Supplementary Information

Facile Fabrication of Tough Hydrogels Physically Crosslinked by Strong Cooperative Hydrogen Bonding

Guoshan Song[†], *Lei Zhang*[‡], *Changcheng He*[†], *De-Cai Fang*[*,‡] *Philip G. Whitten*[§], *Huiliang Wang*[*,†]

†Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China.

‡Key laboratory of Theoretical and Computational Photochemistry, Ministry of Education, College of Chemistry, Beijing Normal University, Beijing 100875, China

§School of Mechanical, Materials & Mechatronic Engineering, Faculty of Engineering, University of Wollongong, NSW 2522, Australia

Contents:

Results and discussion

Supporting Table

Table S1. The Y_p, M_n, M_w and PDI of the PAAm's synthesized with different C_{AAm}.

Supporting Figures

Figure S1. Photograph showing the elongation of a PVP-*in situ*-PAAm hydrogel with hand.

Figure S2. The resilience of the PVP-*in situ*-PAAm hydrogels.

Figure S3. The true tensile strengths (σ_{true}) of the as-prepared PVP-*in situ*-PAAm hydrogels as a function of C_{AAm}.

Figure S4. A photograph of the as-prepared and equilibrium swollen PVP-*in situ*-PAAm hydrogel specimens.

Figure S5. Photographs of the reacted solutions containing an identical molar concentration of NVP and AAm after being tilted for some times.

Figure S6. The tensile properties of the as-prepared P(AAm-*co*-NVP) hydrogels synthesized with a fixed AAm concentration (5 mol L^{-1}) but varying NVP concentrations (C_{NVP}).

Figure S7. The optimized geometries and relative energies (in kJ/mol) of two stable conformers for the molecule of MP (top) and PP (bottom).

Figure S8. (a): DSC thermograms of the blends of PVP and PAAm with different PVP/PAAm ratios, (b): the T_g's of the blends.

Figure S9. DSC thermograms of dried PVP-*in situ*-PAAm hydrogels with PVP mass ratios more than 50 wt.%.

Supporting Movie

Movie S1. The elongation of a PVP-*in situ*-PAAm hydrogel with hand.

Results and discussion

Supporting Table

Table S1. The Y_p, M_n, M_w and PDI of the PAAm's synthesized with different C_{AAm}.

C_{AAm} (mol L^{-1})	Y_p (%)	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI
2[a]	99.3	1.34×10^6	1.70×10^6	1.27
4[a]	96.9	1.16×10^6	1.48×10^6	1.28
5[a]	98.2	8.21×10^5	1.07×10^6	1.31
6[a]	97.2	7.10×10^5	8.01×10^5	1.13
2[b]	38.4	5.83×10^4	1.12×10^5	1.92
6[b]	84.3	5.62×10^4	1.27×10^5	2.26

[a]: The PAAm's were isolated from the PVP-*in situ*-PAAm hydrogels.

[b]: The PAAm's were syntehsized with neat AAm solutions (without PVP).

Supporting Figures

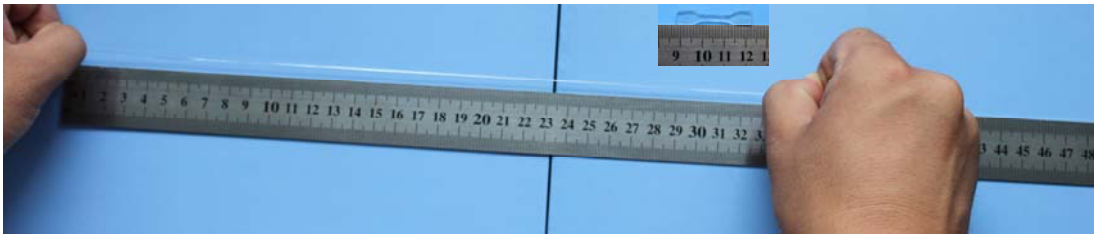

Figure S1. Photograph showing the elongation of a PVP-*in situ*-PAAm hydrogel with hand. The inset shows the original size of the specimen with a gauge length of 10 mm. The reaction conditions were: PVP concentration 0.017 g mL^{-1}, AAm concentration: 5 mol L^{-1}.

