Supplementary Information (SI) for ChemComm.

Supporting Information

Ultra-stiff and tough glassy eutectogel

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Experimental Section

Materials. Methacrylic acid (MAAc), methacrylamide (MAAm), glucose, fructose, xylose, choline chloride (ChCl), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (I2959), N, N'-methylenebis(acrylamide) (MBAA) were purchased from Aladdin and used as received without further purification.

Synthesis of DES. Powdered hydrogen bond donor (HBD, glucose) and hydrogen bond acceptor (HBA, ChCl) were mixed at a molar ratio of 2:5 to prepare ChCl/Glc type DES. The mixture was heated to 80 °C with magnetic stirring for 4 h until a homogeneous colorless liquid formed. The resulting DES was stored in a sealed glass container at room temperature for subsequent use.

Fabrication of glassy eutectogel. A precursor solution was prepared by dissolving methacrylic acid (MAAc) and methacrylamide (MAAm) in the DES. Subsequently, N, N'-methylenebisacrylamide (MBAA) and photoinitiator I2959 were added and kept as 0.1 mol%. After centrifugation to remove air bubbles, the solution was transferred into 1 mm-thick silicone mold, polymerized under UV light for 1 h to obtain the poly(methacrylamide-co-methacrylic acid) (P(MAAm-*co*-MAAc)) glassy eutectogel. For comparative analysis, fructose (Fru) and xylose (Xyl)-based DES were synthesized by substituting glucose for glucose with an equal molar amount of Fru or Xyl, while maintaining a ChCl/HBD molar ratio of 2:5. The corresponding glassy eutectogels, denoted as ChCl/Fru type DES and ChCl/Xyl type DES, were manufactured following the same procedure described in this article. Additionally, chemically cross-linked P(MAAm-*co*-MAAc) hydrogels were prepared as reference materials. Specifically, MAAc, MAAm were dissolved in deionized water with N, N'-methylenebis-acrylamide (MBAA, 0.1 mol%), and photoinitiator I2959 (0.05 mol%). The solution was degassed by sonication for 15 min to being transferred into silicone molds. Photopolymerization was conducted under UV light for 1 h to obtain the final hydrogel.

Characterizations. The chemical compositions of PMAAm, PMAAc, and P(MAAm-*co*-MAAc) synthesized in ChCl/Glc type DES were analyzed by Fourier transform infrared (FTIR) spectroscopy (Nicolet iS50, Thermo Scientific). All spectra were scanned 32 times in the range of 4000-400cm^{-1} with a resolution of 4cm^{-1}. Optical transmittance of 0.5 mm-thick gel discs was measured from 400 to 800 nm by a UV-vis spectrophotometer ((UV-2600, Shimadzu). Mechanical properties and cyclic tensile tests were evaluated with a universal testing machine (Instron 5300). Rectangular specimens (10 mm × 7 mm × 1 mm) were clamped and stretched at 50 mm/min. Young's modulus E was calculated from the slope of the initial linear region (<1% strain) of stress-strain curves, while toughness W was determined by integrating the area under the curves. Stability tests compared DES-based and aqueous P(MAAm-*co*-MAAc) gels (3 cm × 3 cm × 1 mm) stored at 25°C/50% RH. Mass loss, tensile strength, and elongation at break were measured at 1, 3, and 5 days. Shape retention was further evaluated by stretching dumbbell-shaped gels to 50% strain (original strain ε_0), releasing the load for 30 s (residual strain ε_1), then heating at 60°C for 20 min (final strain ε_2). Shape fixation ratio ($R_f = \varepsilon_1/\varepsilon_0 \times 100\%$) and recovery ratio ($R_r = (\varepsilon_0 - \varepsilon_2)/\varepsilon_0 \times 100\%$) were quantified. Dynamic thermomechanical analysis (DMA) of gels was performed using a dynamic thermomechanical analyzer (DMA850, TA Instruments). Prepare glassy gel rectangular samples (50 mm× 7 mm×1 mm). The temperature was increased from 40 °C to 180 °C (heating rate: 5 °C/min) at a frequency of 1 Hz, and the test was performed in a single cantilever mode.

