

Supporting information for

Self-healing, Mechanically Robust, and 3D Printable Ionogel for Highly Sensitive and Long-Term Reliable Ionotronics

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Experimental section

Materials: Isophorone diisocyanate (IPDI) and 2-hydroxyethyl acrylate (HEA) were purchased from Beijing Innochem Co., Ltd. Polyethylene glycol (PEG, Mn~2000) was purchased from Xilong Scientific Co., Ltd. Polycaprolactone diol (PCL, Mn~2000) was purchased from Jining Baichuan Chemicals Co., Ltd. Bis(2-hydroxyethyl) disulfide (HEDS, 90%) was purchased from Alfa. Dibutyltin dilaurate (DBTDL), hydroquinone (HQ), and acetone were provided from Sinopharm Chemical Reagent Co., Ltd. 4-Acryloylmorpholine (ACMO), 2-Hydroxy-2-methyl-phenyl-propane-1-one

(PI 1173) and phenyl bis (2,4,6-trimethylbenzoyl) phosphine oxide (PI 819) were purchased from Energy Chemicals Co., Ltd. 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([EMIM][TFSI], 97%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

Synthesis of Polyurethane Acrylate Containing Disulfide Bonds (PUA) : IPDI (25.00 g, 112.50 mmol), PEG (50.00 g, 25.00 mmol), PCL (25.00 g, 12.50 mmol), HEDS (10.71 g, 62.50 mmol), and acetone (50 mL) were added into a 250 mL three-necked flask and stirred at 60 °C for 0.5 h under a N₂ atmosphere. Then, catalyst DBTDL (0.05 g) was added into the system and the mixture was further stirred for 2 h. Afterwards, the mixture of HEA (2.90 g, 25.00 mmol) and HQ (0.05 g) was added into the system and the reaction was continued until the absorption peak of NCO groups disappeared on the FTIR spectrum. Finally, the polyurethane acrylate containing disulfide bonds (PUSA) was obtained after rotary evaporation (Mn ~ 5323, PDI ~ 2.21 from GPC).

Synthesis of Polyurethane Acrylate without Disulfide Bonds : IPDI (9.42 g, 42.40 mmol), PEG (45.82 g, 22.91 mmol), PCL (22.91 g, 11.45 mmol), and acetone (50 mL) were added into a 250 mL three-necked flask and stirred at 60 °C for 0.5 h under a N₂ atmosphere. Then, catalyst DBTDL (0.04 g) was added into the system and the mixture was further stirred for 1 h. Afterwards, the mixture of HEA (1.86 g, 16.00 mmol) and HQ (0.04 g) was added into the system and the reaction was continued until the absorption peak of NCO groups disappeared on the FTIR spectrum. Finally, the polyurethane acrylate without disulfide bonds (PUHA) was obtained after rotary evaporation (Mn ~ 5875, PDI ~ 1.84 from GPC).

Preparation of Ionogels: The photopolymer resin was prepared using ACMO as the reactive diluent, PI 1173 as the photoinitiator, and [EMIM][TFSI] as the ionic liquid. PUA, ACMO, and [EMIM][TFSI] were mixed with different mass ratios. Then, PI 1173 (1 wt%) was added into the mixture. After removing the bubbles with a centrifuge, the photopolymer resin was poured into a PTFE mold (60 mm × 50 mm × 2 mm) and then irradiated for 10 min using a UV curing machine (CL-1000, wavelength 365 nm, light intensity 5.6 mW/cm²).

Fabrication of the I-TENG: The I-TENG with a sandwich-like structure was fabricated in which the ionogel was encapsulated with two plates of PDMS elastomer and an aluminum plate was attached into the ionogel for the electrical connection. Sylgard 184 was used to prepare PDMS elastomer through mixing 10A:1B by weight and cured at 80 °C for 1h in a vacuum oven. The PDMS plate with a dimension of 30 × 50 × 1 mm was firstly prepared, and then a piece of ionogel with a dimension of 20 × 40 × 1 mm was cured on the top of the PDMS plate, and afterwards, another PDMS layer was coated on the ionogel layer to get I-TENG.

3D Printing of the Ionogel by DLP: PI 819 (1 wt%) was used as photoinitiator in the photopolymer resin for 3D printing. All the complex structures were printed using a DLP 3D printer (EvoDent S110, Shanghai Union Technology Corporation) with a light source of 405 nm.

