

## ***Supporting Information***

### **High-performance Poly(acrylic acid) Hydrogels Formed with Block Copolymer Crosslinker Containing Amino-acid Derivatives**

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## **2. Experimental Section**

### **2.1 Materials.**

Photoinitiator 2-hydroxy-1-[4(-2-hydroxyethoxy)phenyl]-2-methyl-propanone (Irgacure 2959), N,N,N,N',N'-Pentamethyldiethylenetriamine (PMDETA) were purchased from Acros. Monomethoxy poly (ethylene oxide) (PEO 5000, molecular weight=5.0×10<sup>3</sup>) was purchased from Sigma. Acryloyl chloride (C<sub>3</sub>H<sub>3</sub>ClO), 1-dodecanethiol (C<sub>12</sub>H<sub>26</sub>S), oxalyl chloride (C<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub>), 2-bromo-2-methylpropionyl bromide (BIB), acrylic acid (AA), L-aspartic acid (Asp), methyl trioctyl ammonium chloride (Aliquot 336) and 2, 2'-azobisisobutyronitrile (AIBN) were purchased from Adamas. Chloroform (CHCl<sub>3</sub>), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), diethyl ether (C<sub>4</sub>H<sub>10</sub>O), acetone (C<sub>3</sub>H<sub>6</sub>O), isopropanol (IPA), petroleum ether (PET), hexane (Hex), acetic acid glacial (AcOH), methanol (MeOH), ethanol (EtOH), triethylamine (Et<sub>3</sub>N), tetrahydrofuran (THF), N,N-dimethylformamide (DMF), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), potassium hydroxide (KOH), potassium chloride (KCl), hydrochloric acid

(HCl, 36 wt%), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), calcium hydride ( $\text{CaH}_2$ ), aluminum oxide ( $\text{Al}_2\text{O}_3$ ), sodium hydroxide (NaOH), sodium bisulfate ( $\text{NaHSO}_4$ ) and carbon disulfide ( $\text{CS}_2$ ) were all purchased from Greagent. Dopamine hydrochloride (DOPA) and cuprous chloride ( $\text{CuCl}$ ) was purchased from Macklin and the methyl L-leucinate hydrochloride (H-Leu-OMe-HCl) was obtained from GL Biochem (Shanghai) Ltd. Ultrapure water was obtained from the UP Water Purification System. Acrylic acid (AA) was purified by filtrating through an  $\text{Al}_2\text{O}_3$  column.  $\text{CuCl}$  was stirred with AcOH, filtered, and washed with EtOH at least 3 times<sup>[1]</sup>.  $\text{CH}_2\text{Cl}_2$  was purified by distillation over  $\text{CaH}_2$  and AIBN was purified by recrystallization using the hot EtOH. Other reagents were used without further purification.

## 2.2 Preparation of Monomer LAC or AAC

Block copolymer PEO-b-PLAA was synthesized via ATRP presented in Scheme 1. The monomer LAC or AAC was prepared by traditional method of amidation reaction. Briefly, 9.084 g (50 mmol) methyl L-leucinate hydrochloride or 6.655 g (50 mmol) L-aspartic acid was dissolved in the  $\text{K}_2\text{CO}_3$  solution (40.0 mL, 3.0 mM). Then the pH of the mixture was adjusted to 10.0 and pH value was remained stably during reaction by using 2.0 M KOH solution and 5.0 mL (60 mmol) acryloyl chloride which was added dropwisely with vigorous stirring to the chilled solution. After reaction for 2 h, the pH value of solution was acidified with 5.0 M HCl to 2.0. Then the solution was extracted using  $\text{CH}_2\text{Cl}_2$  for 3 times, and the solution was dried with  $\text{Na}_2\text{SO}_4$ . Finally, the solvent was evaporated to give an oily residue named as LAC (8.7 g, 73.8%) or ACC (6.8 g, 72.7%).