Table 1. Synthesis of deep eutectic solvent with different compositions.

solvent	H-bond acceptor (HBA)	H-bond donor (HBD)	molar ratio (HBD : HBA)
ChCl/Grc type	choline chloride	glucose	2 : 5
ChCl/Fru type	choline chloride	fructose	2 : 5
ChCl/Xyl type	choline chloride	xylose	2 : 5

Table 2. Synthesis of poly(methacrylic acid-co-methacrylamide) [P(MAAc-*co*-MAAm)] eutectogels with different compositions using ChCl/Glc type deep eutectic solvent as the solvent.

sample	Solvent(g)	MAAc(g)	MAAm(g)	I2959(mg)	MBAA(mg)
PMM-0.3-3 (ChCl/Grc)	3.567	0.540	0.231	1.997	1.372
PMM-0.3-4 (ChCl/Grc)	3.159	0.718	0.308	2.657	1.826
PMM-0.3-5 (ChCl/Grc)	2.745	0.899	0.385	3.326	2.286
PMM-0.3-6 (ChCl/Grc)	2.334	1.079	0.463	3.994	2.745
PMM-0.3-7 (ChCl/Grc)	2.009	1.258	0.539	4.654	3.199
PMM-0.1-6 (ChCl/Grc)	2.334	1.388	0.154	3.994	2.745
PMM-0.2-6 (ChCl/Grc)	2.334	1.234	0.308	3.994	2.745
PMM-0.4-6 (ChCl/Grc)	2.334	0.925	0.617	3.994	2.745
PMM-0.5-6 (ChCl/Grc)	2.334	0.771	0.771	3.994	2.745

Table 3. Synthesis of poly(methacrylic acid-co-methacrylamide) [P(MAAc-co-MAAm)] eutectogels with different compositions and P(MAAc-*co*-MAAm) hydrogels using other deep eutectic solvents as the replacement solvents.

sample	Solvent(g)	MAAc(g)	MAAm(g)	I2959(mg)	MBAA(mg)
PMM-0.3-6 (DMSO)	2.334	1.079	0.463	3.994	2.745
PMM-0.3-6 (H_2O)	2.334	1.079	0.463	3.994	2.745
PMM-0.1-6 (ChCl/Fru)	1.749	1.388	0.154	3.994	2.745
PMM-0.2-6 (ChCl/Fru)	1.749	1.234	0.308	3.994	2.745
PMM-0.3-6 (ChCl/Fru)	1.749	1.079	0.463	3.994	2.745
PMM-0.4-6 (ChCl/Fru)	1.749	0.925	0.617	3.994	2.745
PMM-0.1-6 (ChCl/Xyl)	1.908	1.388	0.154	3.994	2.745
PMM-0.2-6 (ChCl/Xyl)	1.908	1.234	0.308	3.994	2.745
PMM-0.3-6 (ChCl/Xyl)	1.908	1.079	0.463	3.994	2.745
PMM-0.4-6 (ChCl/Xyl)	1.908	0.925	0.617	3.994	2.745