Material Characterization: FTIR-ATR measurements were performed with a Bruker Tensor-27 FTIR spectrometer from 500 to 4000 cm⁻¹. ¹H-NMR measurements were performed on a Bruker Advance 400 MHz spectrometer using deuterated chloroform (CDCl₃) as the solvent. The molecular weight and molecular weight distribution were determined by GPC (WATERS, 1515) using polystyrene as the standard and 1-Methyl-2-pyrrolidinone (NMP) as the eluent. The transparency of the ionogel sample (1 mm thickness) was measured with a UV-visible spectrophotometer (SHIMADZU, UV-2600) in the wavelength range of 400-800 nm at room temperature.

Thermal Properties: The thermogravimetric (TGA) analysis was performed on a TGA Q50 instrument in a N₂ atmosphere from 50 to 800 °C. Dynamic mechanical analysis (DMA) measurements were performed on a DMA Q800 instrument in the film tension mode at a heating rate of 5°C/min in a N₂ atmosphere from -100 to 60 °C.

Mechanical Properties: Mechanical properties of ionogels at RT were measured using universal testing machine Instron 5567. Dumbbell-shaped specimens (50 mm × 4 mm × 2 mm) were prepared for tensile and cyclic tensile tests at a rate of 100 mm/min and at least five specimens per sample were tested. Cylindrical specimens (10 mm diameter and 10 mm height) were printed for cyclic compression tests at a rate of 10

mm/min. Cyclic tensile tests at -10 °C (low temperature) or 150 °C (high temperature) were performed using dynamic mechanical analysis (DMA Q800) in the film tension mode at a strain rate of 100%/min.

Scratch Healing Test: The scratch healing images of the ionogels were observed under an optical microscope (Olympus Microscope BX-51).

Ionic Conductivity Test: The ionic conductivity of ionogels and its temperature dependence were determined by sandwiching the samples (1 mm thickness) between two stainless steel electrodes (15 mm diameter) via electrochemical impedance spectroscopy (EIS) using Zahner Zennium electrochemical workstation with a frequency range of 5×10^6 to 1 Hz. The ionic conductivity was calculated according to the following equation:

$$\sigma = \frac{L}{RA}$$

where L is the thickness of the sample, R is the impedance value, A is the contact surface area with stainless steel electrodes.

Sensing Test: The strain sensing properties were measured by combining a digital source meter (Keithley 2450) and a universal testing machine (Instron 5567). The relative resistance change ($\Delta R/R_0$) was calculated according to the following equation:

$$\frac{\Delta R}{R_0} = \frac{R - R_0}{R_0} \times 100\%$$

where R_0 and R are the resistance values before and after the deformation. The gauge factor (GF) was calculated according to the following equation:

$$GF = \frac{\Delta R/R_0}{\varepsilon}$$

where ε is the tensile strain of the ionogel. The pressure sensitivity (S) was calculated according to the following equation:

$$S = \frac{\Delta R/R_0}{P}$$

where P is the pressure applied on the ionogel.

The electric signal of TENG was measured by a Keithley 6514 electrometer and drove by a linear motor.

Results

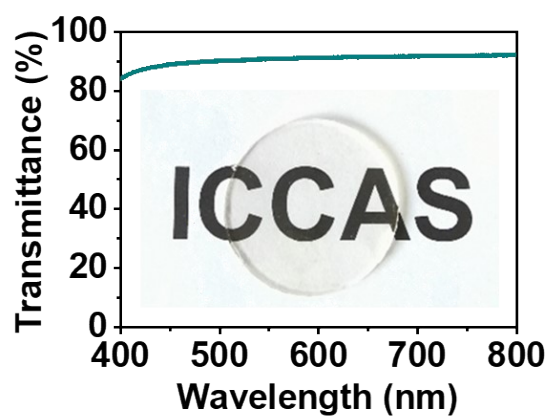


Figure S1. The transmittance of the synthesized ionogel in the wavelength of 400 to 800 nm.