## 2.3 Preparation Diblock Copolymer of PEO-b-PLAA

The amphiphilic diblock copolymers PEO-b-PLAA were prepared though ATRP as followed. Firstly, the macro-initiator prepared in step 2 in scheme 1. 20.0 g PEO5000 (4.0 mmol) was dissolved in 40 mL anhydrous  $\text{CH}_2\text{Cl}_2$ , and then 1.12 mL (8.0 mmol)  $\text{Et}_3\text{N}$  were added in the system to obtain a homogeneous solution. After the complete dissolution of PEO5000, the solution was immersed in the ice bath under

stirring. Meanwhile, 1.5 mL (12.0 mmol) BIB was added dropwise under the nitrogen atmosphere for 30 min. The obtained solution was further stirred at room temperature for 16 h. The crude product was precipitated from the reaction solution by adding excessive cold diethyl ether, and further washed three times by diethyl ether then dried in vacuum for 6 h. Finally the macro-initiator which was named as PEO-Br was obtained as a white solid (17.4 g, 84.5%).

For the next part, the monomer LAC would be grafted on the PEO chain by the following steps. About 2.50 g (0.5 mmol) PEO-Br, 0.1042 mL (0.5 mmol) PMDETA, 0.05 g (0.5 mmol) CuCl and 7.00 g (35.0 mmol) LAC were added into a 125.0 mL flask containing 15 mL DMF. The bottle, including reactants, was fully degassed with three freeze-pump-thaw cycles and sealed under nitrogen atmosphere. Then it was immersed in a thermostated oil bath at 80 °C for 12 h. After completion of the reaction, the system was then cooled down to room temperature followed by added 30.0 mL CH<sub>2</sub>Cl<sub>2</sub> and filtered through an Al<sub>2</sub>O<sub>3</sub> column to remove the catalyst. Herein, the copolymer was precipitated using the mixtures solution of diethyl ether and PET. Though dried in vacuum, the block copolymer named as PEO-b-PLAC was obtained as a white solid (2.3 g, 42.6%).

At last, 2.0 g PEO-b-PLAC was dissolved in MeOH and NaOH (1.0 M, 2 equiv per ester group) solution. The mixture was stirred overnight at room temperature and then neutralized with 1.0 M NaHSO<sub>4</sub> solution. After removing excessive solution, the crude product was dispersed in MeOH to separate salt. The pure diblock copolymer named as PEO-b-PLAA could be obtained by evaporation of the MeOH solution. (1.7 g, 87.9%)

#### **2.4 Preparation Diblock Copolymer of PEO-b-PAAC**

The other amphiphilic diblock copolymer PEO-b-PAAC was synthesized through RAFT process as followed. Firstly, the chain transfer agent was prepared by following steps<sup>[2]</sup>. 20.20 g 1-Dodecanethiol (0.100 mol), 1.62 g Aliquot 336 (0.004 mol) and 61.30 mL acetone (0.827 mol) were mixed in three-neck flask. Then 4.20 mL NaOH

solution (25.0 M) was added dropwisely with vigorous stirring under nitrogen atmosphere followed by adding CS<sub>2</sub> of acetone solution which was contained 7.60 g CS<sub>2</sub> (0.1 mol) and 12.80 mL acetone. Then 12.00 mL chloroform and 20.00 mL above NaOH solution were added dropwisely in the system during 30 minutes. After reaction for 10h, the mixture was blended with 150 mL deionized water, and then the solution was acidified by using 25 mL hydrochloric acid. Most of acetone was evaporated with vigorous stirring under nitrogen atmosphere, and then crude products were obtained by filtration and then dispersed into IPA to remove impurities. After evaporating the residual solution, the chain transfer agent, DMP, was collected as a yellow solid (26.8 g, 73.6%) though the recrystallization with hexane.