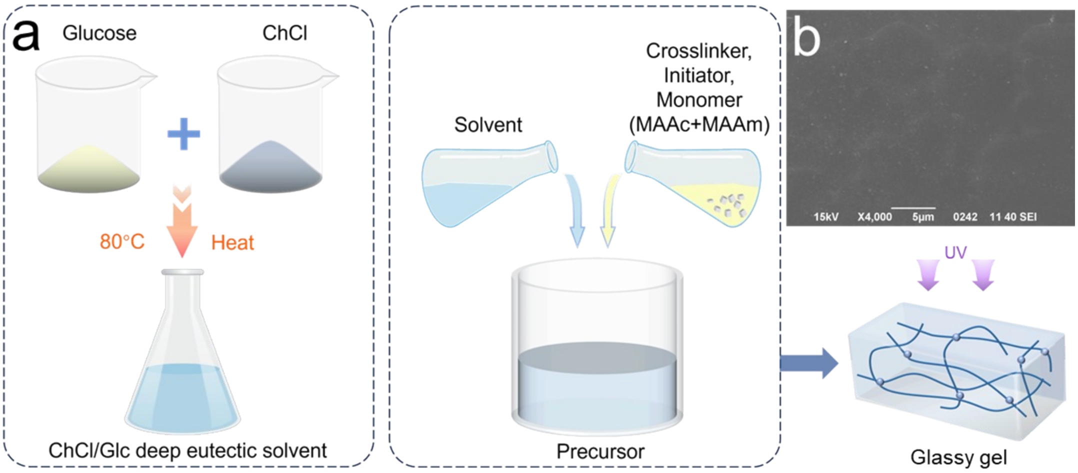

Figure S1. (a) Schematic diagram of the synthesis of P(MAAm-*co*-MAAc) gel and deep eutectic solvent. (b) SEM image of the PMM-0.3-6 eutectogel.

Figure S2. The prepared PMM-0.3-6 eutectogel (with a thickness of 1 mm) withstands the tensile force of a 5 kg weight.

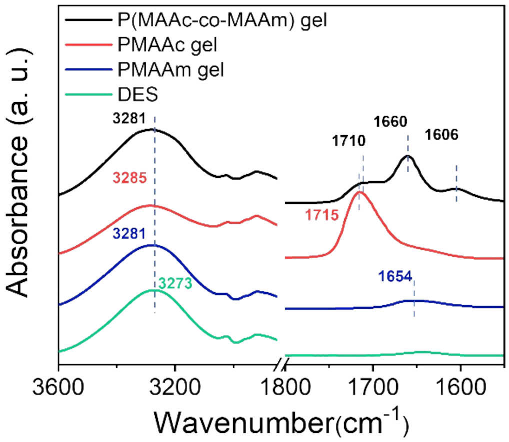

Figure S3. FTIR spectra of different eutectogels and DES.

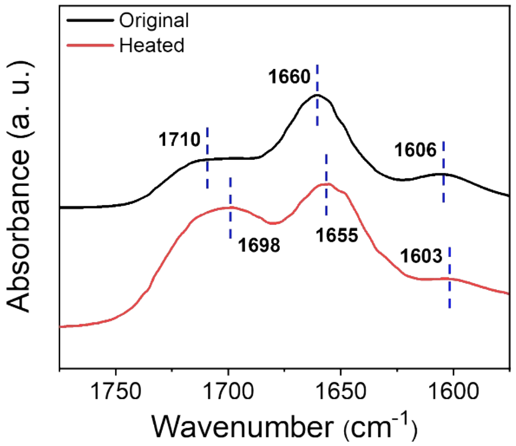

Figure S4. FTIR spectra of the original eutectogels and heated in nitrogen at 80°C for 12 hours. The *v*(C═O) of MAAc at 1710 cm^{-1} shift to 1698 cm^{-1}, and the *v*(C═O) of MAAm at 1660 cm^{-1} and 1606 cm^{-1} shift to 1655 cm^{-1} and 1603 cm^{-1}. It indicates that more hydrogen bonds can be formed in eutectogel after heating.

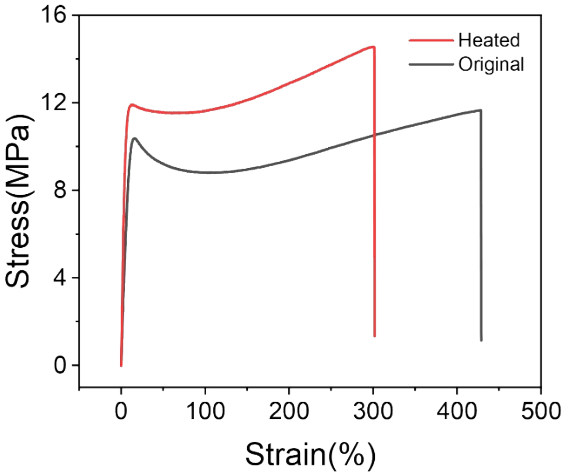

Figure S5. The stress-strain curves of the original eutectogels and heated in nitrogen at 80°C for 12 hours. The breaking strength of eutectogel reaches 14.5 MPa, which is 25% higher than the original of 11.6 MPa.