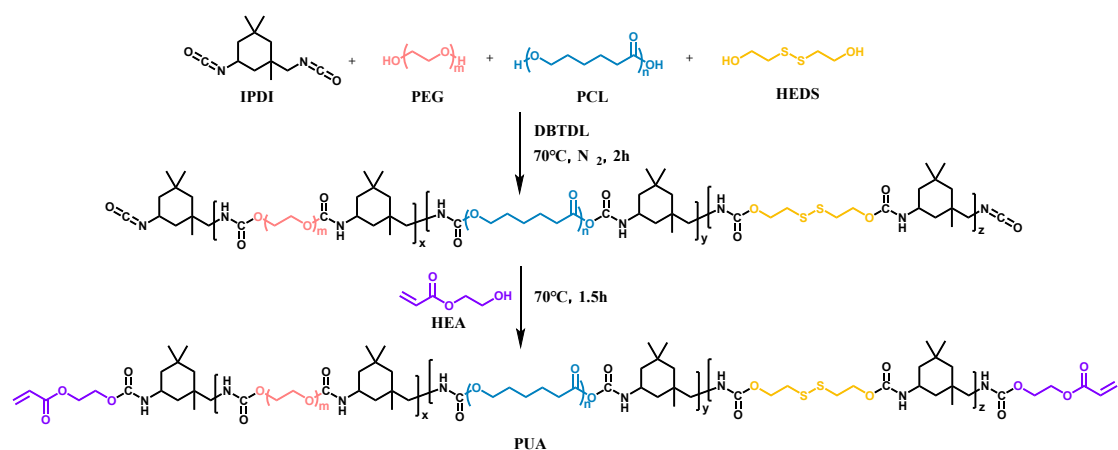


Figure S2. Schematic illustration of the synthesis and structure of the PUA.

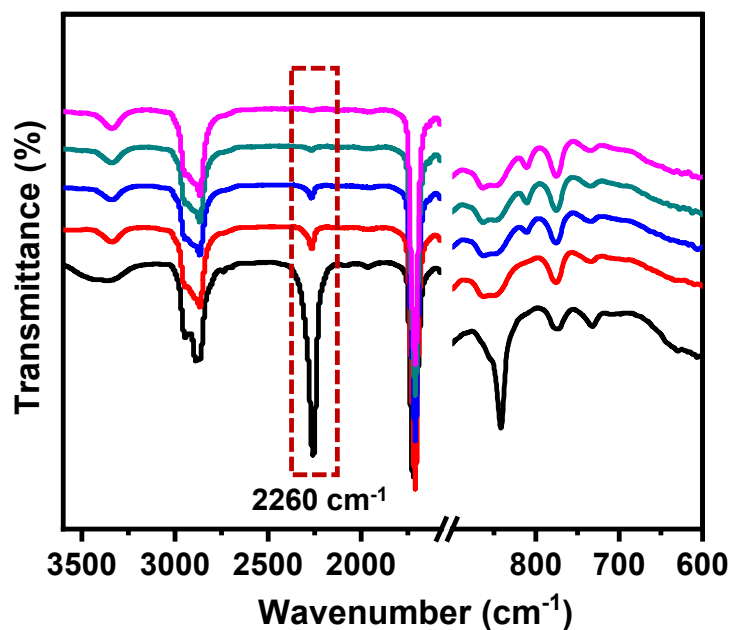


Figure S3. FTIR spectra measured during the synthesis process of the polyurethane acrylate.

