Electronic Supplementary Information

A self-healing polymeric material: From gel to plastic

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Materials and Methods

Materials.

2-acrylamido-2-methyl-1-propanesulfonic acid, guanidine chloride, and Sudan Blue II were purchased from Aladdin and used as received. 3-sulfopropyl methacrylate acid was prepared from 3-sulfopropyl methacrylate potassium (Sigma-Aldrich) by cation exchange resin (Aladdin). All organic solvents (AR grade) were purchased from Sinopharm and used as received. The water used was purified by filtration through a Millipore Gradient system after distillation, giving a resistivity of 18.2 MΩ cm.

Preparation of PAMPSA samples.

The saturated concentration of AMPSA in water is around 60 wt%. In the preparation of a PAMPSA sample, 5.0 g AMPSA was dissolved in 5.0 g water (50 wt%) to get a homogenous solution and then the solution was degassed for ~ 30 min before polymerization to avoid the formation of air bubbles in the sample during polymerization. The polymerization was triggered by simply heating the solution at 80 °C for 30 min. A smaller concentration of

AMPSA in water during polymerization will lead to a less stiff material (Figure S12). Samples with different shapes were prepared by pouring the degassed solution into different molds, followed by heating the molds directly to trigger the polymerization. The samples were weighed to determine the wet weight, and then dried in vacuum oven at 80 °C for 24 h, cooled under vacuum, and weighed again to determine the water content of the samples.

Instrumental measurements.

^{1}H NMR spectra were recorded on a Bruker AV400 NMR spectrometer using deuterium water as solvent at 60 °C. The SEM measurements were carried out on a Sirion200 field emission scanning electron microscope. The sample was fixed on an aluminum plate and was sputtered with gold for 70 s at a current of 5 mA before the SEM measurements. For the tensile tests, the mechanical properties of the samples were measured using a TA Instruments DMA Q800 in standard stress/strain experiments at 20 ºC with the RH of 40%. The specimens were extended at a force ramp rate of 0.5 N min^{-1}. The Young's modulus was determined from the initial slope of the stress-strain curves. For the self-healing tests of the stiff material, a sample was cut into two separate pieces using a razor blade. The cut faces were gently pressed together for several seconds after spraying water, and then left in a chamber at 20 ºC with the RH of 40% for various times. The healed samples were then subjected to the tensile tests at a force ramp rate of 0.5 N min^{-1}.