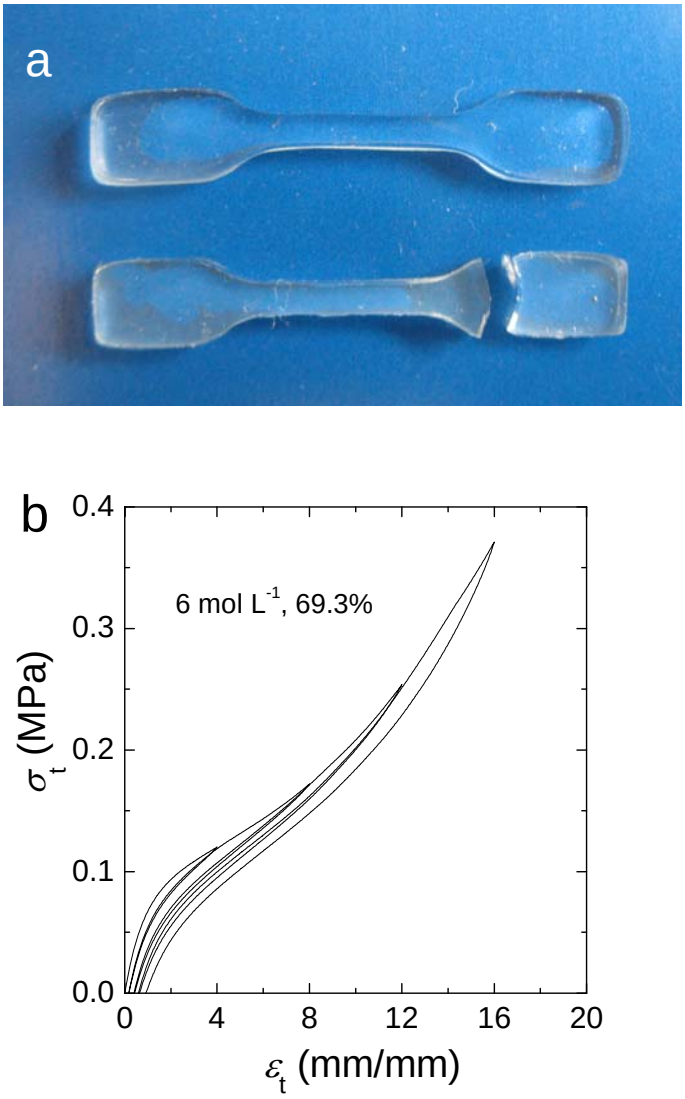

Figure S2. The resilience of the PVP-*in situ*-PAAm hydrogels. (a): Photo showing the appearance of PVP-*in situ*-PAAm gel specimens before and after being elongated. The top one is an original specimen, the bottom one is a specimen after being elongated to the fracture strain of 3000 %. (b): typical successive loading-unloading cycles in extension of the gel sample to different strains. The reaction conditions were: PVP concentration: 0.017 g mL^{-1}, AAm concentrations: 5 mol L^{-1} (a) and 6 mol L^{-1} (b).

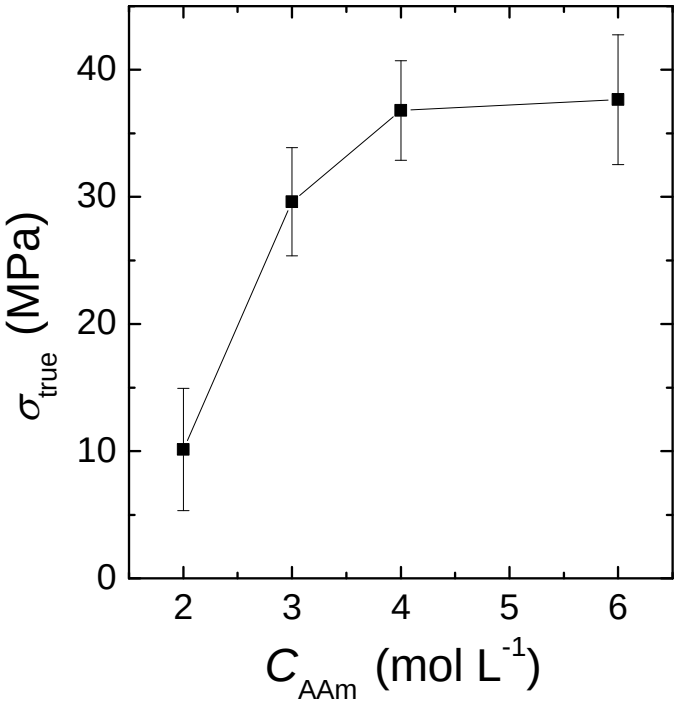

Figure S3. The true tensile strengths (σ_{true}) of the as-prepared PVP-*in situ*-PAAm hydrogels as a function of C_{AAm}.