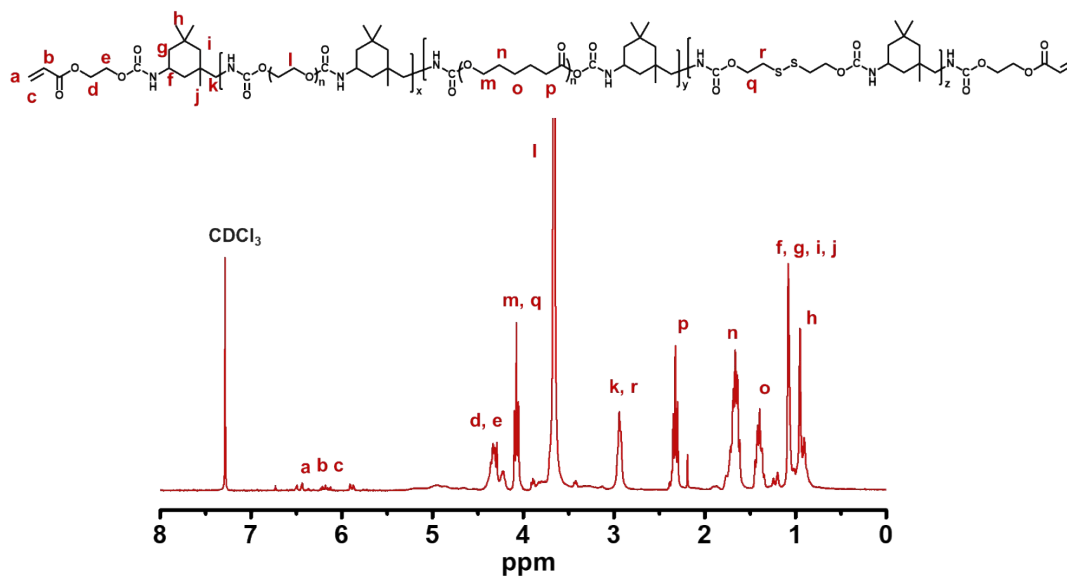


Figure S4. $^1\text{H-NMR}$ spectrum of the synthesized polyurethane acrylate.

Table S1. The compatibility of ionic liquid and diluents.

Diluents	AA	HEMA	IBOA	ACMO	TBA
Compatibility	bad	bad	bad	good	good

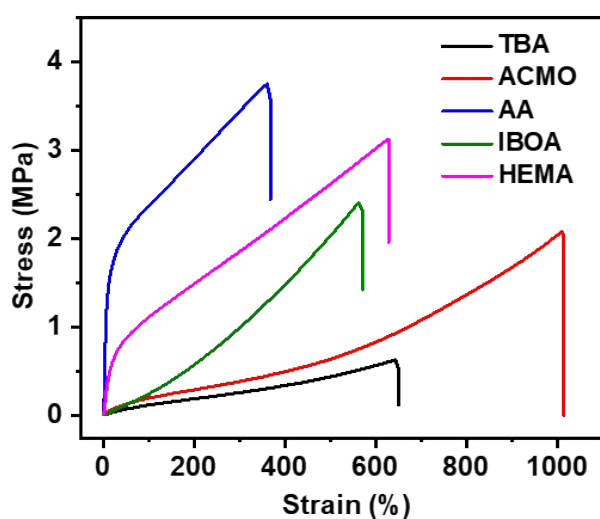


Figure S5. Tensile properties of ionogels with different diluents (PUA:diluent=1:1, with 50% of ionic liquid).

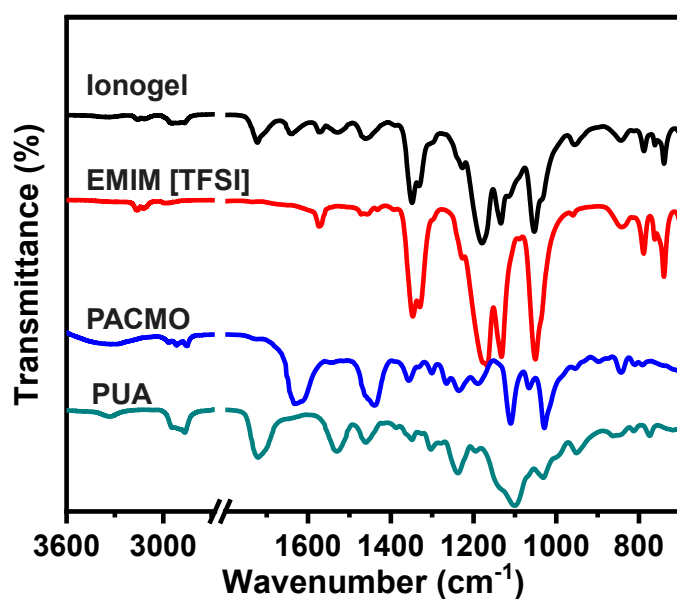


Figure S6. FTIR spectra of the synthesized PUA, PACMO, ionic liquid ([EMIM][TFSI]) and ionogel.

The characteristic peaks at 1347, 1330, and 1132 cm^{-1} were attributed to the bending vibration of S=O groups on IL. The absorption peaks at 1228 and 1167 cm^{-1} were responding to the bending of C-F and the peak at 1058 cm^{-1} was for the bending vibration of S-N-S on IL. On the spectrum of PACMO, these peaks at 1633, 1439, and 1116 cm^{-1} were corresponding to the stretching vibration of C=O, the in-plane bending of C-C on the main chain of polymer, and stretching vibration of C-O-C. On the

spectrum of PUA, the absorption peaks at 1721 and 1101 cm^{-1} were attributed to C=O of the ester groups and C-O-C of the ether groups.