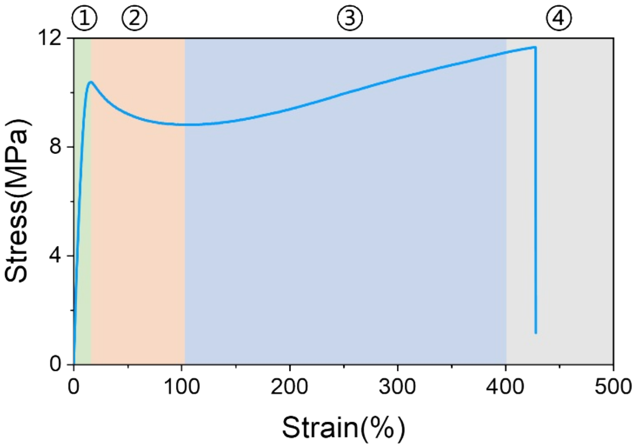

Figure S6. The tensile stress-strain curve of the eutectogel (PMM-0.3-6) is divided into four regions. Firstly, the material demonstrates linear elastic behavior characterized by an exceptionally high Young's modulus (slope of the curve), attributed to the dominance of robust non-covalent interactions within the network. Secondly, the eutectogel network undergoes yielding, initiating chain elongation accompanied by a notable stress reduction. Then, the eutectogel forms a stable neck and undergoes cold drawing with dramatic strain amplification from 100% to 400% in the thirdly regime. Finaly, the covalent bond fracture within the polymer network, which eventually leads to the break of the eutectogel.

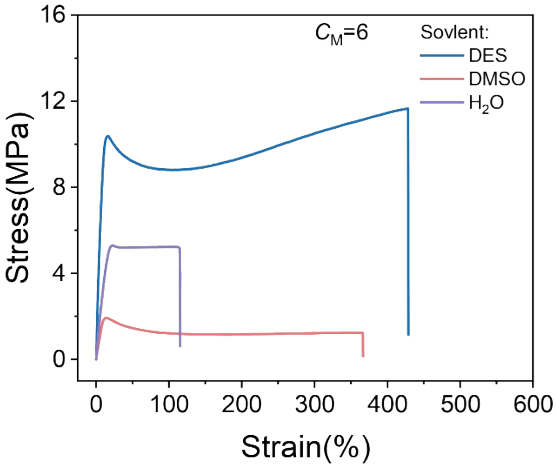

Figure S7. Tensile stress-strain curves of gels with different solvents.

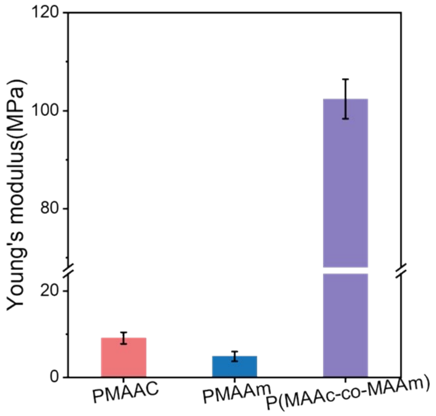

Figure S8. The young's modulus of the chemically cross-linked PMAAm eutectogel, PMAAc eutectogel and the P(MAAM-*co*-MAAC) eutectogel with the same monomer concentration ($C_M = 6$).

