
Supplementary information

Glassy gels toughened by solvent

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Supplementary Information for:

Glassy Gels Toughened by Solvent

Meixiang Wang^{1#}, Xun Xiao^{2#}, Salma Siddika³, Mohammad Shamsi¹, Ethan Frey¹, Wen Qian⁴,
Wubin Bai², Brendan T. O'Connor⁵, Michael D. Dickey^{1*}

¹ Department of Chemical and Biomolecular Engineering, North Carolina State University, 911 Partners Way, Raleigh, NC 27695, USA;

² Department of Applied Physical Sciences, University of North Carolina, Chapel Hill, NC 27599, USA;

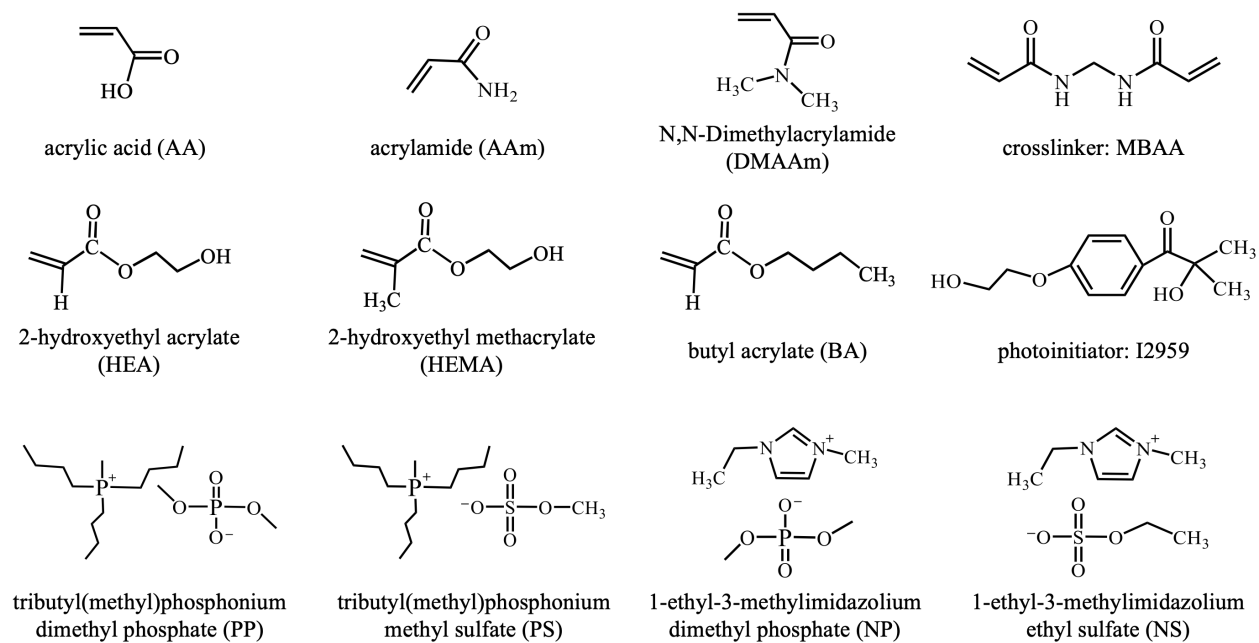
³ Department of Materials Science and Engineering and Organic and Carbon Electronic Laboratories (ORaCEL), North Carolina State University, Raleigh, NC 27695, USA;

⁴ Department of Mechanical & Materials Engineering, University of Nebraska-Lincoln, Lincoln, NE 68588, USA.

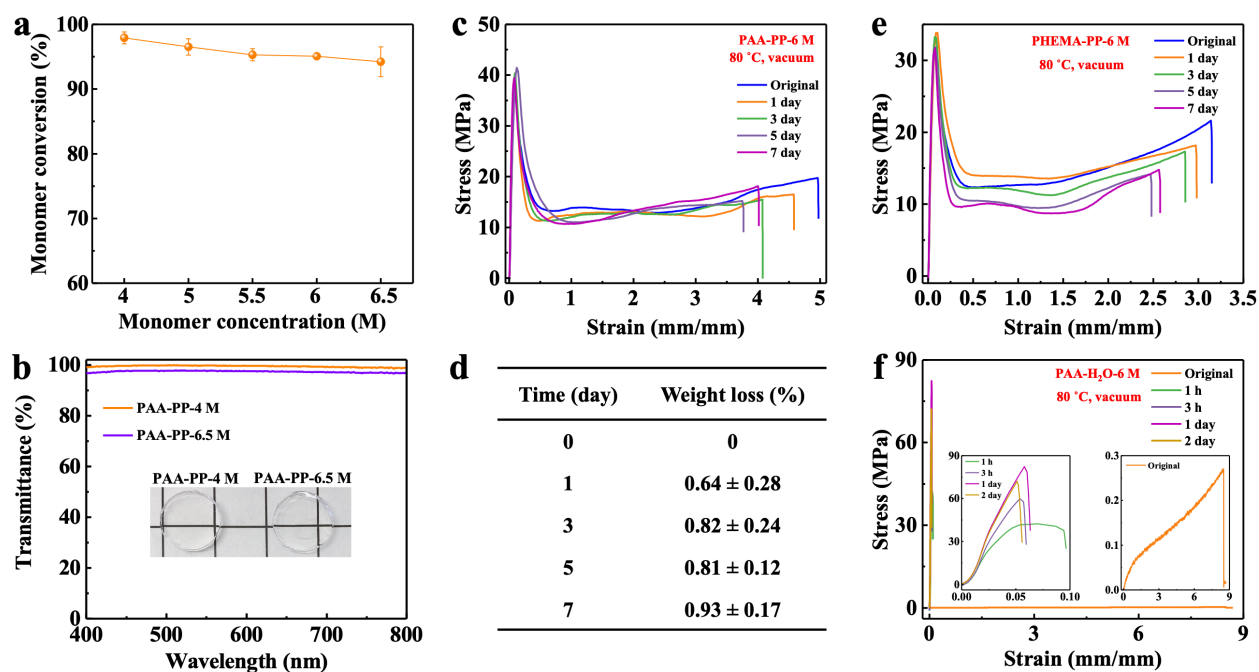
⁵ Department of Mechanical and Aerospace Engineering and Organic and Carbon Electronic Laboratories (ORaCEL), North Carolina State University, Raleigh, NC 27695, USA;

[#] These authors contributed equally.

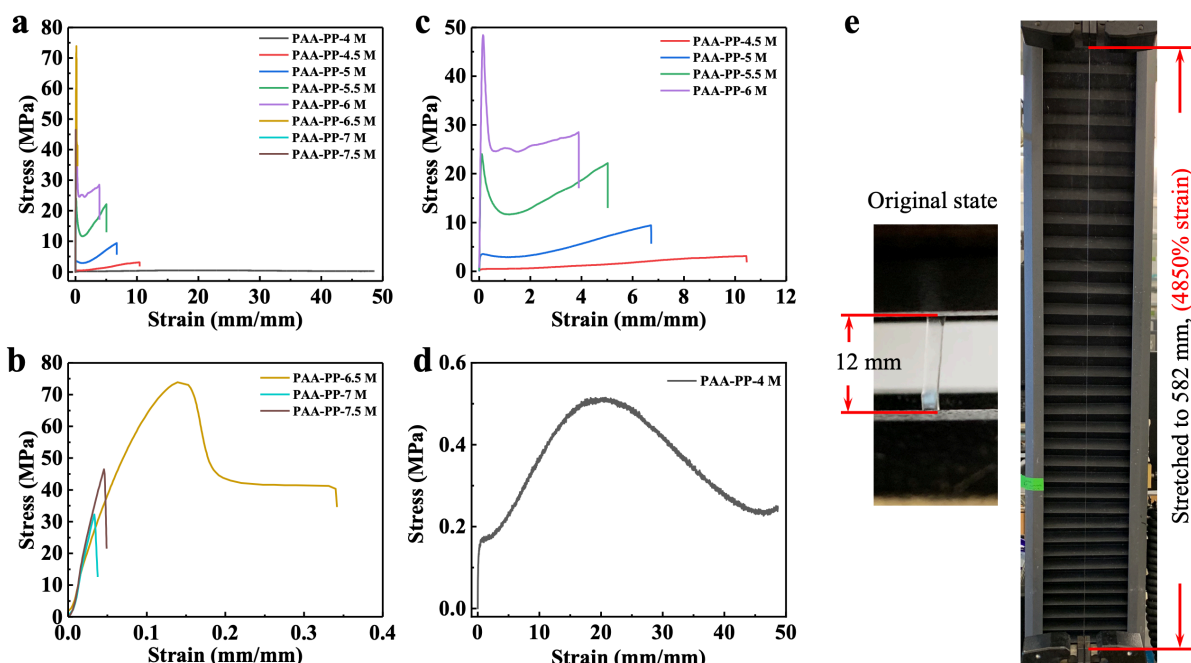
* Correspondence to M.D. (email: mddickey@ncsu.edu)



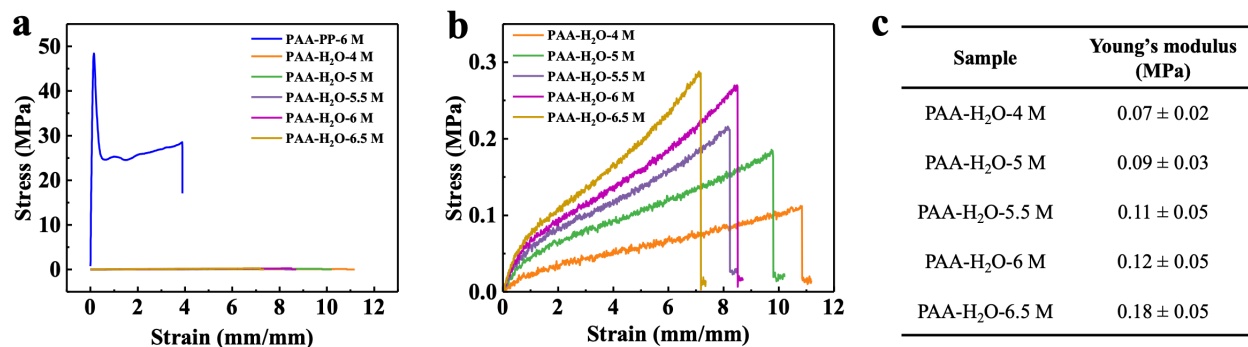
Supplementary Figure 1. Chemical structures of materials used in this work.