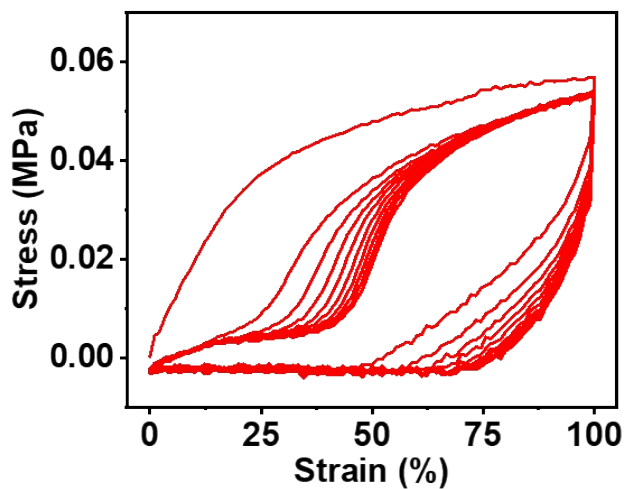


Figure S7. Consecutive cyclic tensile test result of the ionogel PACMO-60 at 100% strain for 10 times.

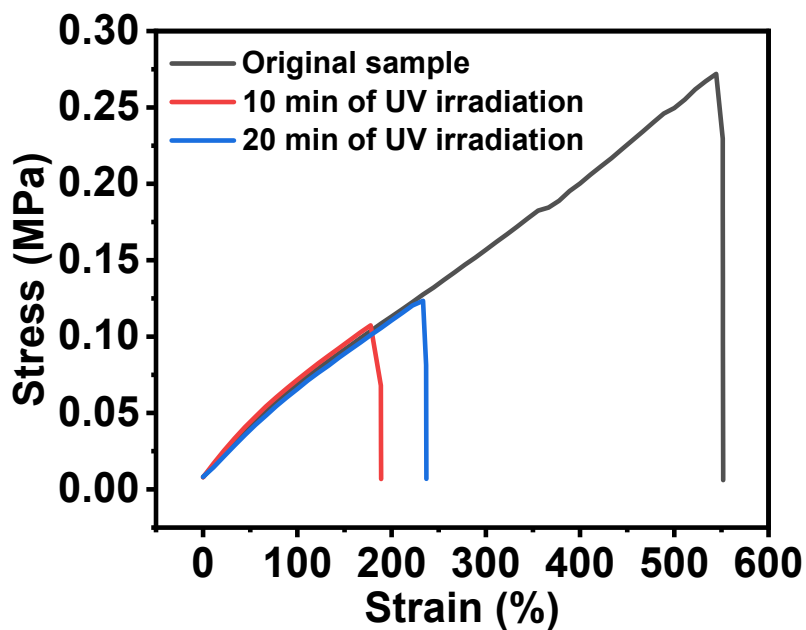


Figure S8. The healing property of the ionogel without disulfide bonds in the network of polyurethane acrylate.

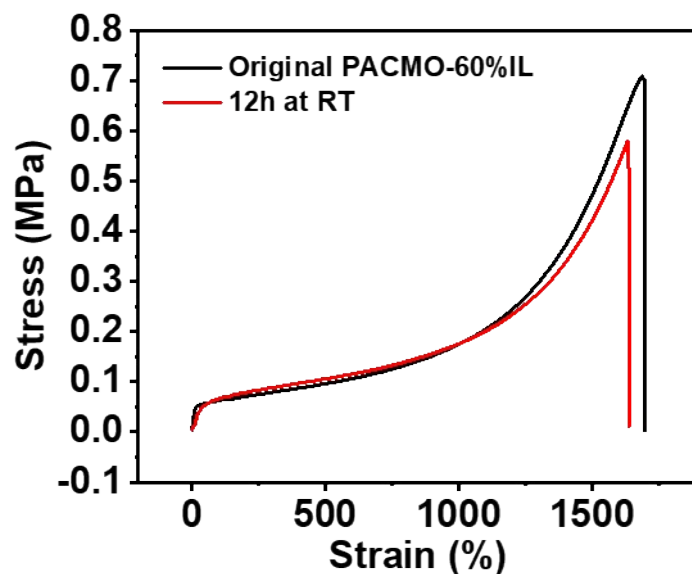


Figure S9. The healing property of the ionogel PACMO-60.

