07	2.4	1.6	1.2
$PAA_{0.7}DN_{0.017}$	0.07	2.8	1.2	1.4
$PAA_{0.8}DN_{0.017}$	0.07	3.2	0.8	1.6

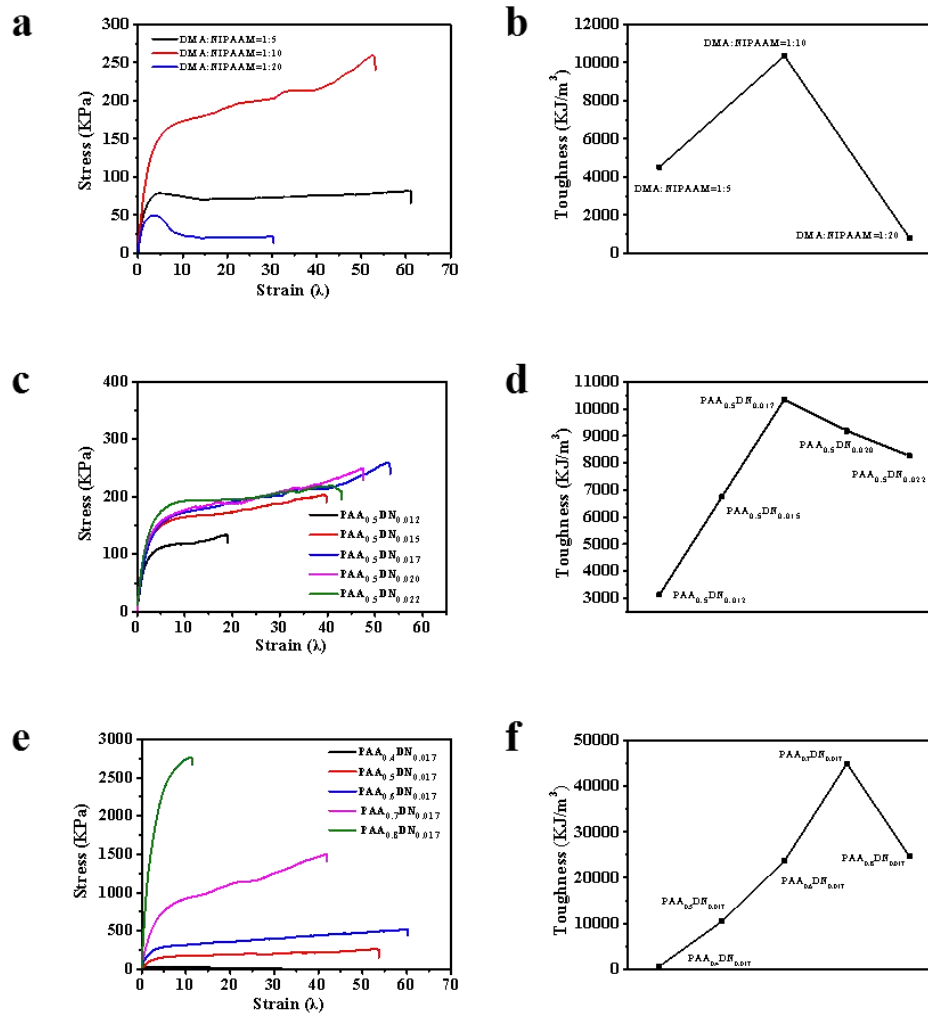**Fig S3.** DSC thermograms of PAA/NIPAAM-co-DMA hydrogels during heating.

Fig S4. (a) Typical tensile stress-strain curves and (b) toughness of hydrogels with different rates of DMA and NIPAAM. (c) Typical tensile stress-strain curves and (d) toughness of hydrogels with different NIPAAM-co-DMA concentration. (e) Typical tensile stress-strain curves and (f) toughness of hydrogels with different AA content.
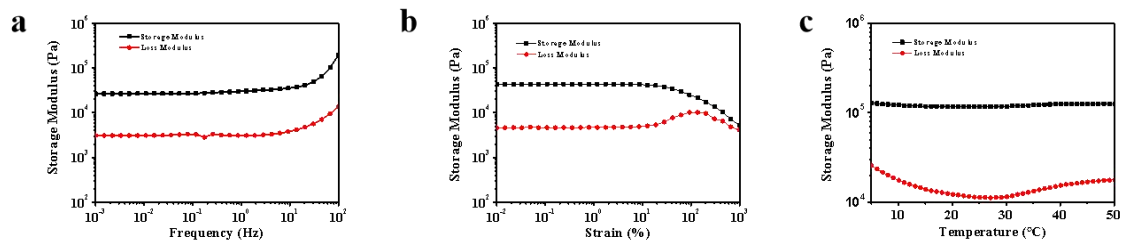
Fig S5. (a)Storage modulus (G′) and loss modulus (G″) as a function of frequency (f) for hydrogel (γ = 0.005). (b) G′ and G″ as a function of strain (γ) for hydrogel (ω = 1 Hz). (c)Dependence of G′ and G″ on temperature during a temperature sweep at a heating and cooling rate of 1 ℃/min for the hydrogel.