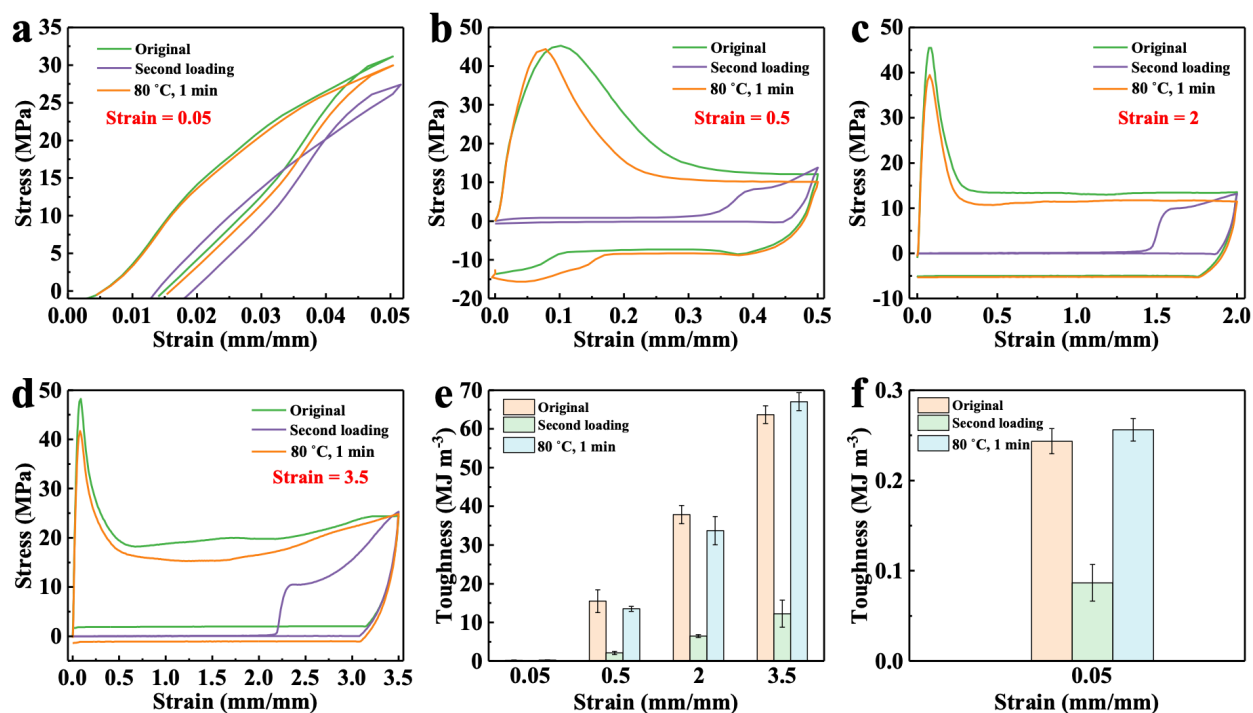
Supplementary Figure 2. Monomer conversion, transmittance, tensile properties, and weight loss of various gels. (a) Monomer conversion of PAA-PP gels with different monomer concentration. (b) Transmission spectra of PAA-PP gels. Inset in a is a photograph of two different gels (thickness = 2 mm, diameter = 12 mm). Tensile stress-strain curves of (c) PAA-PP-6 M, (e) PHEMA-PP-5.5 M, and (f) PAA-H₂O-6 M gels under vacuum at 80 °C for different durations. (d) The weight loss of PAA-PP-6 M gel over time under vacuum at 80 °C. Insets in f are the zoom in of tensile curves of PAA-H₂O-6 M gel. Error bars on the data show standard deviation from three independent samples.



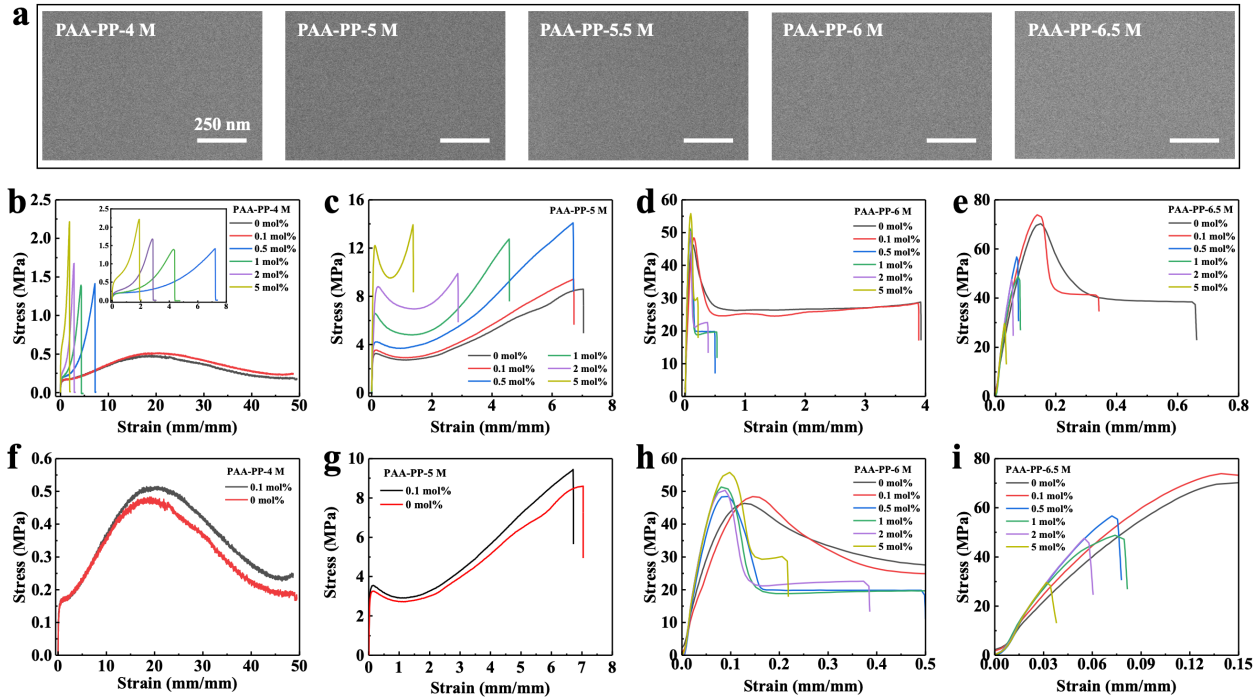
Supplementary Figure 3. Tensile properties of PAA-PP gels. (a-d) Tensile stress-strain curves. b and d: zoom in of a. Depending on the concentration of AA, the gels can vary from being either (b) stiff and brittle, (c) stiff and tough, or (d) soft and stretchable. Inset in d is the zoom in of the stress-strain curve of PAA-PP-4 M gel. (e) Photos of the stretching process of PAA-PP-4 M gel.



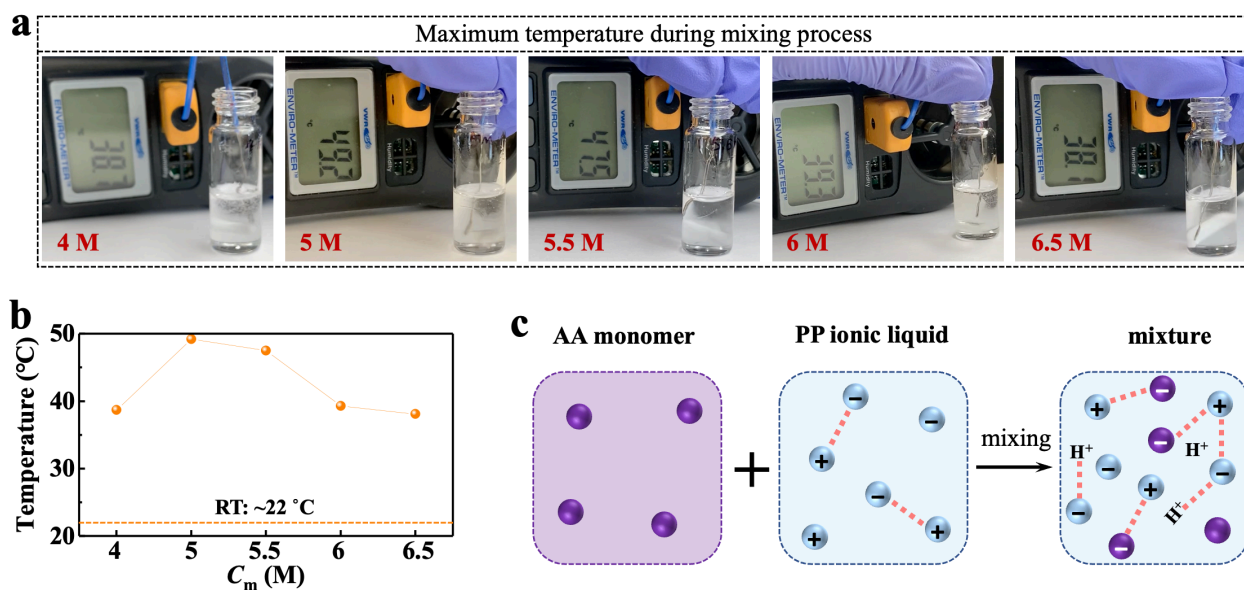
Supplementary Figure 4. Tensile properties of glassy gel versus hydrogel. (a) Tensile stress-strain curves of PAA-PP-6 M glassy gel and PAA-H₂O hydrogels. (b) Zoom in of a. (c) Young's modulus of PAA-H₂O hydrogels.