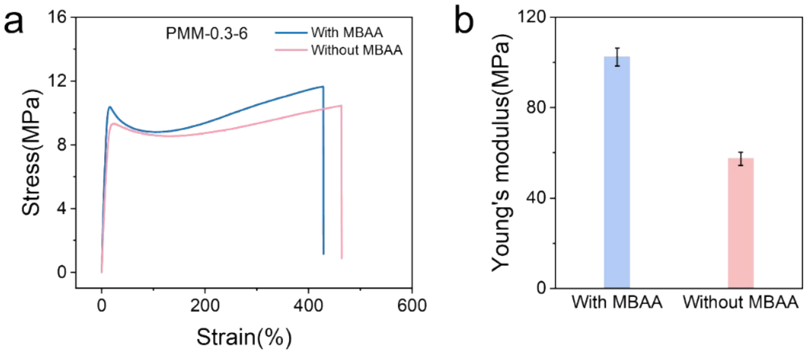

Figure S9. Tensile stress-strain curves (a) and modulus (b) of the PMM-0.3-6 gel with 0.1 mol% MBAA and without MBAA.

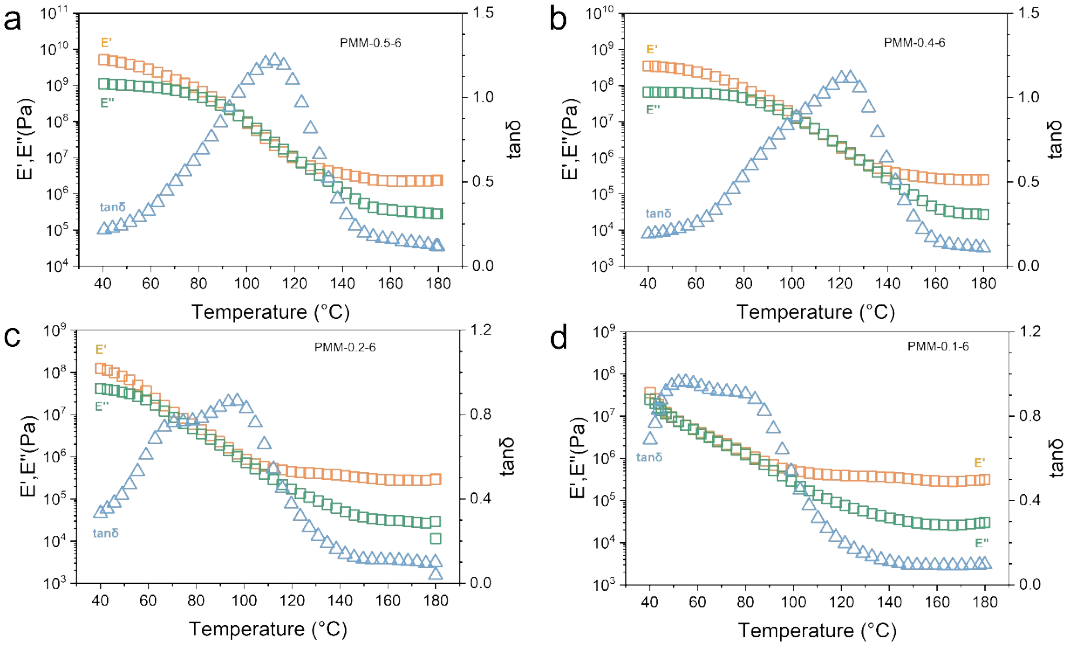

Figure S10. The DMA spectra of other glassy gels during the heating process from 40 to 180°C. Heating rate: 10 °C/min. The DMA test is carried out in a single cantilever mode with a frequency of 1 Hz.