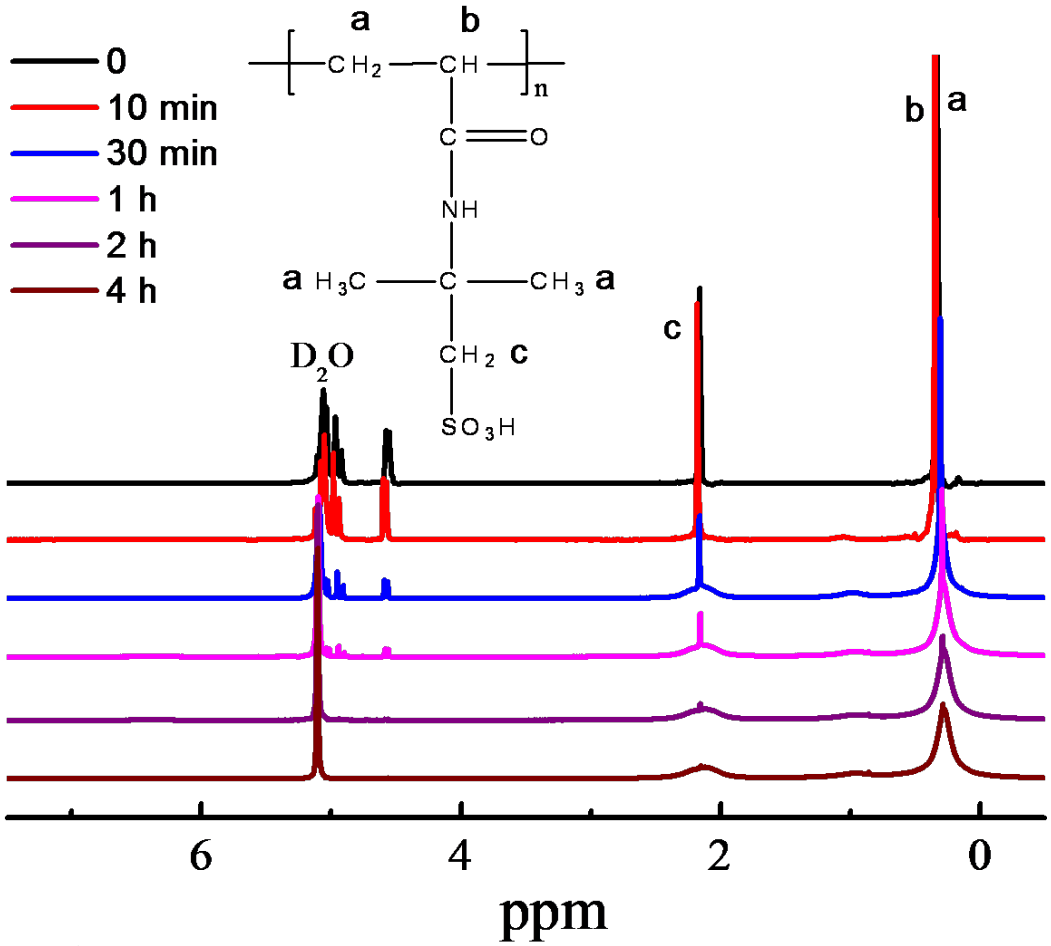

Figure S1. ^{1}H-NMR spectra recorded during the polymerization of AMPSA as a function of time at 60 °C.

The polymerization of AMPSA is completed within 30 min at 80 ºC due to the high activity of monomer, so that it is difficult to use common ^{1}H-NMR to follow the polymerization at this temperature. Because the rate of polymerization becomes slower at a lower temperature, ^{1}H-NMR spectra were recorded at 60 °C to follow the polymerization of AMPSA. The gradual disapperance of the olefinic proton peaks at 4.6 and 4.9 ppm indicates the successful polymerization of AMPSA triggered by heating.