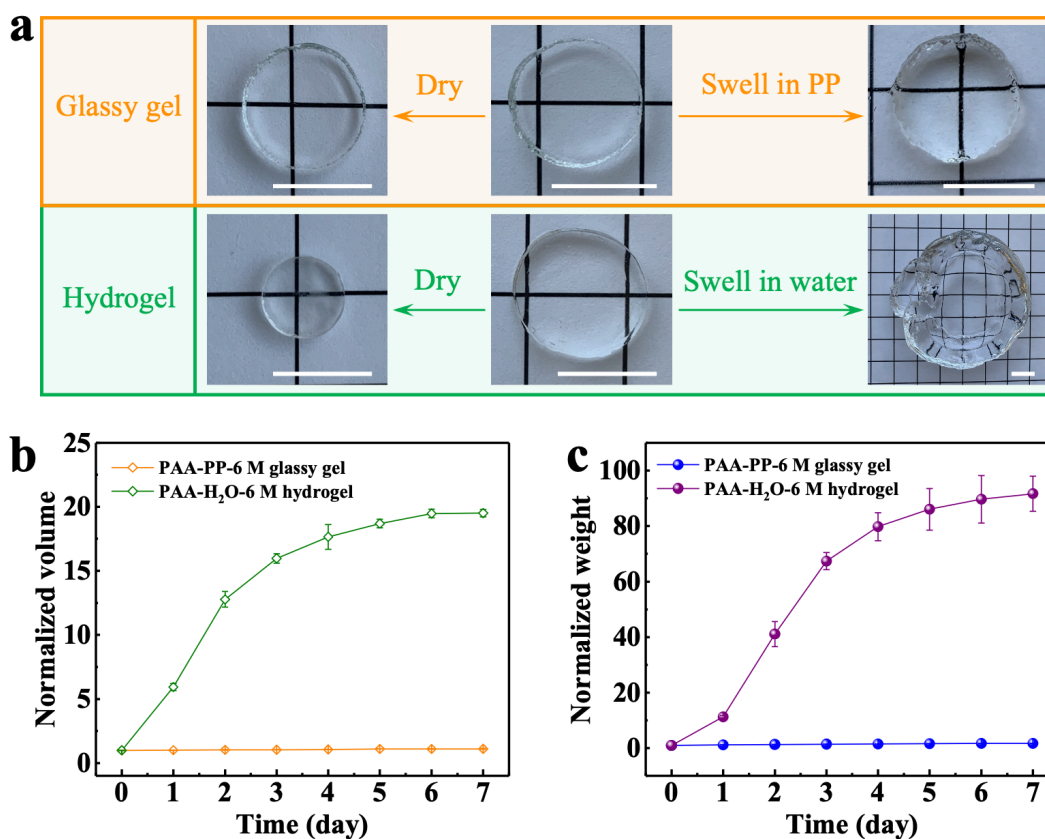
Supplementary Figure 5. Excellent recovery properties of PAA-PP-6 M glassy gel. (a-d) The loading-unloading curves and (e, f) the toughness of glassy gels under different strains. f is zoom in of e. ‘Original’ is the first loading of the glassy gel at room temperature (RT). ‘Second loading’ is the sample at RT without allowing time for recovery after the prior loading. ‘80 °C, 1 min’ is the sample strain cycled at RT after allowing it to recover at 80 °C for 1 min after the prior loading. Error bars on the data show standard deviation from three independent samples.



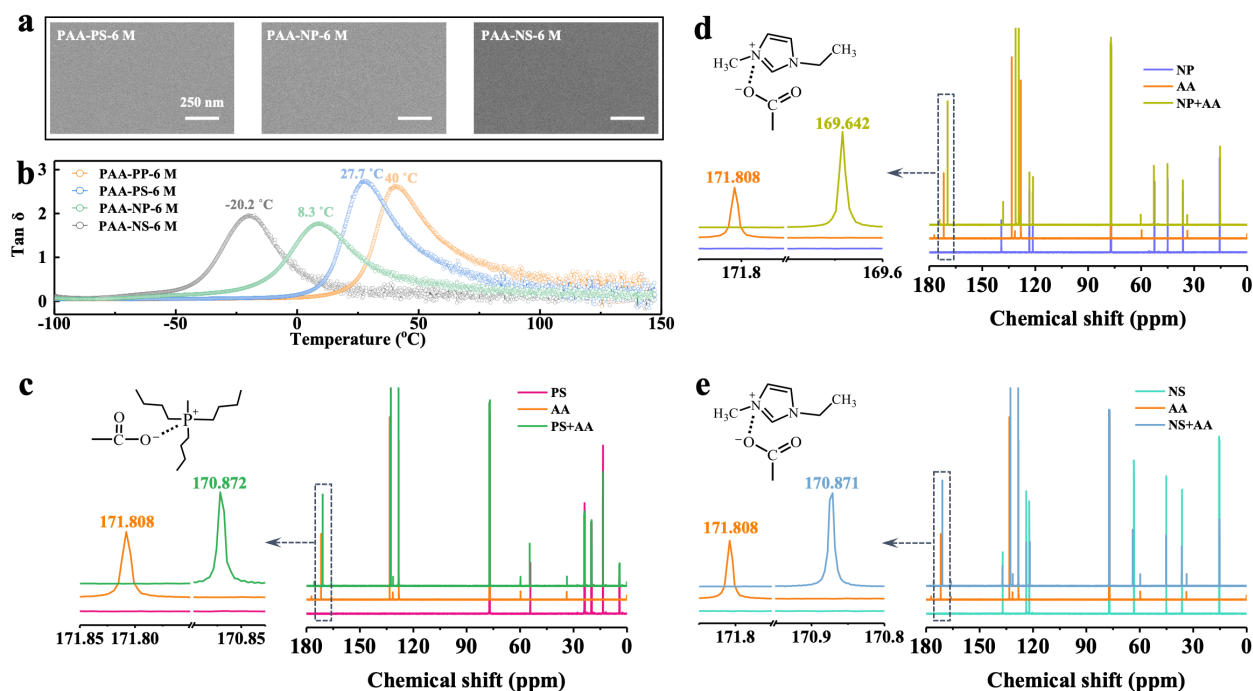
Supplementary Figure 6. SEM images and tensile properties of PAA-PP gels. (a) SEM images show a homogeneous morphology, which implies there is no phase separation in the gel. (b-i) Tensile stress-strain curves of various gels with different MBAA crosslinker concentrations. Inset in b is the zoom in of the tensile stress-strain curves in b. f-i are the zoom in of b-e, respectively. Note that there is no significant difference between the tensile stress-strain curves when crosslinker concentration is ≤ 0.1 mol%. This result indicates when the crosslinker concentration is ≤ 0.1 mol%, the crosslinker does not play an important role in the mechanical properties.



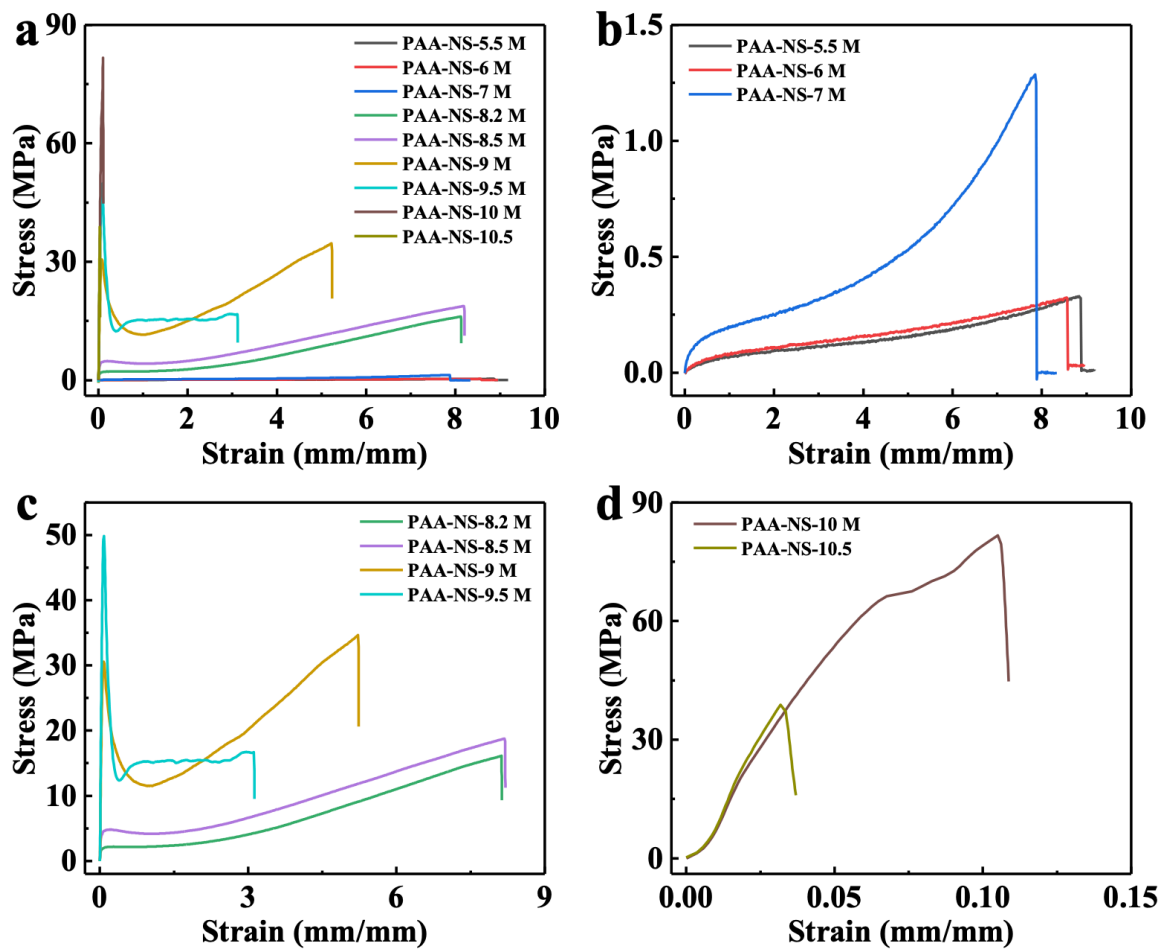
Supplementary Figure 7. Interactions between AA and PP. (a) Photos of the maximum temperature during mixing in air resulting from exothermic mixing. The temperature is measured by a thermometer (enviro-meter, VWR). (b) The maximum temperature of precursors with different AA monomer concentrations. (c) Proposed exothermic interactions between AA and PP from mixing. The dashed lines represent associations between the cation and anion in the ionic liquid, anion of the ionic liquid with the proton from the disassociated AA, or between the cation of the ionic liquid and the disassociated AA.