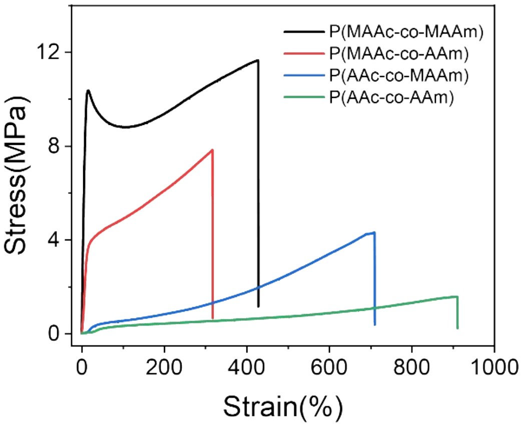

Figure S11. Stress-strain curves of eutectogels with different monomers. The decrease of hydrophobic α-methyl in eutectogels significantly reduces the rigidity of the chain. Furthermore, the α-methyl group on the carboxylic acid unit strengthens the hydrogels more significantly than that on the acrylamide unit.

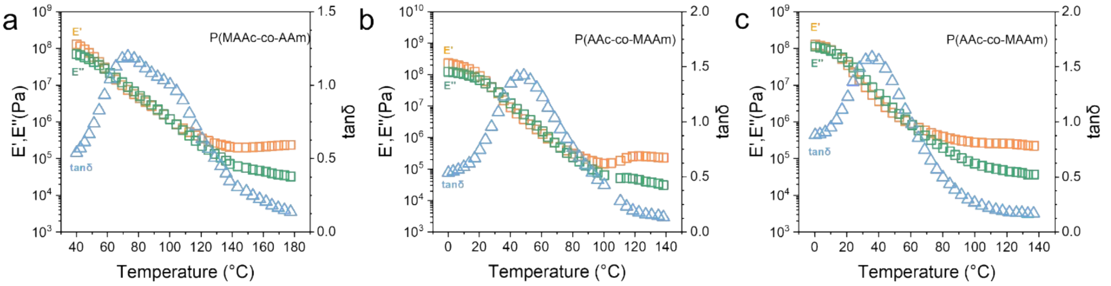

Figure S12. DMA spectra of the as-prepared P(MAAc-co-AAm), P(AAc-co-MAAm) and P(AAc-co-AAm) eutectogels. The T_g of the P(MAAc-co-AAm) eutectogel decreased to 73 °C. It is further decreased to 48 °C and 36 °C in P(AAc-co-MAAm) and P(AAc-co-AAm) eutectogels. It demonstrates that the presence of α-methyl group has a significant impact on the mobility of chain segment. In summary, the number and position of α-methyl groups are crucial for the chain rigidity and strength of the eutectogels.

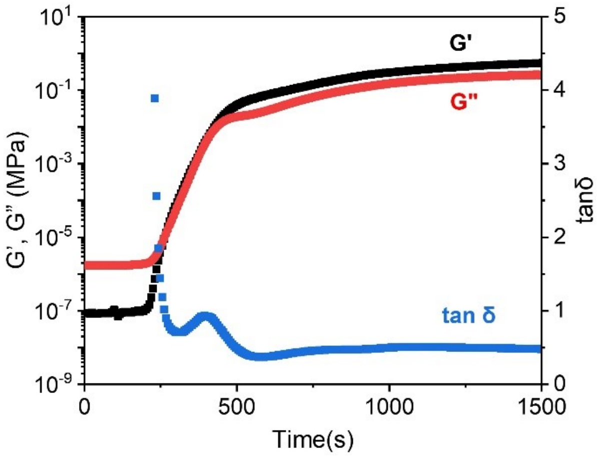

Figure S13. Time-sweep spectra of storage modulus G', loss modulus G", and loss tangent tanδ during the synthesis of PMM-0.3-6. Initially, the solution exhibited liquid-like behavior, evidenced by G" > G'. As the reaction proceeded, one crossover point of G' and G" emerged, signifying the formation of a solid-like network, with gelation (G' = G") occurring at approximately 260 s. Subsequently,, G' and G" kept increasing and then approached to each other. A dramatic increase (~4 orders of magnitude) in both G' and G" within 250 s, accompanied by a sharp tanδ peak at 394 s, indicated vitrification. The G' and G" gradually reached an equilibrium value beyond the vitrification point.