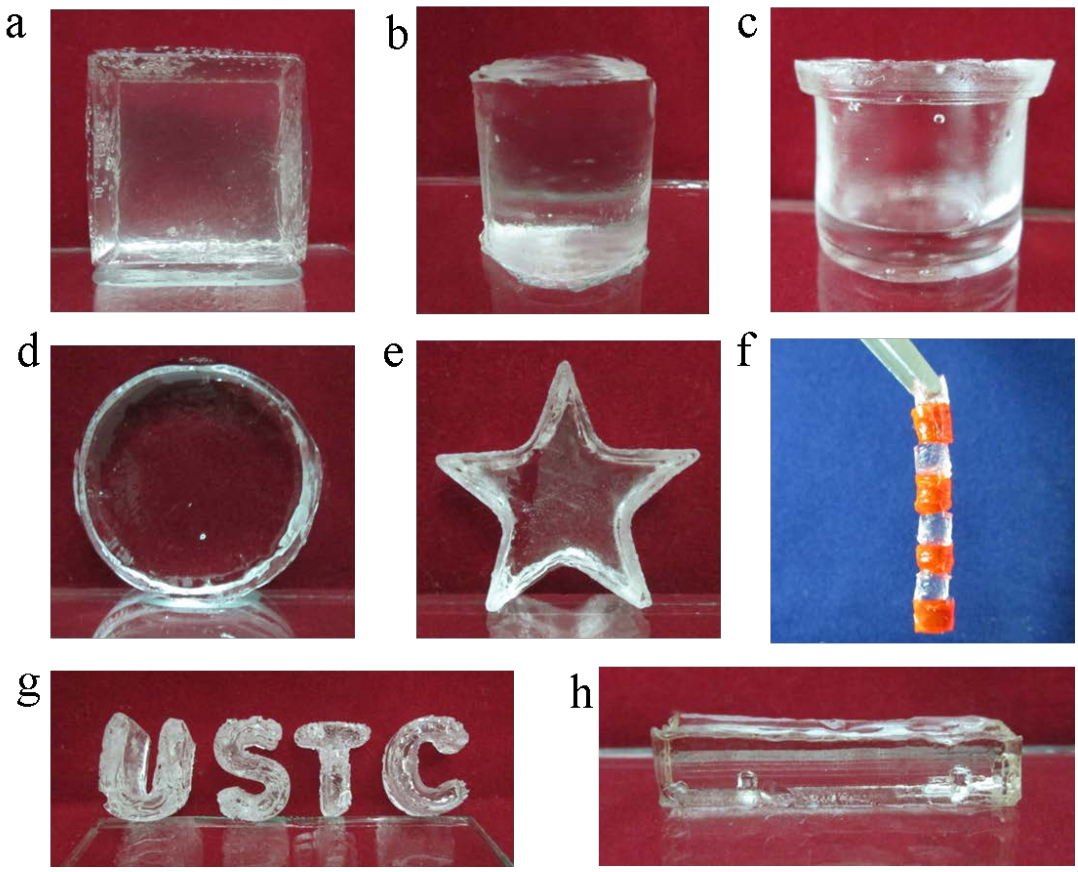

Figure S2. Samples with different shapes were prepared by pouring the degassed solution into different molds, followed by heating the molds directly to trigger the polymerization. Thus, PAMPSA material can be easily processed into any desired shape, which is favorable for the practical applicaitons.

Figure S3. No hydrogel formed from the 2-acrylamido-2-methyl-1-propanesulfonic sodium (AMPSS) aqueous solution (50 wt%) after heating at 80 °C for 2 h, indicating that the high polymerization activity of AMPSA might be due to the catalytic effect of the counterion H^+ of the sulfonic group. Here, AMPSS was prepared from AMPSA by cation exchange resin.

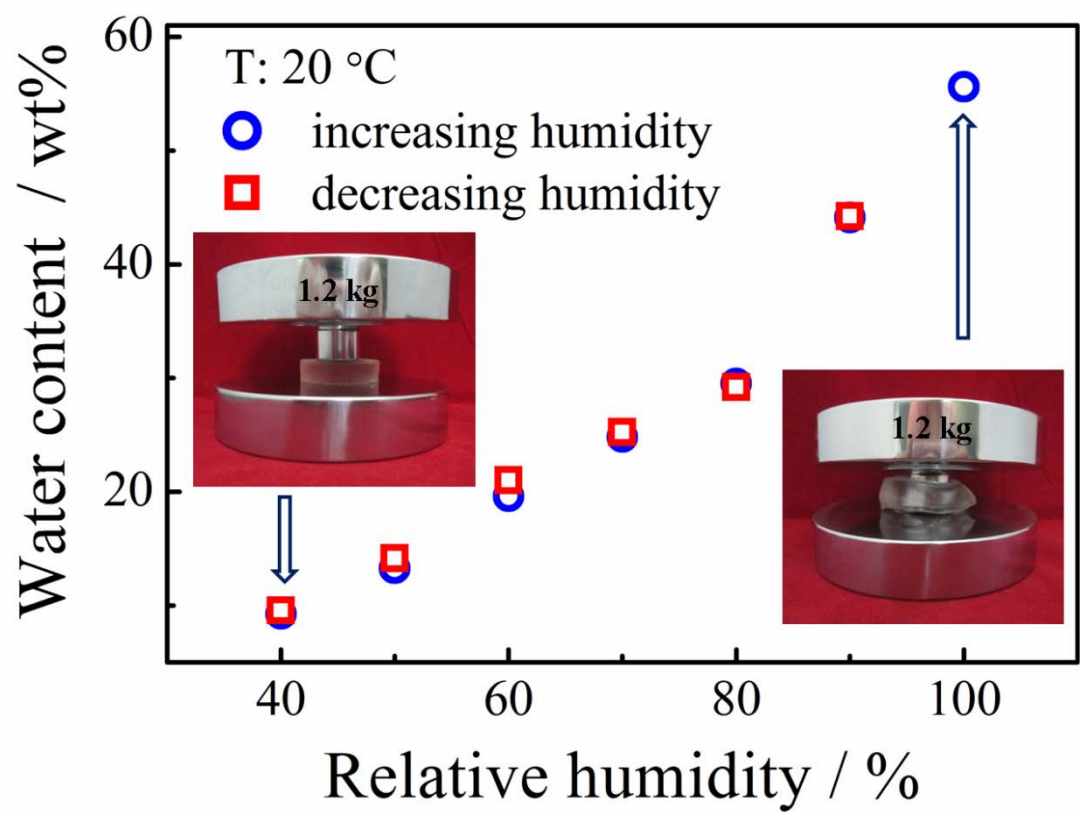

Figure S4. The water content of the PAMPSA sample can be accurately controlled by the relative humidity, which can be used to modulate the mechanical and self-healing properties of the material. Note that the tunable mechanical strength between gel and plastic of the material with varying water content is different from that of the usual swelling/deswelling of polymeric hydrogel. In general, hydrogel has a high water content and the deswelling of the hydrogel will generate a porous and fragile material with a low mechanical strength.[S1] In our study, the homogenous and compact structure and the numerous hydrogen bonds formed throughout the material lead to the stiff properties of the material at the low water content.

