Supporting Information

Ion Induced Ultratough Single-network Ionogel

Zhenchuan Yu,[a] Biaolong Ma [a] and Jiqiang Wang [a]*

[a] State Key Laboratory of Bio-fibers and Eco-textiles, College of Materials Science and Engineering, Collaborative Innovation Center of Shandong Marine Biobased Fibersand Ecological Textiles, Institute of Marine Biobased Materials, Qingdao University, Qingdao 266071, China.

*Corresponding author. E-mail: zhenchuanyu@qdu.edu.cn

Experimental section

Materials: N,N-Dimethylacrylamide (DMAA), acrylic acid (AA), hydroxyethyl methacrylate (HEMA), 2-Hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI), 1-ethyl-3-methylimidazolium acetate (EMIAC), 1-ethyl-3-methylimidazolium methanesulfonate ($EMIMeO_3$) and 1-ethyl-3-methylimidazolium ethyl sulfate (EMIES) were purchased from Sigma-Aldrich.

Preparation of ionogel: The ionogel was synthesized by one-step method using DMAA as monomer and EMITFSI and EMIAC as mixed solvent. In a typical procedure, DMAA with a prescribed concentration of 6 M was dissolved in the mixed solvent with a prescribed volume fraction of EMIAC (x=0.3) to obtain a homogeneous solution. Then, the photoinitiator Irgacure 2959 (0.1 mol% relative to DMAA) was added. The obtained solution was poured into a mold containing two pieces of glass separated by a spacer and then irradiated under ultraviolet light for 2 h to obtain the ionogel. The other ionogels and hydrogels were fabricated in the same way.

Characterization: The transmittance of the ionogel was tested by UV-Vis-NIR spectrometer (UV-2600, Shimadzu) with the thickness of 1 mm. FTIR spectra were recorded on Nicolet iS50 (Thermo Fisher) using attenuated total reflectance (ATR) method. For the time-resolved FTIR spectra, the ATR crystal (diamond) was covered by the sample T/A-0 (about 500 μm), and a certain volume (200 μL herein) of EMIAC was dropped onto the sample while starting the data acquisition. The spectra were collected at a resolution of 4 cm^{-1} with 16 scans. Rheological characterizations of ionogels were performed on a HAAKE MARS modular advanced rheometer with a 25 mm parallel plate at angular frequency from 0.1 to 100 rad/s at 25 °C. Scanning electron microscopy (JSM-6390LV) was used to observe the microstructure of the samples. The universal mechanical test machine (Instron 5300) was used to characterized the tensile stress-strain curves of the ionogels. The stretching rate is 50 mm/min during the stretching process. Tensile toughness of the samples can be defined by integrating the area under the engineering stress-strain curves. To determine the fracture energy, two sets of samples were prepared with the width was w_0 =50 mm and the thickness was t_0 =1.5 mm. One set of samples had no pre-crack, whereas the other set of samples were notched with a 25 mm-long single-edge. The uncut sample was stretched to measure the force-distance curve with the distance between the two clamps was 5 mm. When the two clamps were pulled to a distance of H, the area beneath the force-distance curve gives the work done by the applied force, $U(H)$. Also, the precut sample was stretched until the notch turns into a running crack. The critical distance H_c when the pre-notch starts propagating is recorded. Then the fracture energy of the ionogel can be evaluated by $\Gamma = U(H_c)/w_0t_0$.

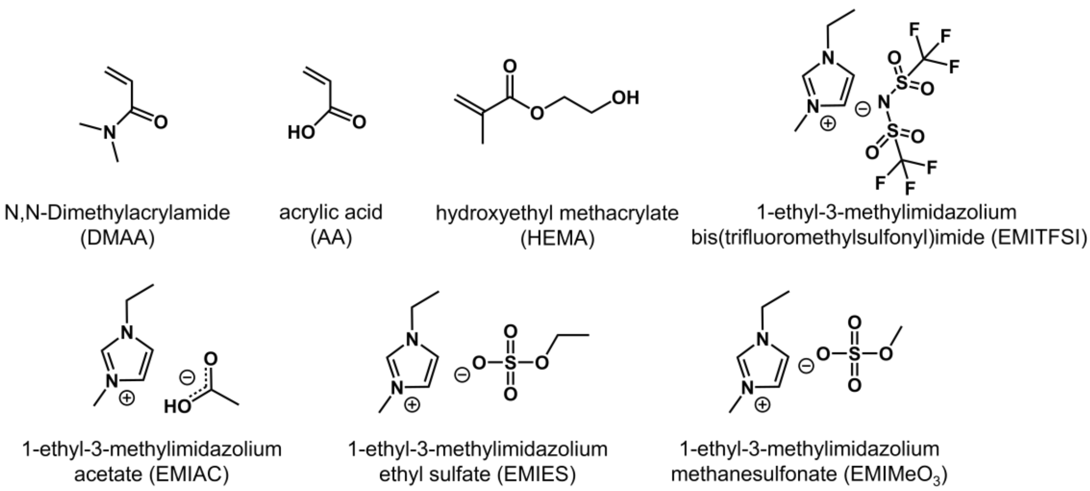

Figure S1. Chemical structures of materials used in this work.