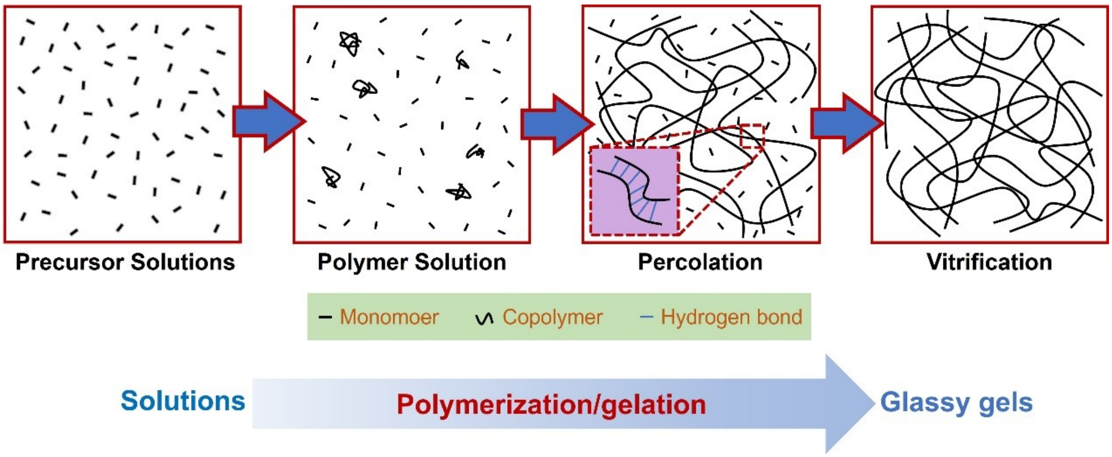

Figure S14. Schematic for the structural evolution during the synthesis of glassy eutectogels with different compositions. Polymerization initially produced random-coiled polymer chains lacking strong intra- and inter-chain hydrogen bonding. As the reaction continued, more polymer chains were produced, leading to chain entanglement and then a sol-gel transition. Further reaction promoted network densification through enhanced entanglement and physical crosslinking via hydrogen bond formation, resulting in the transformation of the gel matrix into a glassy state.

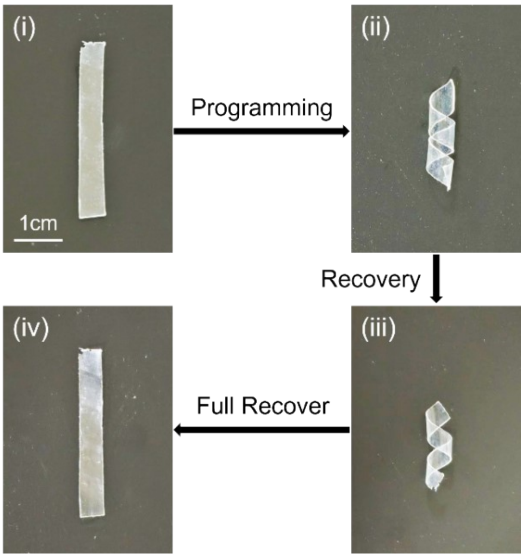

Figure S15. Deformation of the spiral structure of the PMM-0.3-6 gel and recovery.

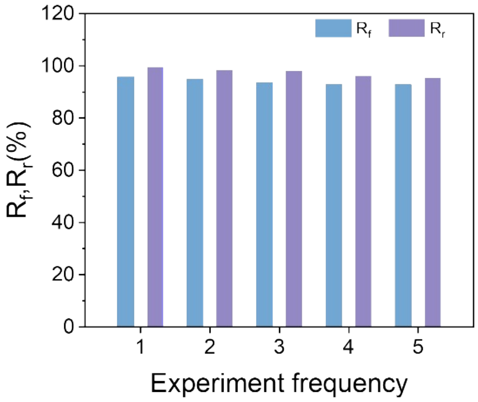

Figure S16. Shape fixity ratio R_f and recovery ratio R_r the eutectogel during the cyclic shape memory and recovery.