The second part was the preparation of macro-initiator. 0.728 g DMP (2.0 mmol) was dissolved in 40.0 mL anhydrous CH<sub>2</sub>Cl<sub>2</sub> under the ice bath, and then 0.338 mL oxalyl chloride (4.0 mmol) was added dropwisely into the solution under nitrogen atmosphere. After mixed completion, the mixture system was further stirring for 2h. Then most of CH<sub>2</sub>Cl<sub>2</sub> and the rest of oxalyl chloride were removed though vacuumizing. The obtained product was dissolved in anhydrous CH<sub>2</sub>Cl<sub>2</sub> containing 10.0 g PEO 5000 (2.0 mmol), then the reaction was carried out at room temperature for 16 h to synthesize the macro-initiator. After reaction completed, the macro-initiator named as PEO-DMP was precipitated by diethyl ether, and the polymer was dried in vacuum to give PEO-DMP as a yellow powder (9.6 g, 90.1%). The last stage was the synthesis of the diblock copolymer PEO-b-PAAC. The 2.65 g (0.50 mmol) PEO-DMP, 9.05 g (0.045 mol) AAC and 0.02 g AIBN were dispersed in 20 mL DMF. Meanwhile the bottle, including reactants, was fully degassed with three freeze pump-thaw cycles and sealed with N<sub>2</sub>. Then the whole system was immersed in a thermostated oil bath at 80 °C for 12 h. After reaction, the system was cooled down to room temperature, and the diblock copolymer was precipitated using diethyl ether. And the final product was dried in vacuum to give PEO-b-PAAC as a yellow powder (2.2 g, 40.0%).

## **2.5 Synthesis of PAA/PEO-b-PLAA and PAA/PEO-b-PAAC Hydrogels**

The PAA/PEO-b-PLAA (PA) or PAA/PEO-b-PAAC (TA) hydrogels were prepared by in situ free radical copolymerization of AA in the present of PEO-b-PLAA or PEO-b-PAAC. The diblock copolymers were dissolved in water to form a homogeneous 10.0 wt% solution. The definite amount of diblock copolymers solution, AA monomers, H<sub>2</sub>O and Irgacure 2959 (Table S1 and S2) were mixed and underwent ultrasonication for 15 min. Then the mixtures were put into molds and exposed to UV light with a wavelength 365 nm for 20 minutes to obtain a series of P<sub>x</sub>A<sub>z</sub> or T<sub>y</sub>A<sub>z</sub> hydrogels. In which x and z was the mass fraction of PEO-b-PLAA polymer and AA monomer in PAA/PEO-b-PLAA hydrogel, while y and z was the mass fraction of PEO-b-PAAC polymer and AA monomer in PAA/PEO-b-PAAC hydrogel. The detail composition of the hydrogels were presented in Table S1 and Table S2.

**Table S1** Composition of five samples of P<sub>x</sub>A<sub>z</sub> hydrogels

<b>Samples</b>	<b>PEO-b-PLAA solution (10.0wt%)/g</b>	<b>AA monomer/g</b>	<b>H<sub>2</sub>O/g</b>	<b>Irgacure 2959/mg</b>
P <sub>0.1</sub> A <sub>0.3</sub>	0.2	0.6	1.2	0.3
P <sub>0.1</sub> A <sub>0.4</sub>	0.2	0.8	1.0	0.4
P <sub>0.1</sub> A <sub>0.5</sub>	0.2	1.0	0.8	0.5
P <sub>0.1</sub> A <sub>0.6</sub>	0.2	1.2	0.6	0.6
P <sub>0.1</sub> A <sub>0.7</sub>	0.2	1.4	0.4	0.7

**Table S2** Composition of five samples of T<sub>y</sub>A<sub>z</sub> hydrogels

<b>Samples</b>	<b>PEO-b-PAAC solution (10.0wt%)/g</b>	<b>AA monomer/g</b>	<b>H<sub>2</sub>O/g</b>	<b>Irgacure 2959/mg</b>
T <sub>0.1</sub> A <sub>0.3</sub>	0.2	0.6	1.2	0.3
T <sub>0.1</sub> A <sub>0.4</sub>	0.2	0.8	1.0	0.4
T <sub>0.1</sub> A <sub>0.5</sub>	0.2	1.0	0.8	0.5
T <sub>0.1</sub> A <sub>0.6</sub>	0.2	1.2	0.6	0.6
T <sub>0.1</sub> A <sub>0.7</sub>	0.2	1.4	0.4	0.7