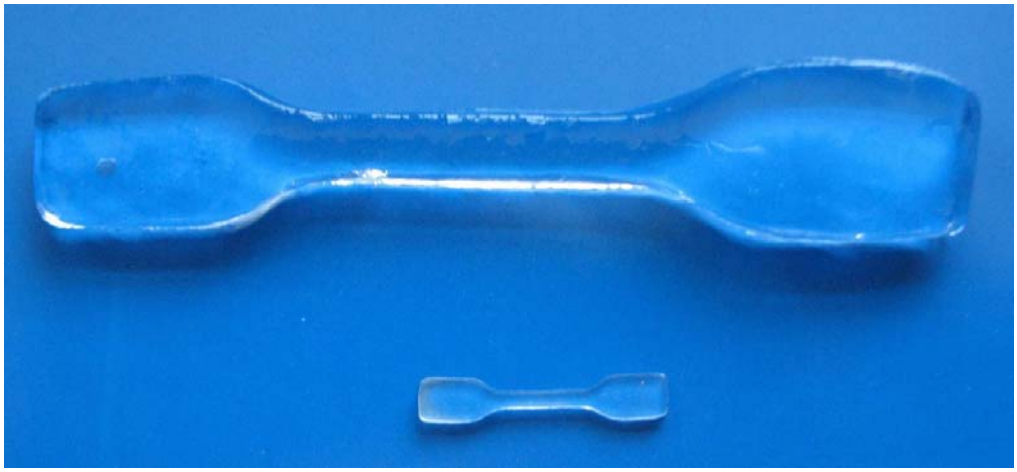

Figure S4. A photograph of the as-prepared and equilibrium swollen PVP-*in situ*-PAAm hydrogel specimens. The hydrogel was synthesized with PVP (0.017 g mL^{-1}) and AAm (6 mol L^{-1}). The bottom specimen was cut from the as-prepared hydrogel, and the top one has been swelled in a large excess amount of deionized water at ambient temperature for eight months.