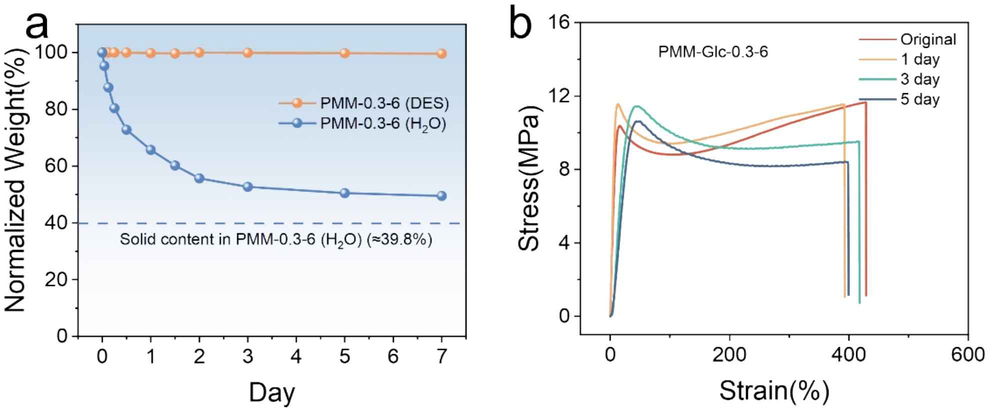

Figure S17. (a) The change in weight relative to the initial weight of the PMM-0.3-6 eutectogel and the PMM-0.3-6 hydrogel in the natural environment. (b) The tensile stress-strain curves of the PMM-0.3-6 eutectogel at different times in the natural environment.

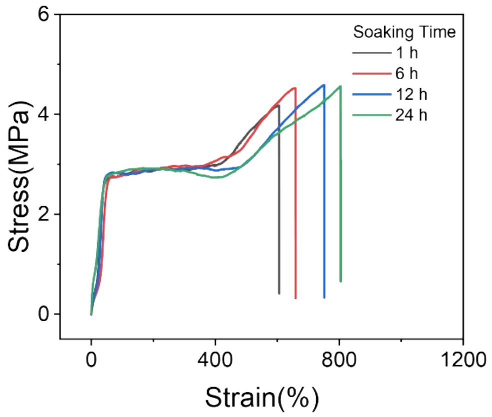

Figure S18. The tensile stress-strain curve of the eutectogel after soaking in water. The tensile strength and Young's modulus of the eutectogels are still as high as 4.6 MPa and 15.2 MPa after soaking in water for 24 h

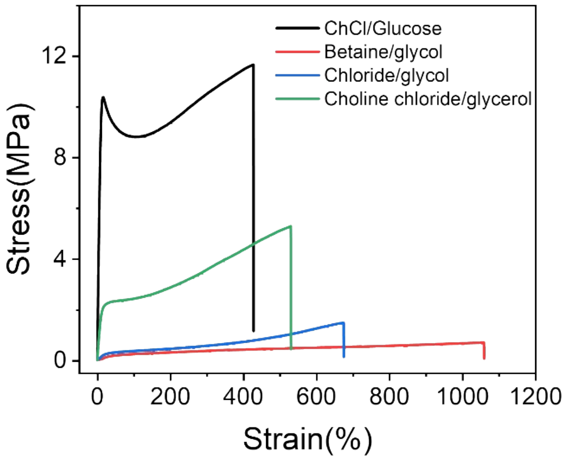

Figure S19. Tensile stress-strain curves of eutectogels with different DES. For comparison, different types of DES were synthesized using glycerol and glycol as hydrogen bond donors, and choline chloride and betaine as hydrogen bond acceptors. The results showed that the strengths of eutectogels prepared by different DES (choline chloride/glycerol, choline chloride/glycol and betaine/glycol) are far below than that of carbohydrate-derived DES. It is because that carbohydrate, such as glucose, fructose, xylose et al., can form more hydrogen bond than glycerol or glycol.