## 2.6 Synthesis of DP-PA and PA-KCl Hydrogels

The gelation of the mixture was similar to above mentioned, PEO-b-PLAA (10.0 wt%) solution, Irgacure 2959, AA monomers, H<sub>2</sub>O and dopamine hydrochloride or KCl were mixed and underwent ultrasonication for 20 min. The mixture was then transferred into molds and exposed to UV light with wavelength 365 nm for 20 minutes to obtain DP-PA or PA-KCl hydrogels.

### 3. Characterization

#### 3.1 <sup>1</sup>HNMR Spectrometer.

<sup>1</sup>HNMR spectrometer was used to determine the structure of LAC, AAC and the diblock copolymers. The <sup>1</sup>HNMR spectra were recorded with an AVANCE 500 NMR spectrometer at 30 °C, and the chemical shifts were referenced to the solvent values ( $\delta = 2.49$  ppm for DMSO and  $\delta = 4.79$  ppm for D<sub>2</sub>O).

#### 3.2 Gel Permeation Chromatography (GPC) Analysis.

The GPC (Waters 1515, United States) test was measured to characterize the molecular weight of the PEO-b-PLAA with THF as standard.

#### 3.3 Scanning Electron Microscope (SEM) Images.

The cross-sections of the freeze-dried PA hydrogels were also imaged with SEM (S4800, Hitachi, Japan) at accelerating voltage of 1.5 kV. Before tests, the hydrogel samples should be freeze-dried in the freeze dryer (SCIENNTZ-10N, Ningbo) for 4 d, and then the hydrogels also should be sprayed with Au film to guarantee samples obtain the electric conductivity.

#### 3.4 Mechanical Properties Tests.

For tensile tests, as-prepared hydrogel samples with 5.5 mm diameter, 50.0 mm length and dyed with Rhodamine B. The distance between clips was 5.0 mm and the crossed speed was 50.0 mm/min at 25 °C. To ensure accuracy, three specimens were tested for each hydrogel sample, and each specimen was coated with a thin layer of silicon oil to prevent water evaporation. During tensile tests, the original cross section (23.75 mm<sup>2</sup>) was used to calculate the tensile stress, and the tensile strain ( $\epsilon$ ) was defined as the length ( $l$ ) relative to the initial gauge length ( $l_0$ ) of the specimen (Equation S1-1)<sup>[3]</sup>.

$$\varepsilon = (l - l_0) / l_0 \times 100\% \quad \text{Equation S1-1}$$

For compressive tests, the cylindrical samples were 12.0 mm in diameter and 7.0 mm in height. The press speed was 10% strain per min. The engineering compressive stress ( $\sigma_c$ ) was calculated as Equation S1-2, where R and  $F_{load}$  was represented the original radius of the cylindrical specimen and the force loaded on the cross-section of hydrogels, respectively<sup>[3]</sup>.

$$\sigma_c = F_{load} / \pi R^2 \quad \text{Equation S1-2}$$

The compression strengths were obtained using the stress at distortion of 85%. And all the mechanical tests were operated with an Instron 5567 machine (Instron Corporation, MA) that is equipped with 100 N load cell and each test was carried out for triplicates.