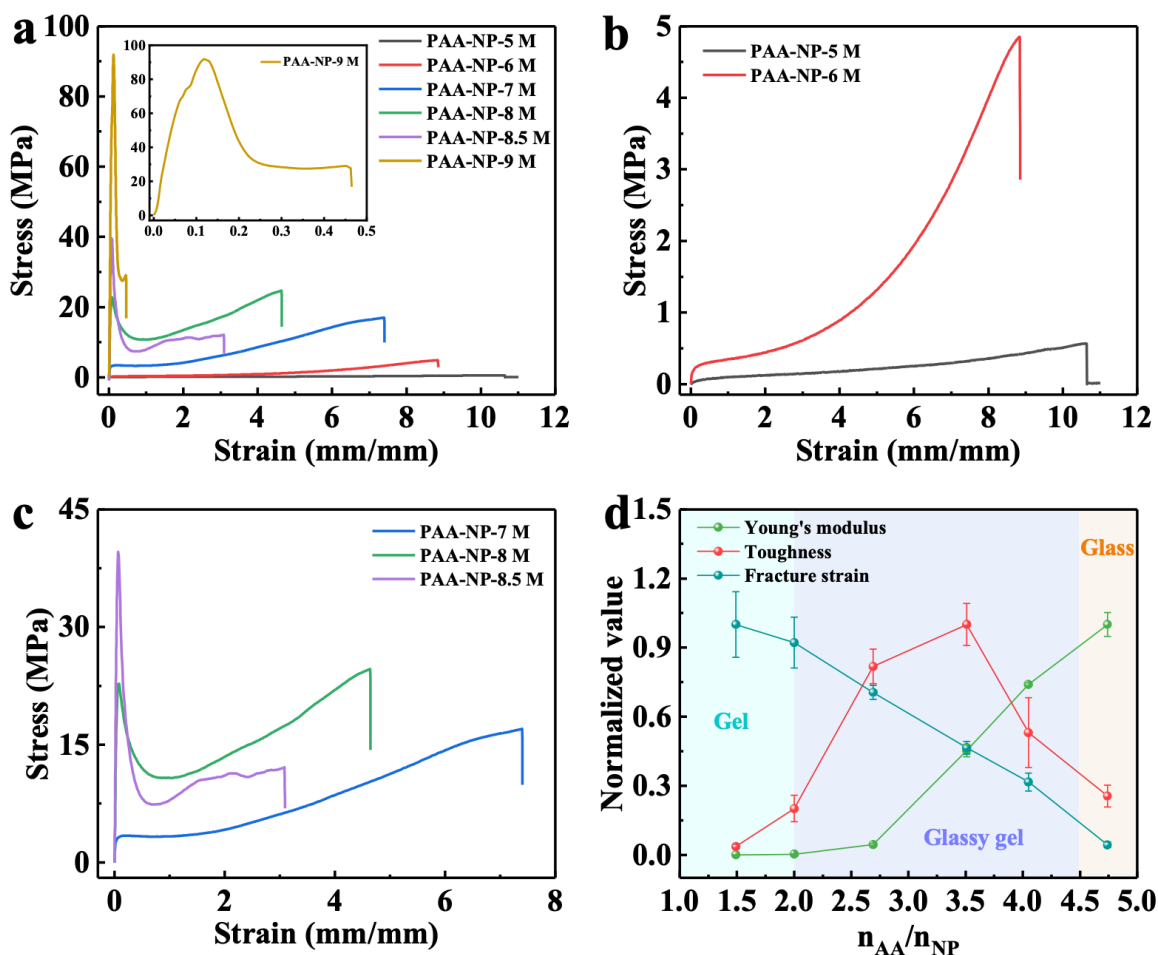
Supplementary Figure 8. Swelling properties of glassy gel compared to hydrogel. (a) The photos of initially 6 M gels after swelling (room temperature for 7 days) and drying (room temperature for 30 days). (b, c) Time dependence of the normalized (b) swelling volume ratio, Q_v , and (c) swelling weight ratio, Q_w . The hydrogel reached equilibrium after 6 days. The scale bar in a is 10 mm. Error bars on the data show standard deviation from three independent samples.



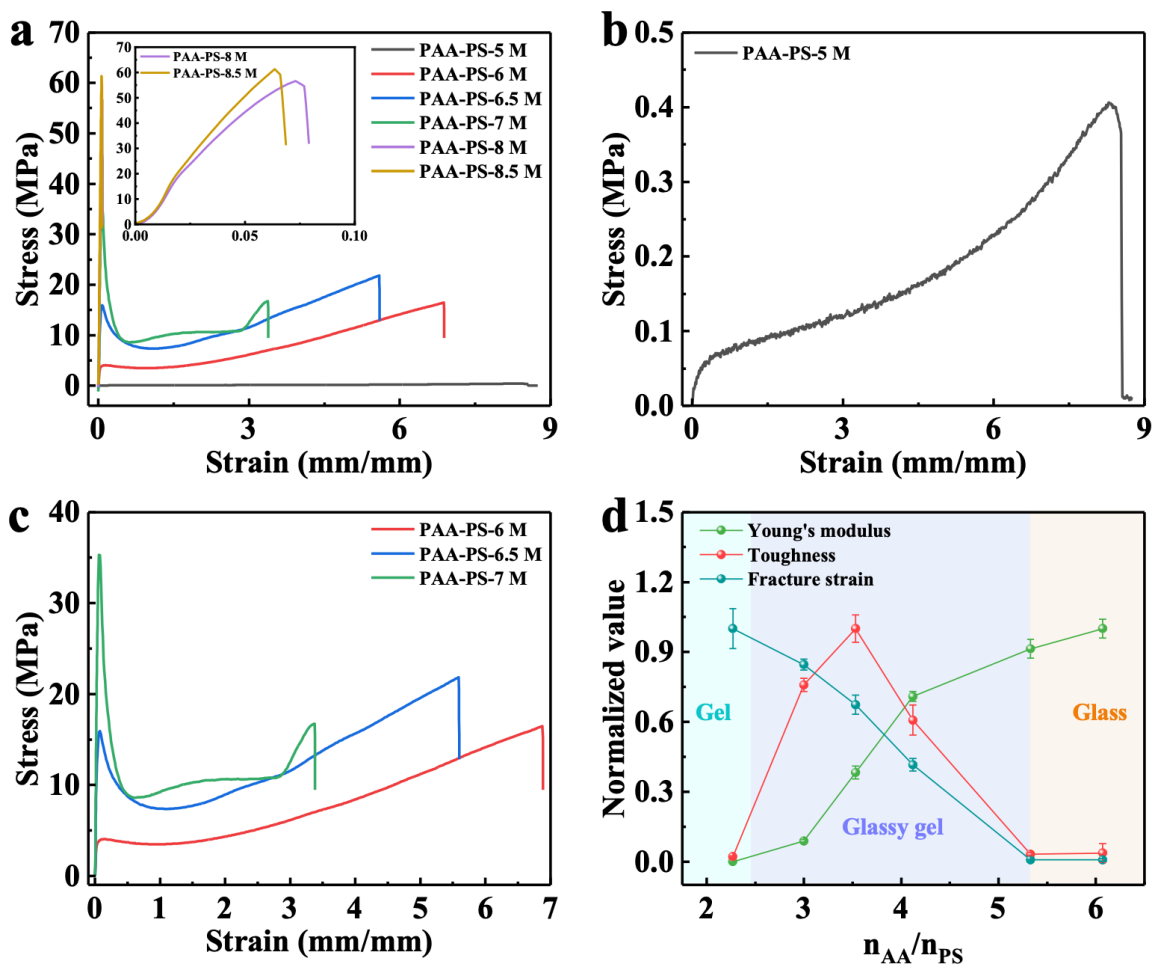
Supplementary Figure 9. Characterizations of PAA gels with different ILs. (a) SEM images and (b) temperature dependence of the loss tangent ($\tan \delta$) of various PAA gels. The uniform SEM image and single T_g peak show that these gels are homogeneous. (c-e) ^{13}C NMR spectra of various ionic liquids, AA monomer, and their mixtures. The upper left schematics show the associations between the cation of ILs and the carboxylic group ($-\text{COO}^-$) of AA. The monomer concentrations for c-e are, respectively, 7, 8.5, and 9.5 M.



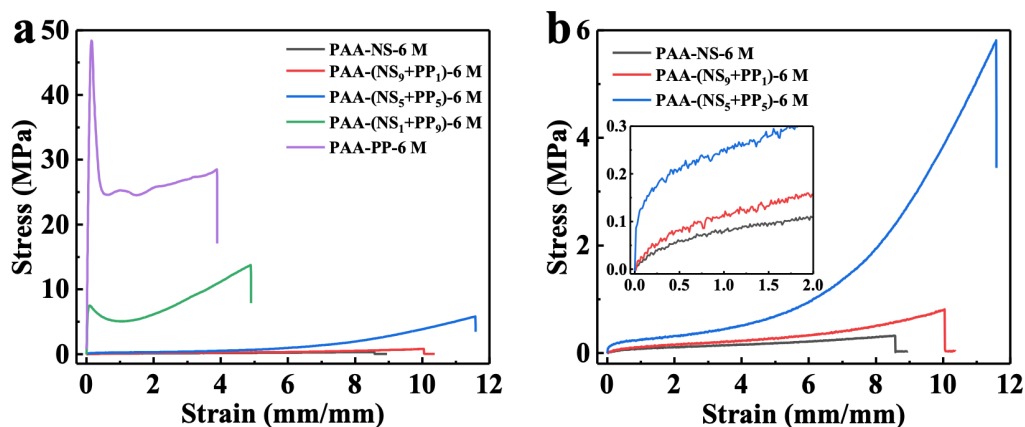
Supplementary Figure 10. Tensile stress-strain curves of PAA-NS gels. b-d: zoom in of a.