Figure S5. A PAMPSA cup filled with common organic solvents. No damage to the cup is observed after filling with organic solvents and waiting for 30 min, indicating that the PAMPSA material has good chemical resistance.

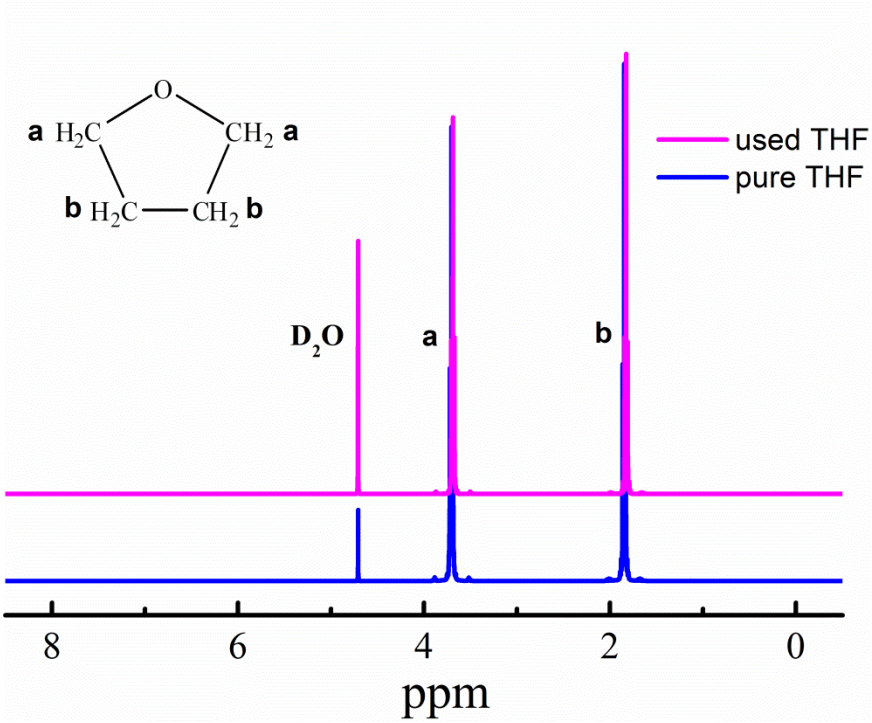

Figure S6. ^{1}H-NMR spectra of pure and used THF.

We have measured the ^{1}H-NMR spectrum of used THF from the PAMPSA cup after this solvent was filled in the cup for 2 days. We find that the ^{1}H-NMR spectrum of the used THF is the same as that of the pure THF. This fact shows that no monomers or polymers from the PAMPSA cup dissolve in THF even after waiting for 2 days. In other words, the cup can resist the corrosion of THF. Also, the weight of the cup doesn't have any obvious change before (~ 12.606 g) and after (~ 12.613 g) filling with THF for 2 days, further suggesting the good organic solvent resistance of the material.

Figure S7. The surface scraped with a razor blade reveals that the fracture healed almost completely to generate a homogeneous material. The line in the region not scraped is visible because of misalignment of the PAMPSA materials when placed together for healing.