**Table S3** Tensile and compressive properties of PAA/PEO-b-PLAA hydrogels

Samples	Fracture strength (KPa)	Fracture elongation (%)	Compressive strength (MPa)	Young's Modulus (KPa)	$\tau_{\alpha=2}$ (Kpa)	N* (mol/m <sup>3</sup> )
P <sub>0.1</sub> A <sub>0.3</sub>	24.28	9800%	—	10.25	2.65	0.61
P <sub>0.1</sub> A <sub>0.4</sub>	48.87	9200%	1.39	19.48	8.37	1.93
P <sub>0.1</sub> A <sub>0.5</sub>	64.09	7800%	1.91	34.47	11.78	2.72
P <sub>0.1</sub> A <sub>0.6</sub>	133.38	3300%	2.58	85.44	24.59	5.67
P <sub>0.1</sub> A <sub>0.7</sub>	194.69	1700%	2.95	112.23	27.59	6.36

**Table S4** Tensile and compressive properties of PAA/PEO-b-PACC hydrogels

Samples	Fracture strength (KPa)	Fracture elongation (%)	Compressive strength (MPa)	$\tau_{\alpha=2}$ (Kpa)	N* (mol/m <sup>3</sup> )
T <sub>0.1</sub> A <sub>0.3</sub>	35.99	7600%	—	16.23	3.74
T <sub>0.1</sub> A <sub>0.4</sub>	65.58	6600%	1.33	19.65	4.52
T <sub>0.1</sub> A <sub>0.5</sub>	87.33	4400%	1.76	24.78	5.71
T <sub>0.1</sub> A <sub>0.6</sub>	162.30	1300%	2.26	32.65	7.52
T <sub>0.1</sub> A <sub>0.7</sub>	283.96	800%	3.28	75.68	17.45

### 3.5 *Self-Healing ability.*

The as-prepared cylindrical samples of  $P_xA_z$  hydrogels were cut into several short rods marked with different colors. The fracture surfaces were close contacted with each other and put in a sealed glass tube at 30°C. The degree of tensile recovery was characterized by the tensile strain of healed samples relative to the initial hydrogels.

### 3.6 *Lap Shear Tests.*

The adhesion properties of the DP-PA hydrogels were also measured through the lap shear tests<sup>[4]</sup>. Briefly, two DP-PA hydrogels were bonded with each other, which overlapping (adhesive bonded) area of around  $1.0 \times 1.0 \text{ cm}^2$  and the thickness of each ribbon hydrogel was 2.0 mm. Then Lap shear test were conducted with an Instron 5567 machine (Instron Corporation, MA) which was equipped with 100 N chucking appliances and each test was carried out for triplicates to avoid errors.

### 3.7 *Swelling Measurements.*

The swelling tests were performed by immersing the hydrogel (small cylinder with 5.0 mm diameter and 2.0 mm height) into 400.0 mL deionized water at room temperature for 14 days to reach equilibrium, with water exchanged every day<sup>[5]</sup>. The swelling ratio (SR) was determined by Equation S1-3.

$$SR = (W_s - W_d) / W_d \times 100\% \quad \text{Equation S1-3}$$

Where  $W_s$  and  $W_d$  was the swollen hydrogels and corresponding dried hydrogels, respectively.

### 3.8 *Conductivity measurement.*

The conductivity of PA-KCl hydrogels was obtained through the two-probe method by using a DC power with 3 voltages as shown in Figure S9A, and the conductivity ( $\kappa$ , S/cm) of hydrogels was calculated according to the Equation S1-4.