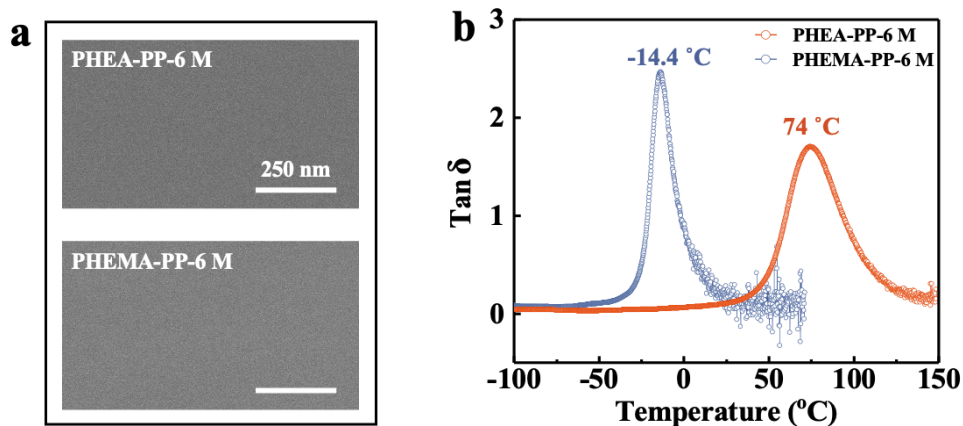
Supplementary Figure 11. Mechanical properties of PAA-NP gels. (a-c) Tensile stress-strain curves of PAA-NP gels. Inset in a is the tensile stress-strain curve of PAA-NP-9 M gel. b and c: zoom in of a. (d) Normalized Young's modulus, toughness, and fracture strain of PAA-NS gels as a function of the molar ratio of AA to NP (n_{AA}/n_{NP}). Clearly, the mechanical behavior of the gels varies from soft and stretchable (gel-like), stiff and tough (glassy gel), to stiff and brittle (glass-like) as molar ratio changes. Error bars on the data show standard deviation from three independent samples.



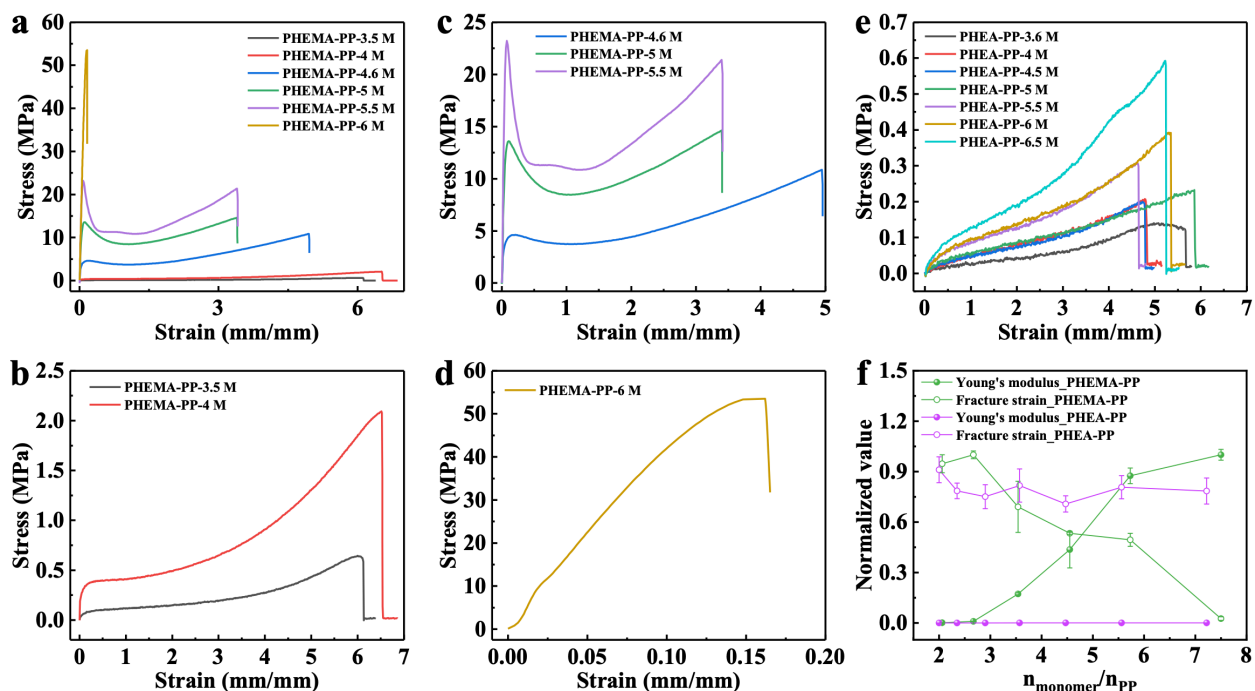
Supplementary Figure 12. Mechanical properties of PAA-PS gels. (a-c) Tensile stress-strain curves of PAA-PS gels. Inset in a is the tensile stress-strain curves of PAA-PS-8 M and PAA-PS-8.5 M gels. b and c: zoom in of a. (d) Normalized Young's modulus, toughness, and fracture strain of PAA-PS gels as a function of the molar ratio of AA to PS (n_{AA}/n_{PS}). It's obvious that the mechanical behavior of the gels varies from soft and stretchable (gel-like), stiff and tough (glassy gel), to stiff and brittle (glass-like) as molar ratio changes. Error bars on the data show standard deviation from three independent samples.



Supplementary Figure 13. Tensile properties of PAA gels using mixed ILs as solvents. (a, b) Tensile stress-strain curves of PAA gels using PP and NS as mixed solvents. Inset in b is the zoom in of b. Note that PP and NS ILs were mixed in volume ratio. For example, PAA-(NS₉+PP₁)-6 M means that the volume ratio of NS to PP is 9:1. PAA-NS-6 M and PAA-PP-6 M gels use pure NS or PP as solvent.



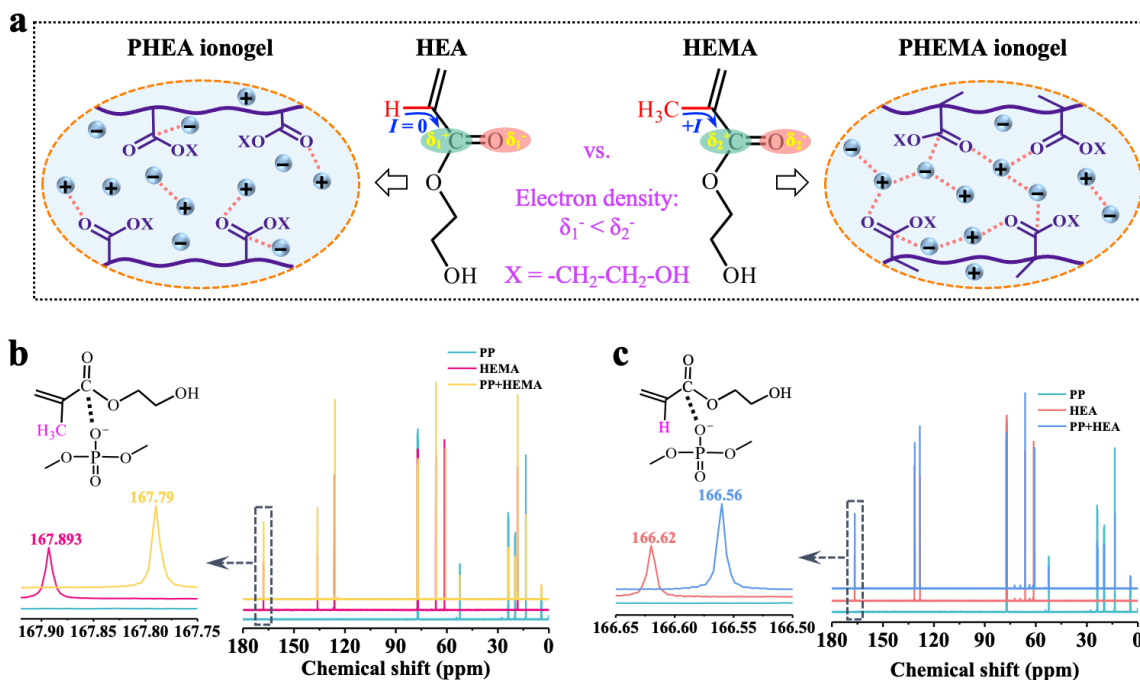
Supplementary Figure 14. Characterizations of gels formed using polymers other than PAA. (a) SEM images and (b) temperature dependence of the loss tangent ($\tan \delta$) of PHEA-PP-6 M and PHEMA-PP-6 M gels. Note that PHEA-PP-6 M gel was too soft to measure at temperature above ~71 °C in b.