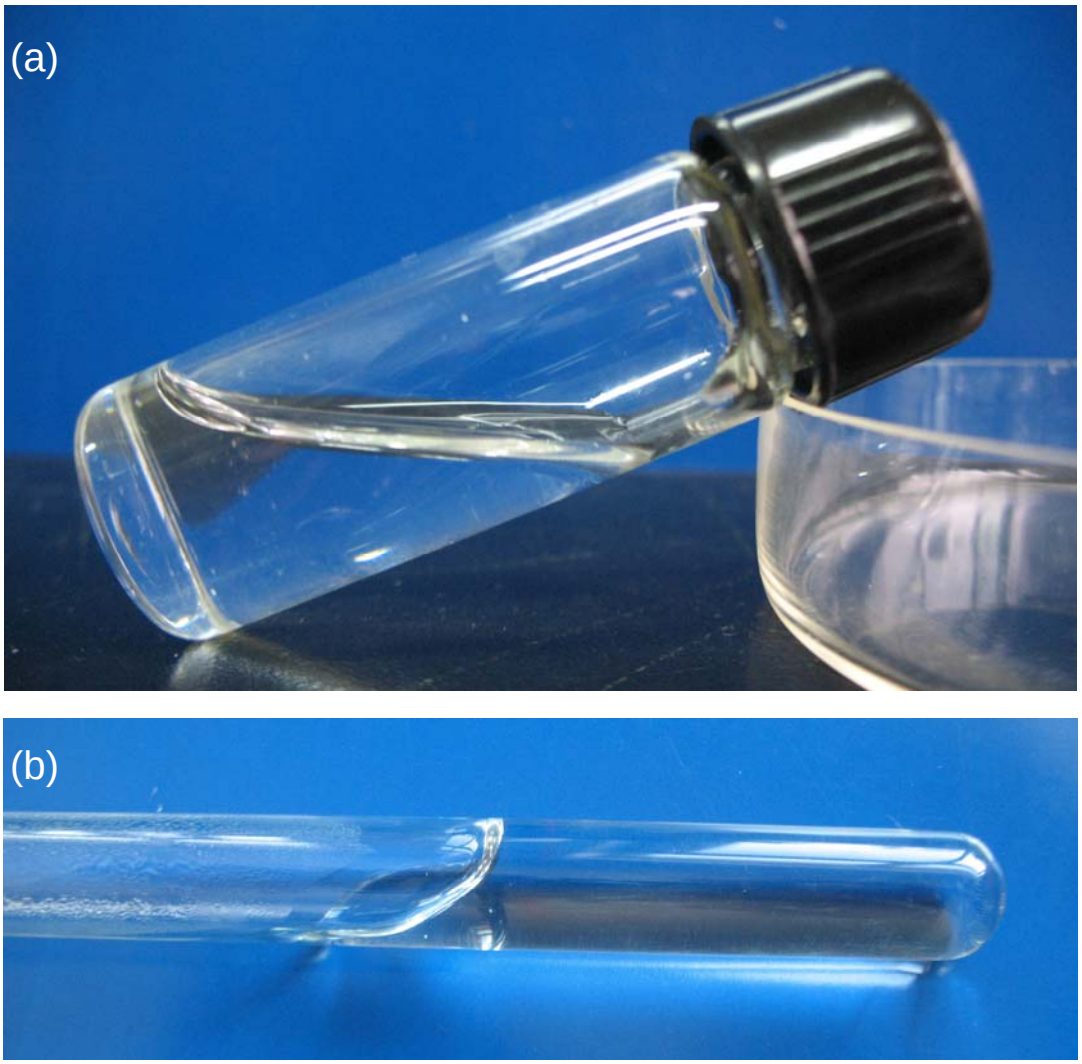

Figure S5. Photographs of the reacted solutions containing an identical molar concentration of NVP and AAm after being tilted for some times. (a): $C_{AAm} = C_{NVP} = 1.8$ mol L^{-1}, 5 min; (b): $C_{AAm} = C_{NVP} = 2.25$ mol L^{-1}, 20 min.

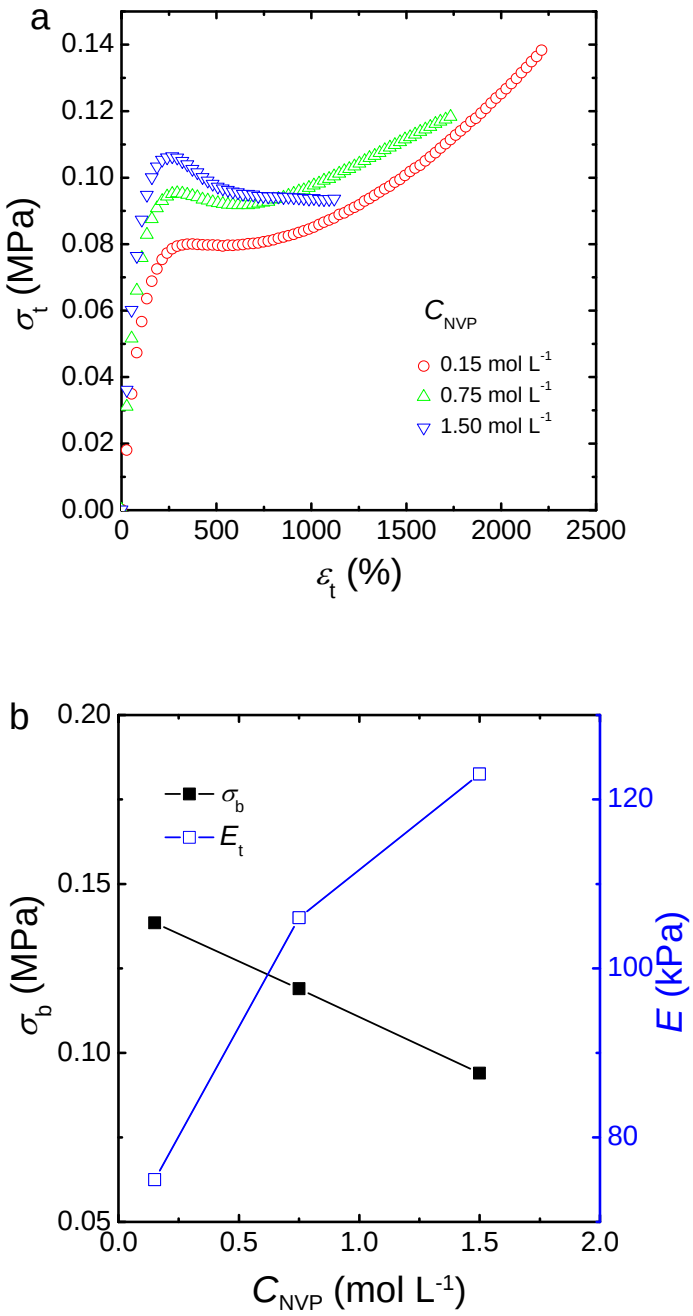

Figure S6. The tensile properties of the as-prepared P(AAm-*co*-NVP) hydrogels synthesized with a fixed AAm concentration (5 mol L^{-1}) but varying NVP concentrations (C_{NVP}). (a): The typical tensile stress-strain (σ_t-ε_t) curves; (b): the tensile strength (σ_b) and the elastic modulus (E) of the hydrogels as a function of C_{NVP}.