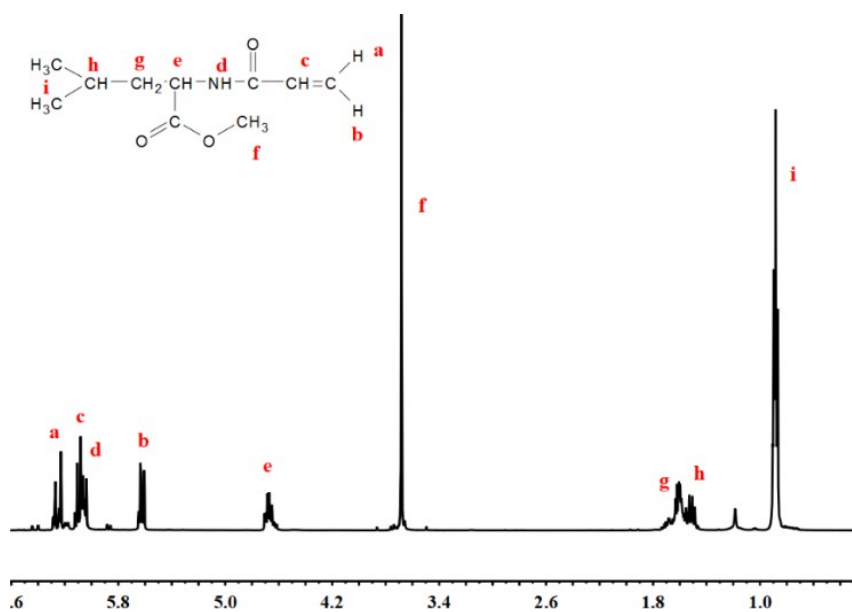


$$\kappa = \left(\frac{I}{U}\right) \left(\frac{L}{A}\right) \quad \text{Equation S1-4}$$

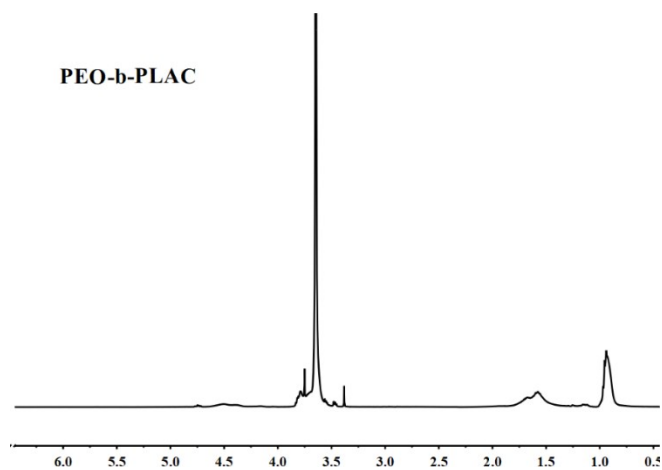
Where  $U(V)$  was the measured voltage;  $I(A)$  was the current provided by the DC power;  $A(\text{cm}^2)$  was the cross-sections area of the hydrogel samples;  $L(\text{cm})$  was the distance between the two probe. Meanwhile the hydrogels were also stretched by cycle tension to explore variation of the conductivity. As shown in Figure S9B, the wires were inserted in the hydrogels. The resistance was recorded when the tensile strain of hydrogels was reached to 500%. The relative resistance change ratio ( $\Delta R/R_0$ ) was obtained though the following Equation S1-5.

$$\Delta R / R_0 = (R - R_0) / R \quad \text{Equation S1-5}$$

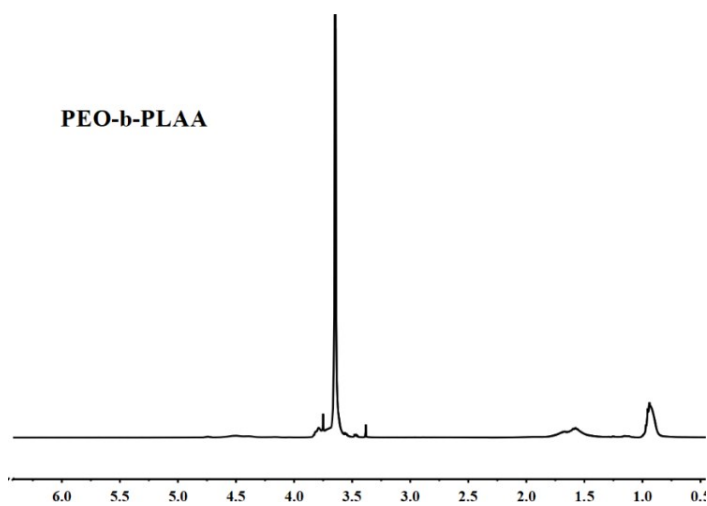
Where  $R_0(\Omega)$  and  $R(\Omega)$  was denoted as resistance without and applied strain, respectively.