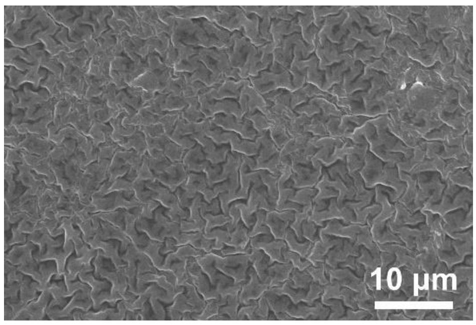

Figure S2. SEM image of T/A-0.4.

Figure S3. (a) The photograph of T/A-1. (b) The T/A-1 failed by brittle fracture without lifting the weight.

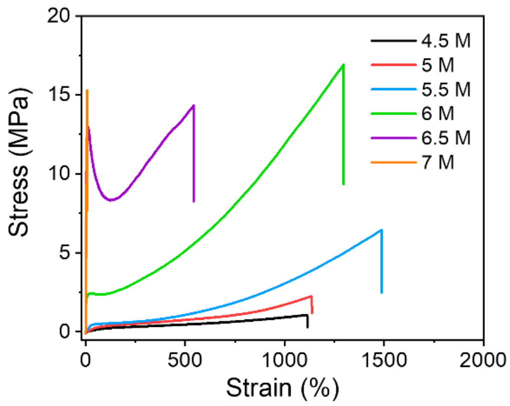

Figure S4. Stress-strain curves of T/A-0.3 with different monomer concentration.

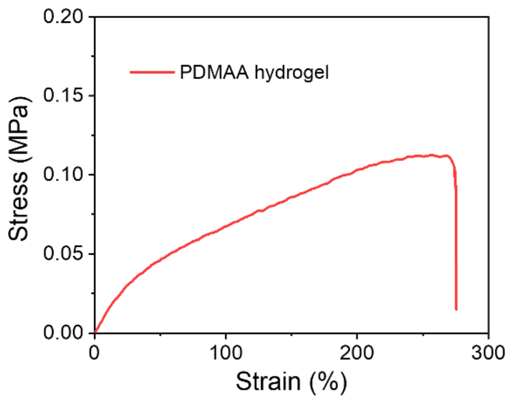

Figure S5. Stress-strain curves of PDMAA hydrogel.

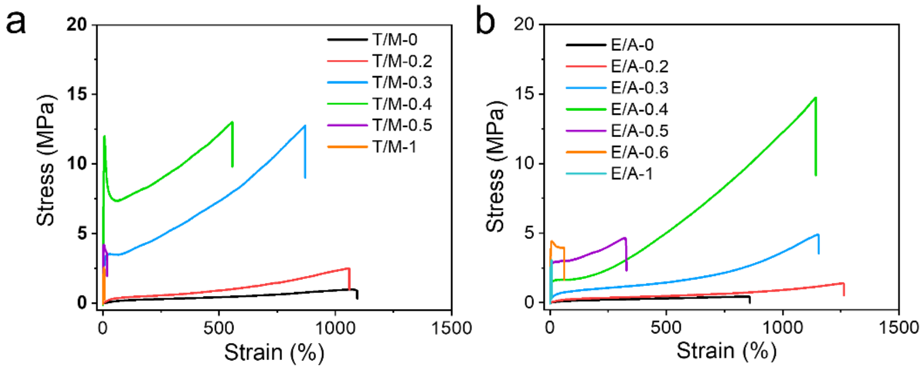

Figure S6. (a) Stress-strain curves of PDMAA ionogel with EMI as the cation, TFSI and methanesulfonate ($MeSO_3$) as mixed anion. T refer to TFSI, M refer to $MeSO_3$ and *x* refer to the volume fraction of $MeSO_3$ in the mixed anion. (b) Stress-strain curves of PDMAA ionogel with EMI as the cation, ethyl sulfate (ES) and AC as mixed anion. E refer to ES, A refer to AC and *x* refer to the volume fraction of AC in the mixed anion.