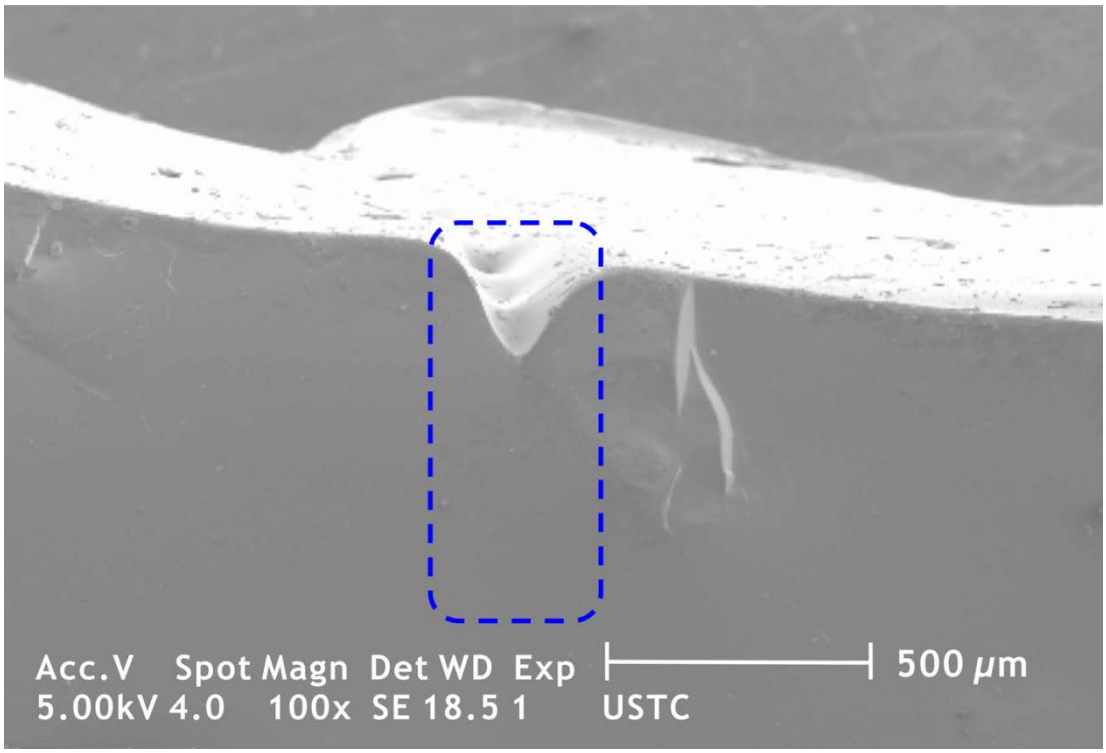

Figure S8. SEM image of the cross-section of the healed PAMPSA material. The healed zone is marked with the rectangle using blue dashed line. Similar to Figure S7, the fracture healed almost completely to generate a homogeneous material. The interface mismatch induced cannelure is still visible.

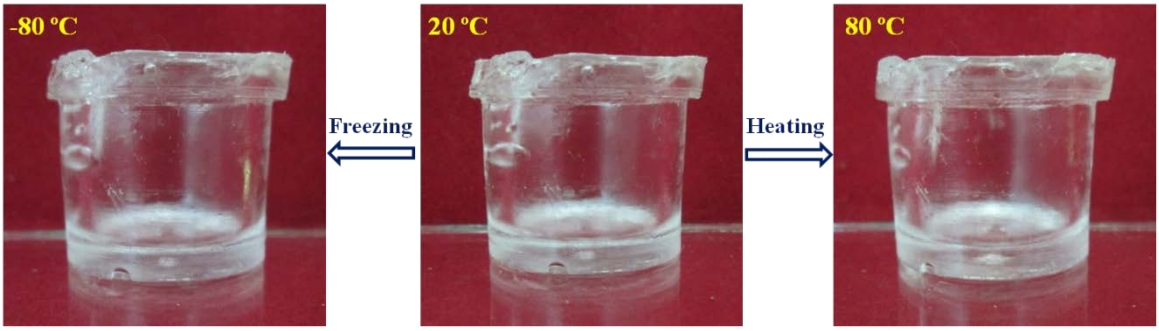

Figure S9. No deformations or cracks are observed in the cup after placing the cup at -80 ºC or 80 ºC for ~ 2h. This insensitivity to temperature implies that this material will find an extensive range of applications.

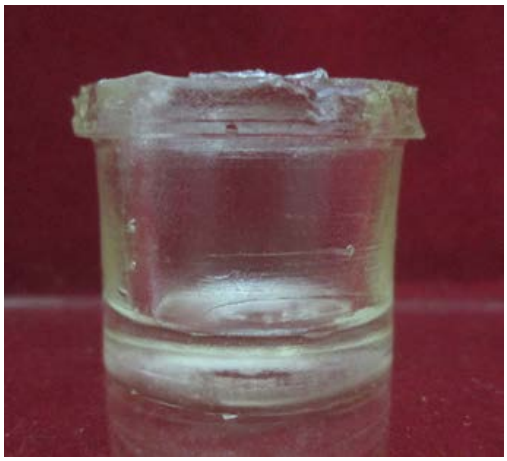

Figure S10. No deformations or cracks are observed in the cup after placing the cup under the relative humidity of 0% for 3 days.