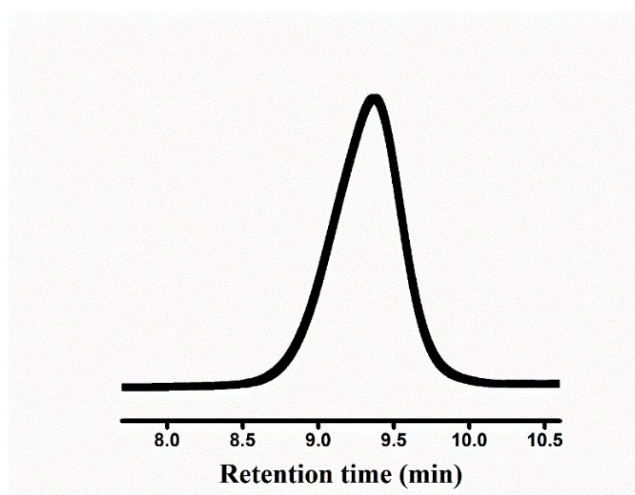
**Figure S1.**  $^1\text{H}$  NMR Spectra of monomer LAC.



**Figure S2.**  $^1\text{H}$  NMR Spectra of PEO-b-PLAC diblock copolymer. The signal (a) at 3.62 ppm is assigned to  $-\text{CH}_2-\text{CH}_2-$  in PEO block.



**Figure S3.**  $^1\text{H}$  NMR Spectra of PEO-b-PLAA



**Figure S4.** GPC traces of diblock copolymer using THF as the eluent.

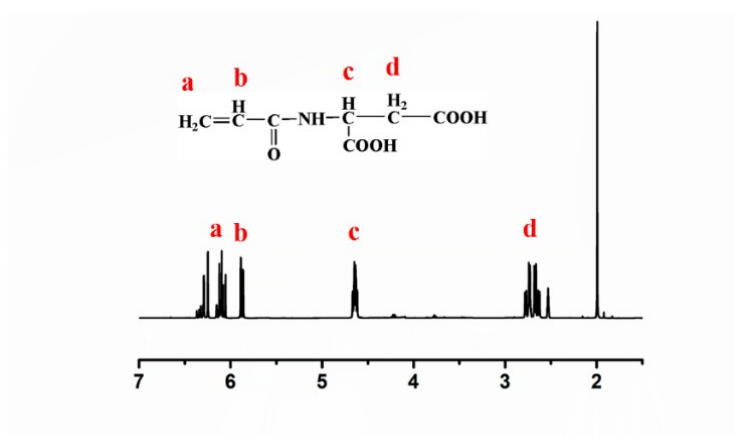


Figure S5.  $^1\text{H}$  NMR Spectra of monomer AAC.

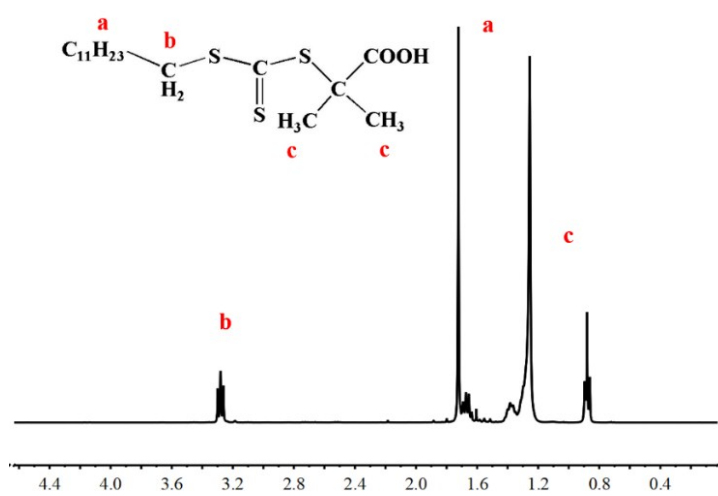


Figure S6.  $^1\text{H}$  NMR Spectra of DMP.