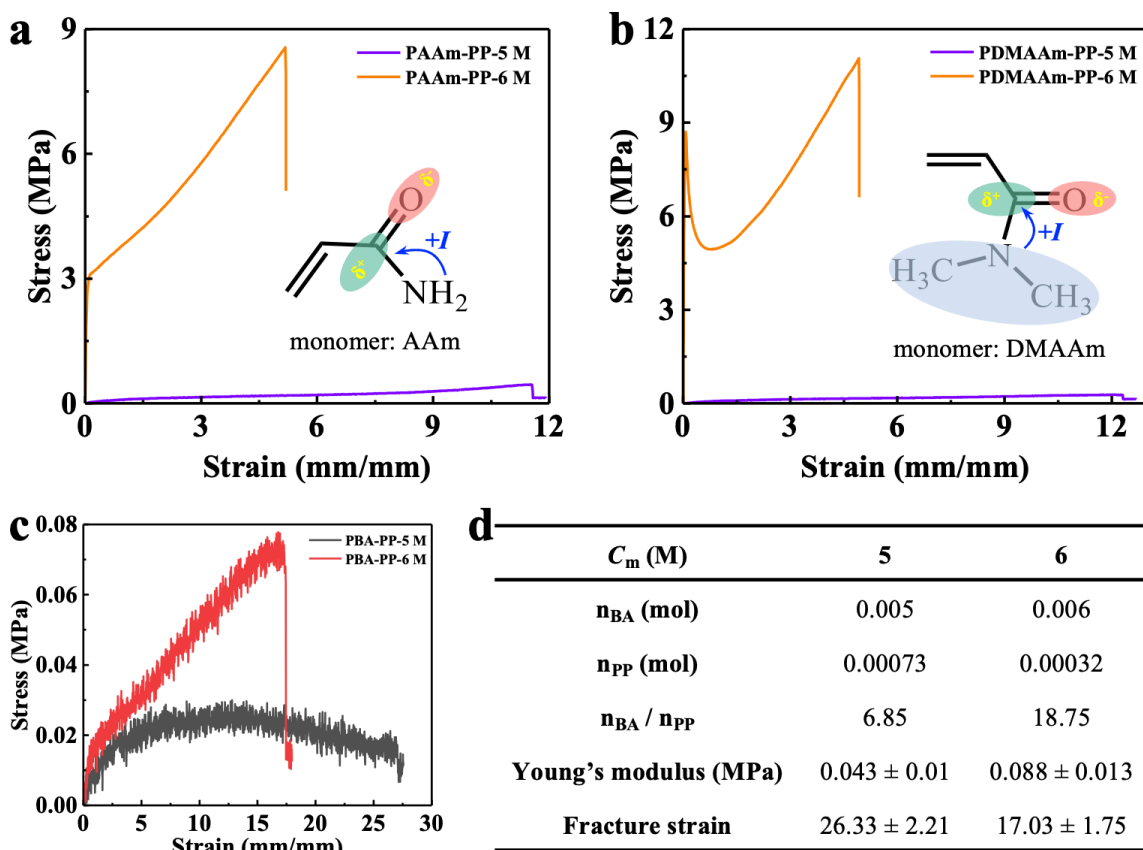
Supplementary Figure 15. Mechanical properties of PHEMA-PP and PHEA-PP gels. (a-c)

Tensile stress-strain curves. b-d: zoom in of a. (f) Normalized Young's modulus and fracture strain of PHEMA-PP and PHEA-PP gels as a function of the molar ratio of monomer to PP ($n_{\text{monomer}}/n_{\text{PP}}$).

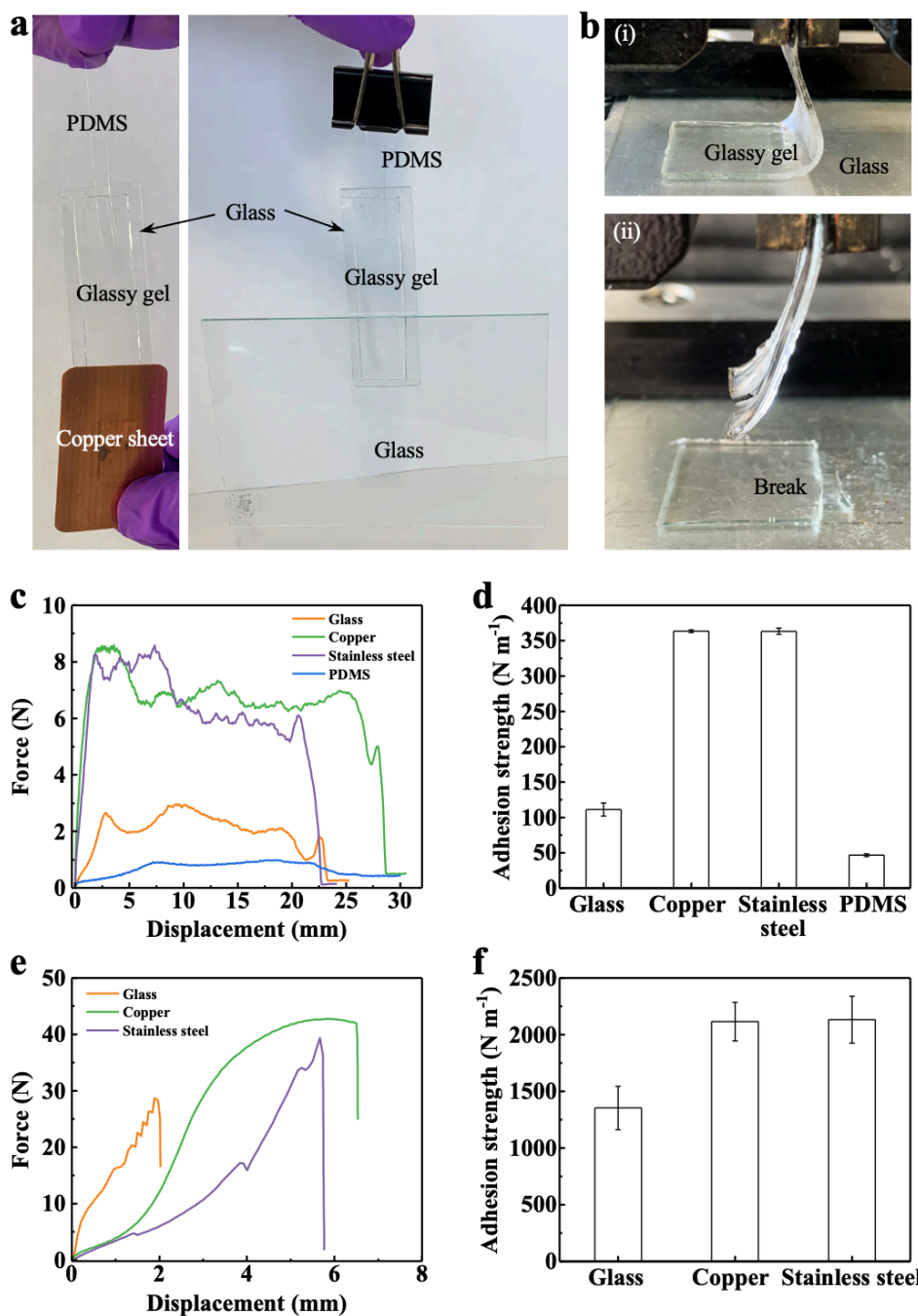
To make a better comparison, both PHEMA-PP and PHEA-PP gels are normalized based on the maximum Young's modulus and fracture strain of PHEMA-PP gels. Error bars on the data show standard deviation from three independent samples.



Supplementary Figure 16. Schematics of dipole-ion interactions and ^{13}C NMR spectra. (a) Schematics illustrating that dipole-ion interactions between HEMA and PP act as physical crosslinks to toughen the PHEMA gel. ^{13}C NMR spectra of (b) PP, HEMA, and their mixture and (c) PP, HEA, and their mixture. The upper left schematics in b and c show the associations between the anion of PP and the carbonyl group ($-\text{C}=\text{O}$) of HEMA and HEA, respectively. The monomer concentrations for b and c are 5.5 and 6 M, respectively.

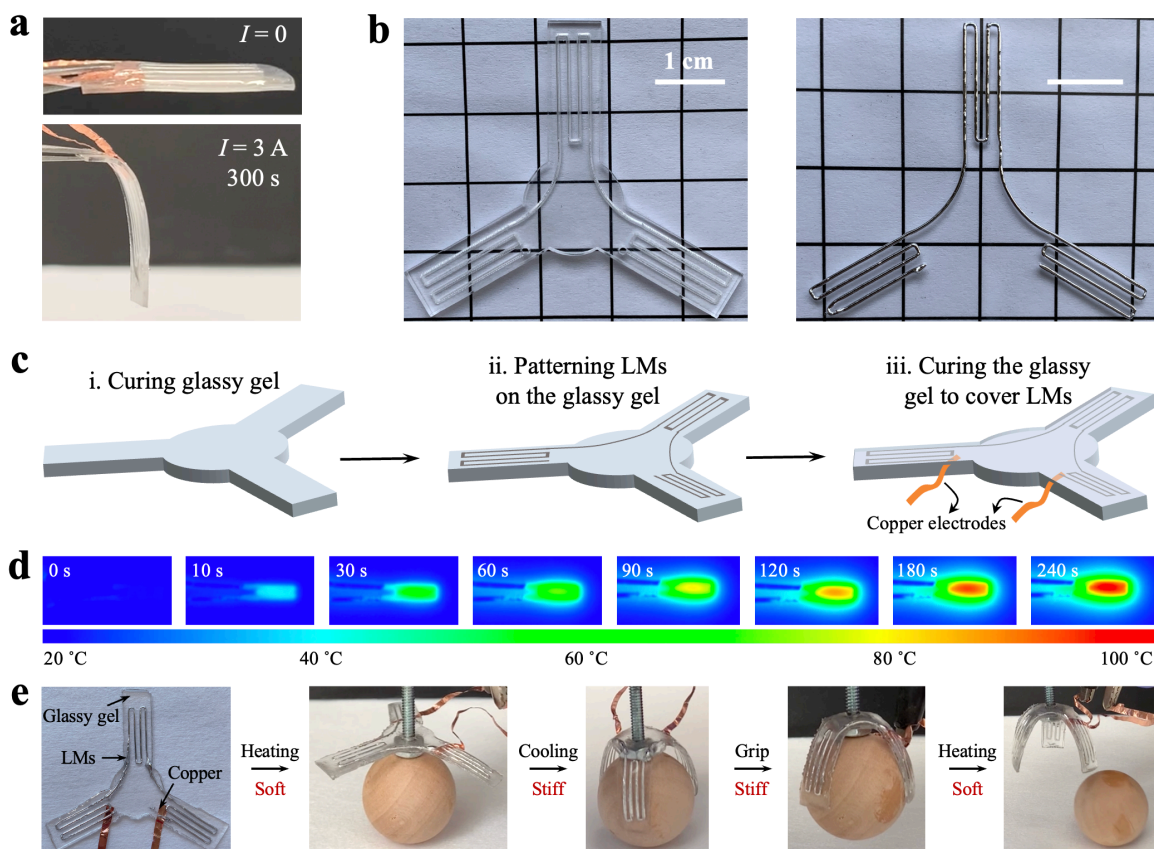


Supplementary Figure 17. Tensile properties of various gels. Tensile stress-strain curves of (a) polyacrylamide (PAAm)-PP and (b) poly(N,N-Dimethylacrylamide) (PDMAAm)-PP gels. These gels can also form polar interactions with the ionic liquid. Insets in b and c to show the +I effect of amide group in AAm and dimethylamino group in DMAAm. (c) Tensile stress-strain curves and (d) summary of mechanical properties of various poly(butyl acrylate) (PBA)-PP gels. BA (I effect = 0: -H) failed to produce a tough gel due to its weak interaction with PP, similar to HEA.