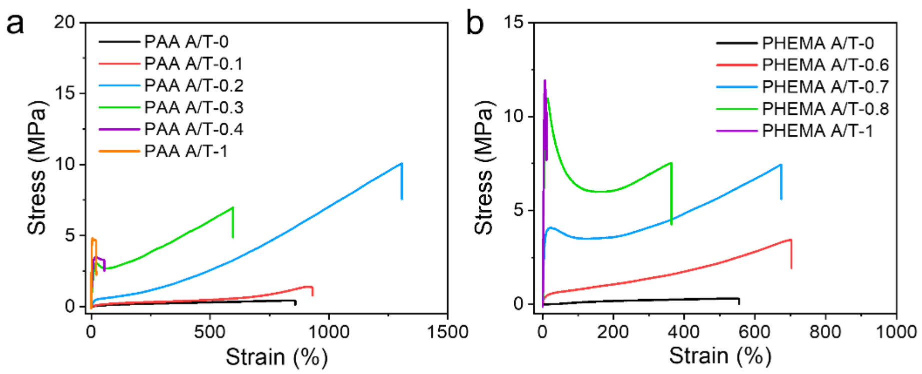

Figure S7. (a) Stress-strain curves of polyacrylic acid (PAA) ionogel with EMI as the cation, AC and TFSI as mixed anion. A refer to AC, T refer to TFSI, and *x* refer to the volume fraction of TFSI in the mixed anion. (b) Stress-strain curves of polyhydroxyethyl methacrylate (PHEMA) ionogels with EMI as the cation, AC and TFSI as mixed anion. A refer to AC, T refer to TFSI, and *x* refer to the volume fraction of TFSI in the mixed anion. EMIAC has good solubility for PAA and PHEMA, while EMITFSI has poor solubility for PAA and PHEMA

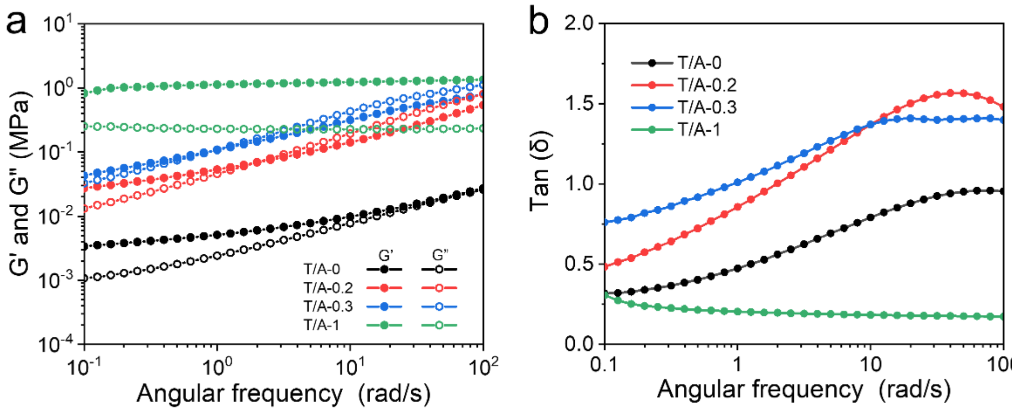

Figure S8. Angular frequency dependence of (a) G', G" and (b) tan δ for the samples T/A-0, T/A-0.2, T/A-0.3, and T/A-1.

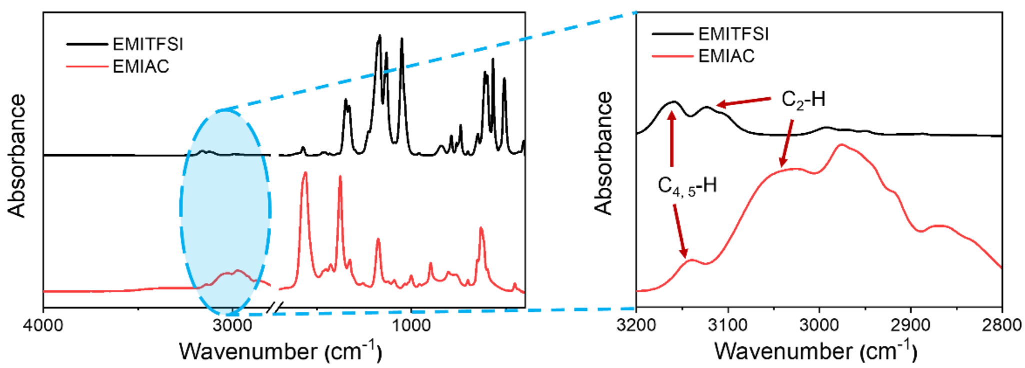

Figure S9 FTIR spectra of EMITFSI and EMIAC.

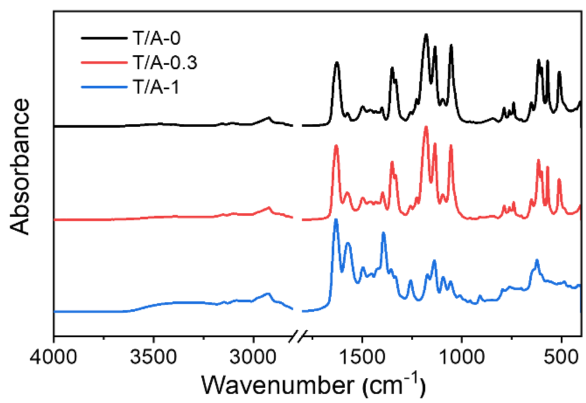

Figure S10 FTIR spectra of the ionogel samples T/A-0, T/A-0.3 and T/A-1.