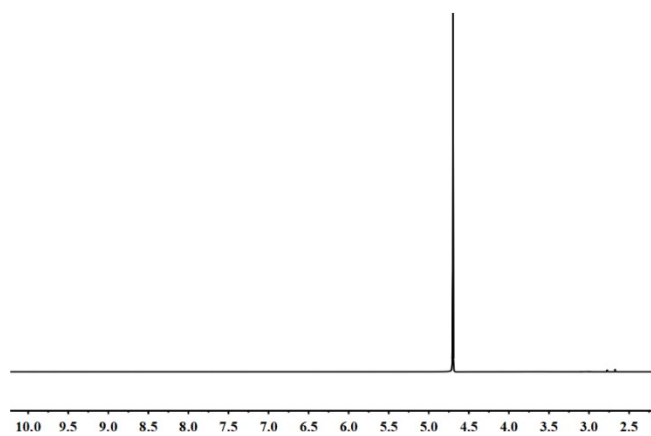
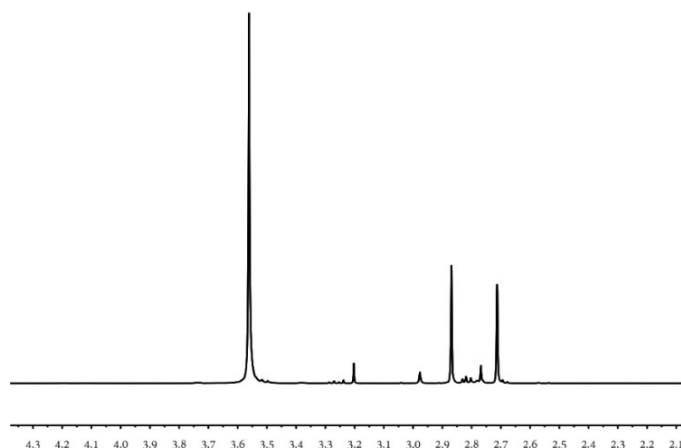
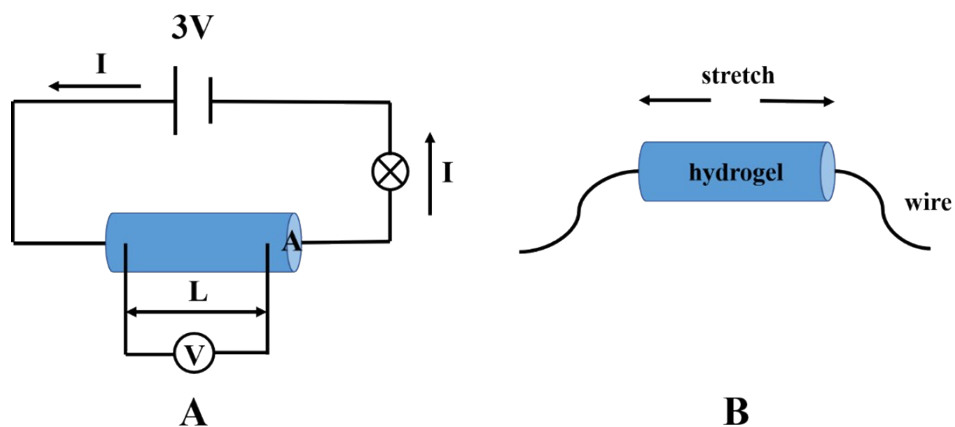


Figure S7.  $^1\text{H}$  NMR Spectra of PEO-DMP.



**Figure S8.**  $^1\text{H}$  NMR Spectra of PEO-b-PAAC.



**Figure S9.** (A) Schematics of the conductivity measurement. (B) Schematic of the relative resistance change of the hydrogels under stretching condition.

**References:**

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