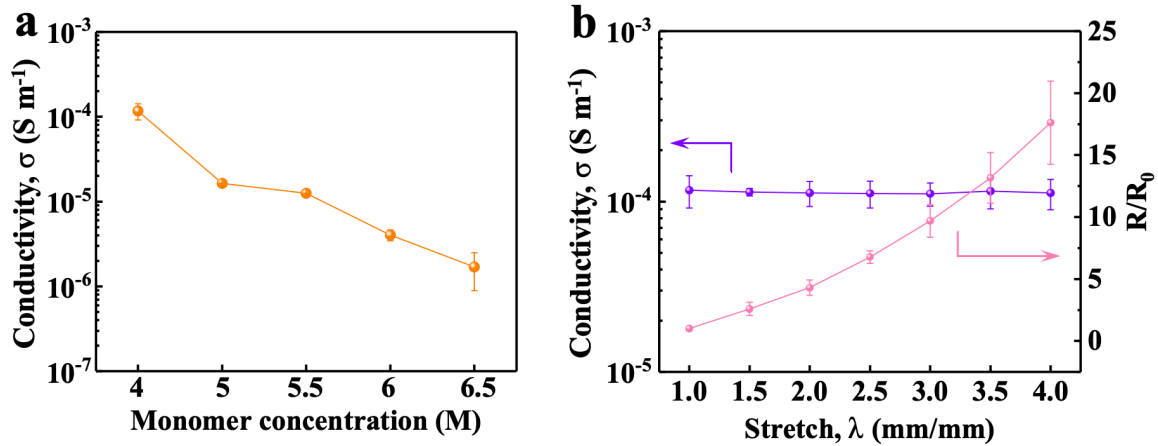


Supplementary Figure 18. Adhesive properties of PAA-PP-6 M glassy gel. (a) The glassy gel could adhere to different substrates. (b) The photos of 90-degree peeling test of glassy gel on glass substrate. (c, e) Peeling curves and (d, f) adhesion strength of glassy gels on different substrates. The thickness and width of the samples are 1 and 19 mm, respectively. Error bars on the data show standard deviation from three independent samples. Note that we prepared samples in two ways:

(1) curing it elsewhere and transferring it to a substrate versus (2) curing the glassy gel directly on a substrate. The former we call “transfer” adhesion. In c and d, the “transfer” adhesion strength of the glassy gel on various substrates was measured after gently pressing the surfaces together by hand for 1 min. In b, e, and f, the adhesion strength of the glassy gel cured directly on the glass substrate is too strong to peel it off the glass, causing the glassy gel to fail cohesively. Thus, the force-displacement curves do not reach a plateau in e (glassy gels cannot be cured on PDMS, so the adhesion strength was not measured). The high adhesion strength may be attributed to the ionic nature of the glassy gels, such as coordination and ionic bonding with the substrate.



Supplementary Figure 19. Joule heat driven gripper. (a) The glassy gel (thickness = 0.7 mm) softens due to Joule heating. (b) The mold of pattern LMs (left) and LMs patterned by the mold (right). The scale bar is 1 cm. The width of LMs path is 500 μm . (c) Schematics showing the fabrication process of the three-arm gripper. (d) The solvent in the glassy gels does not evaporate upon Joule heating the gel (current = 3 A). (e) Heat-driven gripper. The diameter of the wooden ball is 1 inch. The width of LMs line is 500 μm in a and e. PAA-PP-6 M glassy gel was used in a, d, and e.



Supplementary Figure 20. Conductivity of PAA-PP gels. (a) Conductivity of PAA-PP gels with different monomer concentration. (b) Conductivity and resistance of PAA-PP-4 M gel under various stretch (λ , *i.e.*, strain + 1). Error bars on the data show standard deviation from three independent samples.

Supplementary Note 1. Toughening mechanism of PHEMA-PP glassy gel.

The distinct mechanical performance between PHEA-PP and PHEMA-PP gels likely originates from the different structures, and thus, polarity difference between HEA and HEMA. In HEA, it has a hydrogen atom (-H) attached to the carbon near the carbonyl group, while HEMA has a methyl group (-CH₃). This gives rise to different inductive (*I*) effects (*i.e.*, electron donating / withdrawing) on the electron density of the carbonyl group (**Supplementary Fig. 16a**).¹ Since PHEA-PP-6 M gel is in a rubbery state at RT ($T_g = -14.4\text{ }^{\circ}\text{C}$), it can be inferred that the interactions between PHEA chains and PP are weak, consistent with the absence of an inductive effect of -H ($I = 0$). Thus, PP is not an effective crosslinker of PHEA. In contrast, PHEMA has a strong inductive (+*I*) effect due to -CH₃, leading to enhanced dipole-ion interactions between the carbonyl groups of PHEMA chains and PP. The NMR chemical shift of the carbonyl carbon in HEMA and PP mixture (0.1 ppm) is larger than that of HEA and PP mixture (0.06 ppm), indicating that the interaction between HEMA and PP is stronger than HEA and PP (**Supplementary Fig. 16b, c**). The ion-dipole (solvent-polymer) interactions act as noncovalent crosslinks to render the polymer chains in a glassy state at RT, explaining the remarkably high T_g (*e.g.*, $74\text{ }^{\circ}\text{C}$) and excellent mechanical properties of PHEMA-PP gels (**Supplementary Fig. 14b and Fig. 5c**). Finally, the ion-dipole toughening mechanism was further verified with acrylamide (+*I* effect: amide group) and N, N'-dimethylacrylamide (+*I* effect: dimethylamino group) monomers, while butyl acrylate (I effect = 0: -H) monomer failed to produce tough gels due to its weak interaction with PP, similar to HEA (**Supplementary Fig. 17**).

Supplementary Note 2. Multifunctionality of glassy gels.

The glassy gels exhibit exceptional adhesive properties. PAA-PP-6 M gel strongly adheres stainless-steel metal spheres (diameter: 0.25, 0.5, and 1 inch) to a glass slide (**Extended Data Fig. 3a and Supplementary Video 5**). In addition to stainless steel, the gel can also adhere to different materials such as glass, copper, and PDMS (**Supplementary Fig. 18a**). In particular, the adhesion strength of the gel to glass and metal are as high as ~ 1350 and 2100 N m^{-1} , respectively, far exceeding the bonding strength of tendon or cartilage to bone ($\sim 800 \text{ N m}^{-1}$, **Supplementary Fig. 18b-f**).² In principle, glassy polymers such as PMMA or PS can adhere to surfaces via weak interactions, such as van der Waals forces, but slabs of glassy polymers are too rigid to make intimate contact with surfaces, which is usually necessary for bonding. Remarkably, despite being macroscopically rigid, the glassy gels bond to many surfaces due to the strong interactions arising from their ionic nature (*e.g.*, coordination and ionic bonds).³

Since the glassy gels have a T_g above RT, they possess shape-memory, self-healing, and variable stiffness capabilities. At temperatures above T_g , the glassy gel softens, which allows deformation to relax in the case of shape-memory. Likewise, a sample deformed at elevated temperature (*e.g.*, 80°C) and cooled at RT maintains a temporary programmed shape. For instance, a spiral shape was programmed from an otherwise flat gel strip at 80°C for 10 s (**Extended Data Fig. 3b and Supplementary Video 6**). Cooling the gel at RT for 10 s fixed the shape. The gel quickly returns to its original shape within 6 s at 80°C . Likewise, a softened network can heal by reforming noncovalent interactions between polymer chains and IL. Two disc-shaped PAA-PP-6 M samples (dyed black and red) cut in half can heal at 80°C for 60 s (**Extended Data Fig. 3c(i)**). The healed gel can support a 500 g weight (**Extended Data Fig. 3c(ii) and Supplementary Video 7**).

Supplementary Note 3. Joule heat driven grippers.

Due to the thermal stability of the IL solvent, the glassy gels can be heated above T_g to soften them without evaporating the solvent, which makes them useful as substrates for Joule heaters that can vary stiffness by heating or cooling. We used a Joule heater composed of liquid metals (LMs) to soften the glassy gel (PAA-PP-6M) to form a variable stiffness gripper (**Supplementary Fig. 19a-c**). Joule heating elevated the temperature from RT to ≈ 100 °C, well above the T_g (40 °C) of PAA-PP-6 M gel (**Supplementary Fig. 19d**). The softened arms can conform to objects with minimal applied pressure. Upon cooling, the glassy gel retains its shape to create a stiff grip on the object (**Supplementary Fig. 19e and Video 8**). We included a thin coating on the glassy gel to prevent it from adhering to the object; thus, the gripping is a mechanical process.

C_m (M)	n_{AA} (mol)	n_{PP} (mol)	n_{AA} / n_{PP}	Young's modulus (MPa)	Toughness (MJ m ⁻³)	Fracture strain
4	0.004	0.0021	1.90	1.53 ± 0.06	14.91 ± 2.14	48.20 ± 1.43
4.5	0.0045	0.002	2.25	15.34 ± 1.65	17.98 ± 3.12	10.60 ± 1.08
5	0.005	0.0019	2.63	70.20 ± 0.54	37.52 ± 2.10	6.84 ± 0.34
5.5	0.0055	0.0018	3.06	411.70 ± 3.38	78.07 ± 5.21	5.06 ± 0.35
6	0.006	0.0017	3.53	676.49 ± 15.08	110.25 ± 13.82	3.88 ± 0.13
6.5	0.0065	0.0016	4.06	878.35 ± 27.25	15.19 ± 1.09	0.33 ± 0.01
7	0.007	0.0015	4.67	1063.33 ± 76.71	0.50 ± 0.03	0.04 ± 0.01
7.5	0.0075	0.0014	5.36	1206.23 ± 62.21	0.86 ± 0.20	0.04 ± 0.01

Supplementary Table 1. Summary of composition and mechanical properties of PAA-PP gels.