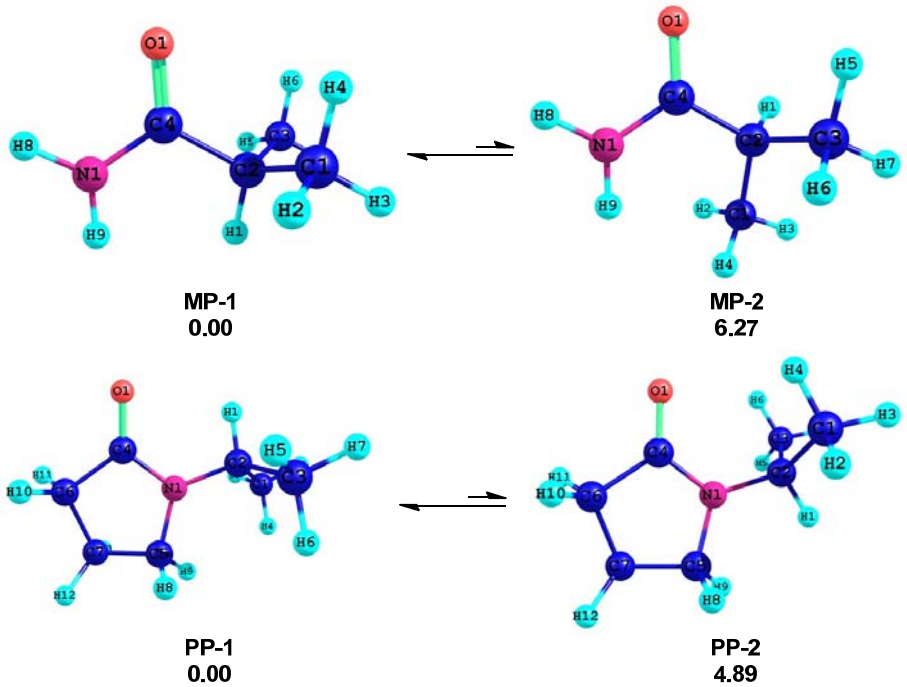

Figure S7. The optimized geometries and relative energies (in kJ/mol) of two stable conformers for the molecule of MP (top) and PP (bottom).

MP-1 was confirmed as the dominant conformation through rotation about C2-C4 bond in MP molecule, in which carbonyl group is gauche to C2-C1 and C2-C3 and near antiperiplanar to C2-H1. Another rotamer **MP-2** with carbonyl group near antiperiplanar to C2-C1 lies 6.27 kJ/mol above **MP-1** in energy. The conformational analyses were mainly focused on rotation along N-C2 bond for PP molecule, which is consistent with the results reported by Sarasua *et al* that the near eclipsed arrangement of carbonyl group with C2-H1 in **PP-1** was energetically favored by 4.89 kJ/mol relative to **PP-2**.[1] Therefore, only the structures **MP-1** and **PP-1** were selected to model PAAm and PVP chains for constructing all the H-bond complexes afterwards.

Reference:

1. Lejardi, A.; Meaurio, E.; Fernández, J.; Sarasua, J.-R. *Macromolecules* **2011,** 44, (18), 7351-7363.

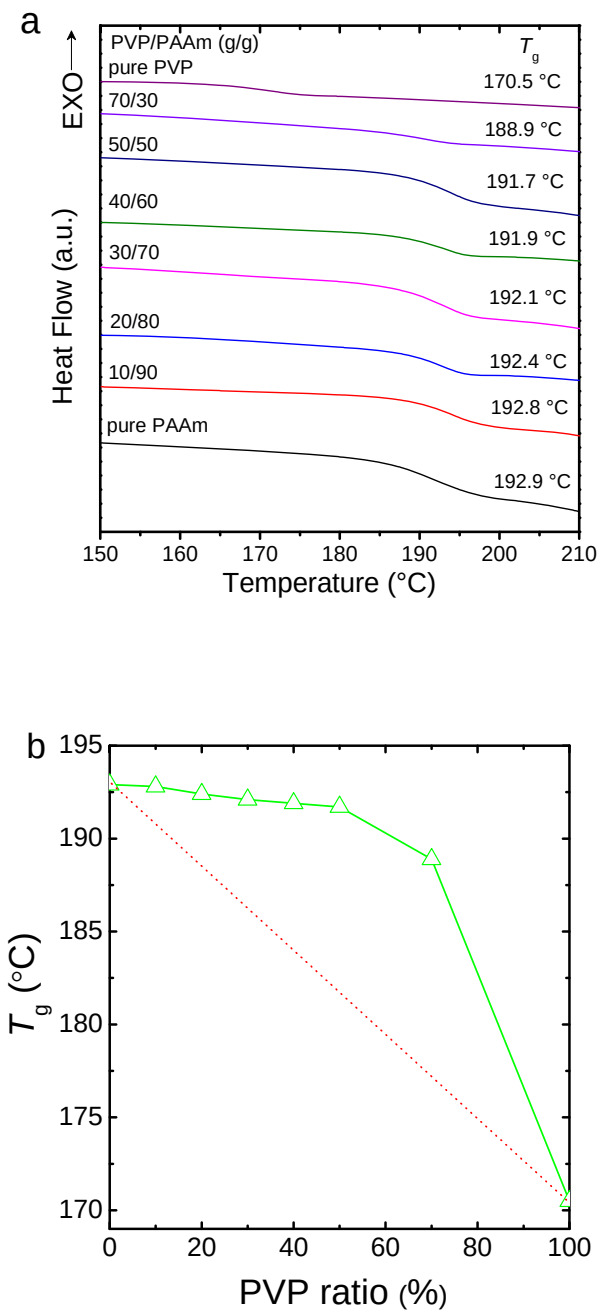

Figure S8. (a): DSC thermograms of the blends of PVP and PAAm with different PVP/PAAm ratios, (b): the T_g's of the blends. The dashed line shows the linearity with blend composition.

Please notice that the T_g of the PAAm is 192.9°C, which is higher than that of the PAAm we prepared (186.3°C). The PAAm (M_w = 8.3×10^5 g mol^{-1}, 10% in water) used for preparing the blends was purchased from TCI (Shanghai, China).

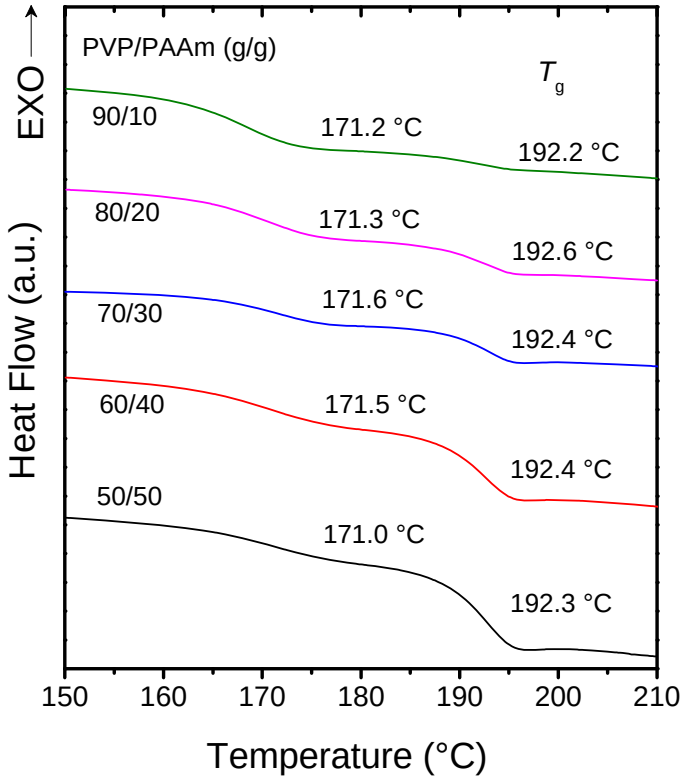

Figure S9. DSC thermograms of dried PVP-*in situ*-PAAm hydrogels with PVP mass ratios more than 50 wt.%.

Supporting Movie

Movie S1. The elongation of a PVP-*in situ*-PAAm hydrogel with hand. The reaction conditions were: PVP concentration: 0.017 g mL^{-1}, AAm concentration: 5 mol L^{-1}.