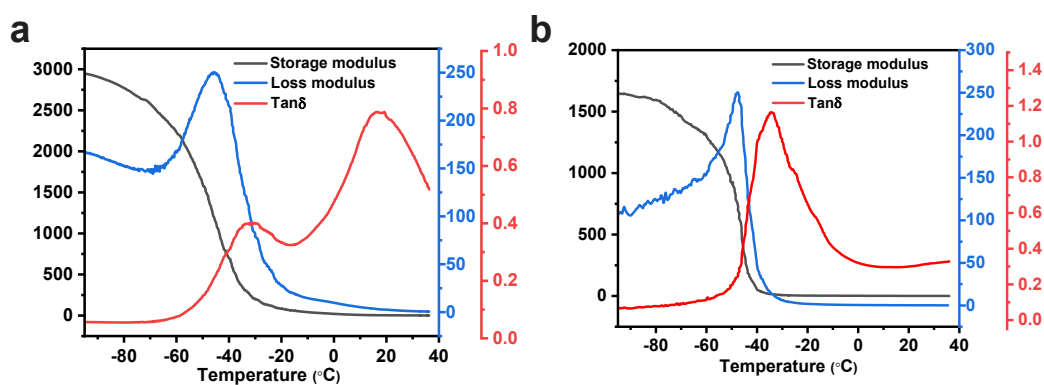


Figure S10. DMA curves of a) P(UA-co-ACMO) ionogel and b) PUA ionogel.

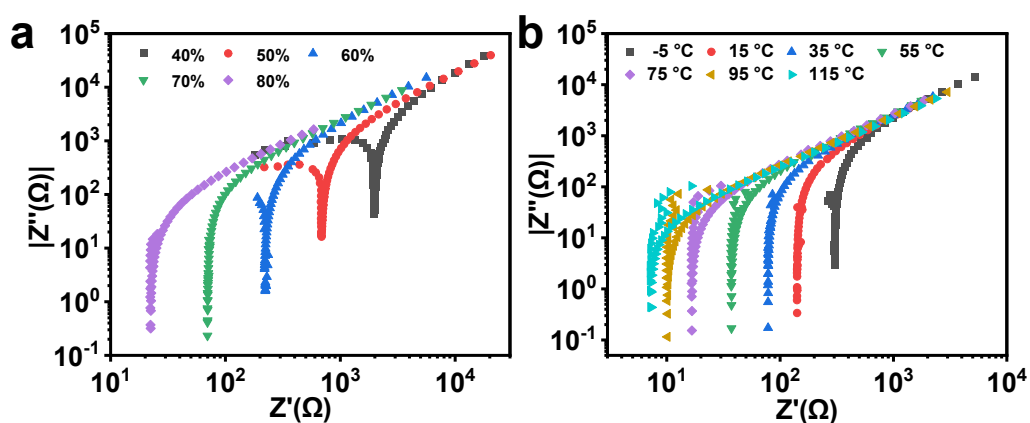


Figure S11. The electrochemical impedance spectroscopy of a) the ionogels with different contents of ionic liquid and b) the ionogel P(ACMO/UA)-60 at a wide temperature ranging from -5 to 115 °C.

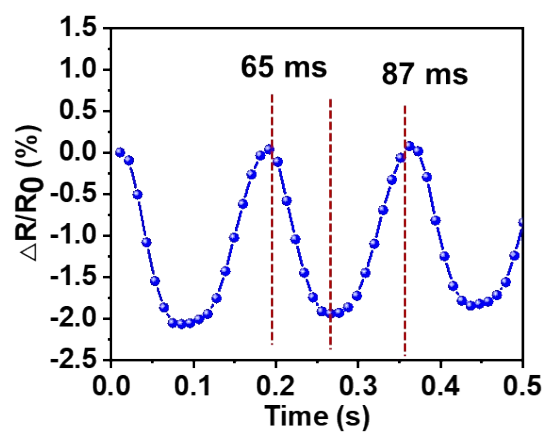


Figure S12. Response and relaxing time of the ionogel.