C_m is the monomer concentration. n_{AA} and n_{PP} are the moles of AA monomer and PP IL, respectively. Note that the moles of AA and PP are calculated based on 1 mL precursor.

References	Toughening mechanism	Interaction	Synthesis	Solvent content (wt%)	Mechanical properties ^b	Materials
[4] Adv. Mater., 2020, 32, 1901244	Hydrogen bond	Polymer-polymer	Multiple steps (~2-7 days): Dissolve-cast-dry (annealing)	0	Young's modulus: ~6 GPa Fracture strength: ~130 MPa Toughness: ~345 MJ m ⁻³	Non-solvated
[5] Adv. Mater. 2021, 33, 2105829	Nanofiller, Hydrogen bond	Polymer-polymer	Multiple steps (~8 days): Organic synthesis, dissolve-cast-dry (annealing)	0	Young's modulus: ~2.3 GPa Fracture strength: ~100 MPa Toughness: ~430 MJ m ⁻³	
[6] Adv. Mater. 2017, 29, 1704661	Phase separation, Hydrogen bond	Polymer-polymer	Multiple steps (~7 days): Organic synthesis, dissolve-cast-dry (annealing)	0	Young's modulus: ~2.2 GPa Fracture strength: ~90 MPa Toughness: ~150 MJ m ⁻³	
[7] Adv. Mater. 2021, 33, 2007371	Metal coordination, Hydrogen bond, Metal chelation	Metal salt-polymer, Polymer-polymer	Multiple steps (~9 days): Organic synthesis, Dissolve-heat-blade coating-dry-dialyze-dry	0	Young's modulus: ~4.7 GPa Fracture strength: ~85 MPa Toughness: ~27 MJ m ⁻³	
[8] Angew. Chem. Int. Ed., 2022, 61, e202212512	Metal coordination, Hydrogen bond	Metal salt-polymer, Solvent-polymer, Solvent-solvent	Multiple steps (~6 days): Organic synthesis, Dissolve metal salt, Free radical polymerization	~40-50 ^a	Young's modulus: ~55 MPa Fracture strength: ~14 MPa Toughness: ~78 MJ m ⁻³	Solvated
[9] Adv. Mater. 2023, 2301383	Entanglement, Crystalline domain, Metal coordination, Hydrogen bond	Polymer-polymer, Metal salt-polymer, Solvent-polymer, Solvent-solvent	Multiple steps (~3 days): Dissolve metal salt, Dissolve polymer-water evaporate-solvent exchange	~10-27 ^a	Young's modulus: ~50 MPa Fracture strength: ~63 MPa Toughness: ~2000 MJ m ⁻³	
[10] Nature, 2021, 590, 594	Crystalline domain, Hydrogen bond	Polymer-polymer	Multiple steps (~5 days): Dissolve-freeze-salting-out	~70-95	Young's modulus: ~2.5 MPa Fracture strength: ~23.5 MPa Toughness: ~210 MJ m ⁻³	
This Work	Electrostatic interaction (e.g., ion-ion, ion-dipole)	Solvent-polymer, Solvent-solvent	One-step (5 mins): Free radical polymerization	~48-65	Young's modulus: ~1.2 GPa Fracture strength: ~42 MPa Toughness: ~110 MJ m ⁻³	

Supplementary Table 2: Comparison between this work and literature.⁴⁻¹⁰ ^a The metal salt content is not included. ^b Maximum values are summarized.

C_m (M)	n_{AA} (mol)	n_{NS} (mol)	n_{AA} / n_{NS}	Young's modulus (MPa)	Toughness (MJ m ⁻³)	Fracture strain
5.5	0.0055	0.00325	1.69	0.26 ± 0.05	1.43 ± 0.26	8.90 ± 0.80
6	0.006	0.0031	1.94	0.28 ± 0.01	1.49 ± 0.19	8.42 ± 1.00
7	0.007	0.0027	2.59	1.04 ± 0.18	3.84 ± 0.09	7.89 ± 0.22
8.2	0.0082	0.0023	3.57	60.03 ± 7.28	49.93 ± 11.10	7.81 ± 0.76
8.5	0.0085	0.0022	3.86	185.78 ± 22.10	78.05 ± 4.72	7.91 ± 0.39
9	0.009	0.0020	4.50	733.47 ± 10.16	97.85 ± 7.96	5.04 ± 0.19
9.5	0.0095	0.0018	5.28	1118.47 ± 37.25	44.08 ± 7.31	3.26 ± 0.53
10	0.01	0.0016	6.25	1292.75 ± 29.47	5.07 ± 0.51	0.11 ± 0.01
10.5	0.0105	0.00147	7.14	1466.67 ± 33.10	2.92 ± 4.33	0.064 ± 0.06

Supplementary Table 3. Summary of composition and mechanical properties of PAA-NS gels. C_m is the monomer concentration. n_{AA} and n_{NS} are the moles of AA monomer and NS IL, respectively. Note that the moles of AA and NS are calculated based on 1 mL precursor.

C_m (M)	n_{AA} (mol)	n_{NP} (mol)	n_{AA} / n_{NP}	Young's modulus (MPa)	Toughness (MJ m ⁻³)	Fracture strain
5	0.005	0.00335	1.49	0.45 ± 0.09	2.73 ± 0.82	10.32 ± 1.47
6	0.006	0.003	2.00	4.32 ± 0.32	15.08 ± 4.32	9.52 ± 1.14
7	0.007	0.0026	2.69	60.46 ± 6.48	61.41 ± 5.59	7.28 ± 0.32
8	0.008	0.00228	3.51	604.08 ± 35.89	75.05 ± 6.86	4.80 ± 0.28
8.5	0.0085	0.0021	4.05	986.97 ± 9.27	39.85 ± 11.34	3.27 ± 0.40
9	0.009	0.0019	4.74	1332.67 ± 68.73	19.17 ± 3.60	0.46 ± 0.12

Supplementary Table 4. Summary of composition and mechanical properties of PAA-NP gels. C_m is the monomer concentration. n_{AA} and n_{NP} are the moles of AA monomer and NP IL, respectively. Note that the moles of AA and NP are calculated based on 1 mL precursor.

C_m (M)	n_{AA} (mol)	n_{PS} (mol)	n_{AA} / n_{PS}	Young's modulus (MPa)	Toughness (MJ m ⁻³)	Fracture strain
5	0.005	0.0022	2.27	0.60 ± 0.06	1.59 ± 0.20	8.10 ± 0.69
6	0.006	0.002	3.00	109.48 ± 9.13	53.37 ± 2.00	6.85 ± 0.19
6.5	0.0065	0.00184	3.53	470.43 ± 33.71	70.34 ± 4.14	5.46 ± 0.33
7	0.007	0.0017	4.12	872.08 ± 26.09	42.74 ± 4.51	3.37 ± 0.21
8	0.008	0.0015	5.33	1123.85 ± 50.18	2.29 ± 0.52	0.07 ± 0.01
8.5	0.0085	0.0014	6.07	1229.77 ± 50.15	2.60 ± 2.84	0.07 ± 0.05

Supplementary Table 5. Summary of composition and mechanical properties of PAA-PS gels.

C_m is the monomer concentration. n_{AA} and n_{PS} are the moles of AA monomer and PS IL, respectively. Note that the moles of AA and PS are calculated based on 1 mL precursor.

C_m (M)	n_{HEMA} (mol)	n_{PP} (mol)	n_{HEMA} / n_{PP}	Young's modulus (MPa)	Toughness (MJ m ⁻³)	Fracture strain
3.5	0.0035	0.0017	2.06	0.78 ± 0.13	1.50 ± 0.19	6.02 ± 0.34
4	0.004	0.0015	2.67	5.98 ± 1.09	5.74 ± 0.30	6.36 ± 0.15
4.6	0.0046	0.0013	3.54	109.67 ± 4.99	31.66 ± 4.05	4.39 ± 0.97
5	0.005	0.0011	4.55	277.59 ± 69.14	34.71 ± 1.65	3.39 ± 0.04
5.5	0.0055	0.00096	5.73	556.79 ± 29.54	43.90 ± 6.96	3.14 ± 0.25
6	0.006	0.0008	7.50	636.26 ± 20.46	6.04 ± 4.02	0.17 ± 0.07

Supplementary Table 6. Summary of composition and mechanical properties of PHEMA-

PP gels. C_m is the monomer concentration. n_{HEMA} and n_{PP} are the moles of HEMA monomer and PP IL, respectively. Note that the moles of HEMA and PP are calculated based on 1 mL precursor.

C_m (M)	n_{HEA} (mol)	n_{PP} (mol)	$n_{\text{HEA}} / n_{\text{PP}}$	Young's modulus (MPa)	Toughness (MJ m ⁻³)	Fracture strain
3.6	0.0036	0.0018	2.00	0.10 ± 0.02	0.38 ± 0.05	5.79 ± 0.49
4	0.004	0.0017	2.35	0.11 ± 0.02	0.48 ± 0.05	5.00 ± 0.29
4.5	0.0045	0.00155	2.90	0.12 ± 0.02	0.42 ± 0.05	4.78 ± 0.45
5	0.005	0.0014	3.57	0.19 ± 0.03	0.76 ± 0.19	5.20 ± 0.63
5.5	0.0055	0.00123	4.47	0.23 ± 0.03	0.67 ± 0.08	4.50 ± 0.31
6	0.006	0.00108	5.56	0.25 ± 0.03	0.90 ± 0.12	5.13 ± 0.44
6.5	0.0065	0.0009	7.22	0.39 ± 0.03	1.30 ± 0.21	4.99 ± 0.49

Supplementary Table 7. Summary of composition and mechanical properties of PHEA-PP gels. C_m is the monomer concentration. n_{HEA} and n_{PP} are the moles of HEA monomer and PP IL, respectively. Note that the moles of HEA and PP are calculated based on 1 mL precursor.

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