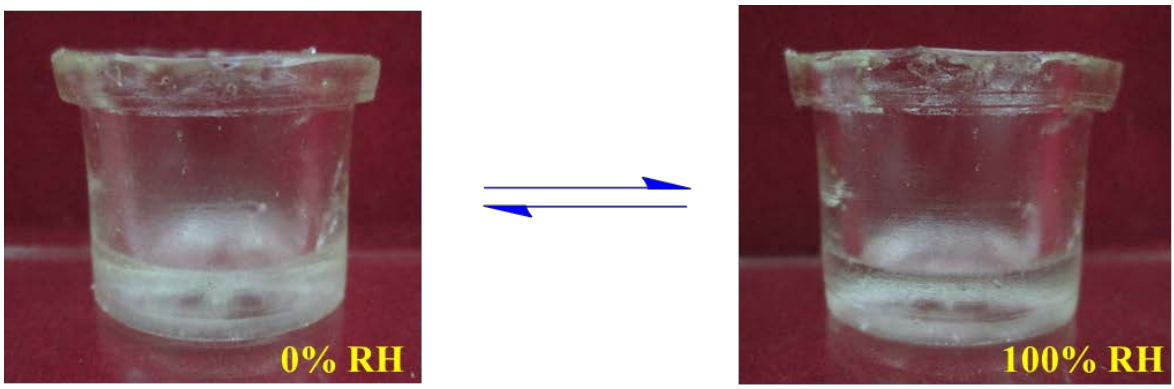

Figure S11. No deformations or cracks are observed in the cup after reversibly switching the relative humidity between 0% and 100% for 5 cycles. In each cycle, the cup was placed under the relative humidity of 0% or 100% for 1 day.

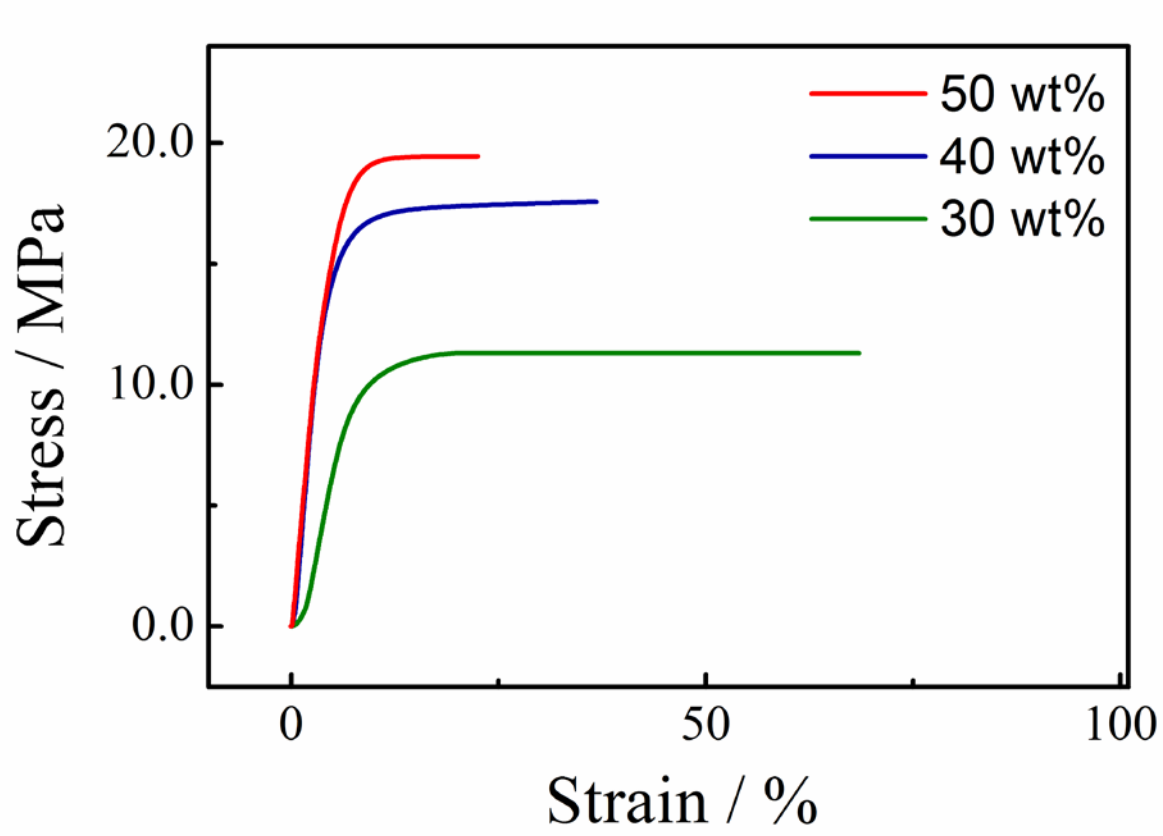

Figure S12. Stress-strain curves of PAMPSA samples with different monomer concentrations during polymerization. Before the tensile tests, the freshly prepared PAMPSA samples were placed at room temperature under RH of 40% for ~ 72 h to reach a steady state. It is evident that the break strength of the PAMPSA sample increases as the monomer concentration increases from 30 wt% to 50 wt%, which might be induced by the increasing density of hydrogen bonds in the material with increasing monomer concentration. To demonstrate the stiff properties of the self-healing polymeric material, we chose to use the sample with a monomer concentration of 50% to investigate the self-healing properties of the PAMPSA material in this study.

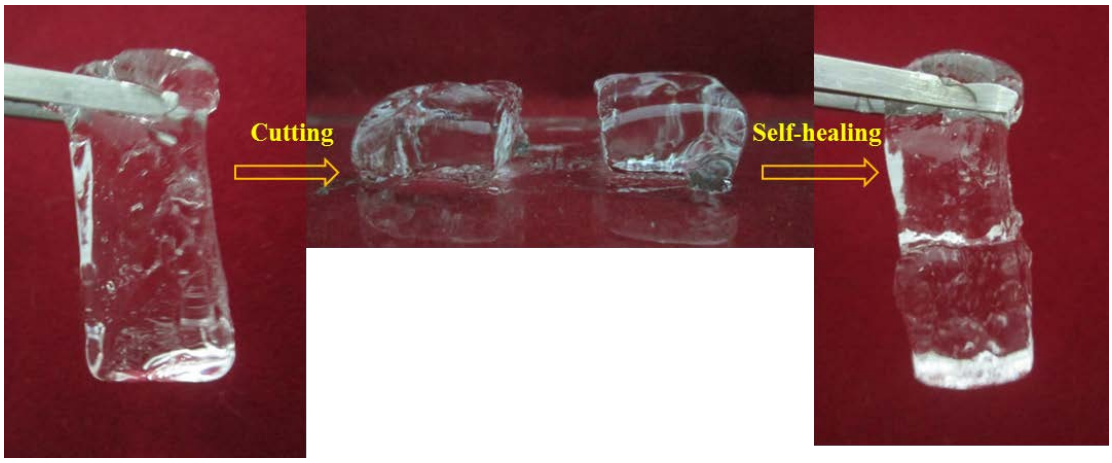

Figure S13. PAMPSA hydrogel with a water content of ~ 82 wt% can self-heal automatically without any external stimulus.

Table S1. The mechanical properties of PAMPSA sample compared with commercial elastomers and plastics.[S2] Here, the mechanical properties of PAMPSA represent the sample which has a water content of 9 wt%. The mechanical properties of the PAMPSA sample fall in the range of commercial plastics. POE: polyoxyethylene, EPDM: ethylene-propylene-diene terpolymer, LDPE: linear low density polyethylene, HDPE: high density polyethylene, HIPS: high impact polystyrene, PP: polypropylene.

Property		Break strength	Young's modulus	Elongation to break
Unit		MPa	MPa	%
PAMPSA		20	387	23
Elastomer	POE	-	18	>1000
	EPDM	6-16	1.2-5.6	100
	Silicone	1.0-5.5	-	200-850
Plastic	LDPE	10.3	165.5	620
	HDPE	19-30	800-1400	10-1000
	HIPS	24	1650	52
	PP	35.5	1380	-

References

S1 J. Chen, H. Park and K. Park, *Journal of Biomedical Materials Research*, 1999, **44,** 53-62.

S2 J. E. Mark, (ed.) *Polymer Data Handbook*, Oxford Univ. Press, New York, 1999, ch. 5, pp. 164-169.