Electronic Supplementary Material (ESI) for Materials Horizons.

Supplementary data for

Amino acid-induced rapid gelation and mechanical reinforcement of hydrogels with low-hysteresis, self-recoverable and fatigue-resistant properties

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Table S1. Compositions of the PLS hydrogels.

Samples	AM (M)	L-serine (M)	MBA (M)	KPS (M)	TMEDA (M)	pH
PLS-0	3.0	0	0.001	0.008	0.016	6.85
PLS-0.5	3.0	0.5	0.001	0.008	0.016	6.72
PLS-1.0	3.0	1.0	0.001	0.008	0.016	6.50
PLS-1.5	3.0	1.5	0.001	0.008	0.016	6.35
PLS-2.0	3.0	2.0	0.001	0.008	0.016	6.10

Table S2. The effect of pH value on the gelation time of the precursor of the PLS-1.0 hydrogel.

pH	Gelation time	pH	Gelation time
6.50	75±10 s	7.50	240±13 s
5.50	30±1.20 min	8.50	partially gelated even after 2 d
4.50	2±0.16 h	9.50	viscous flow state even after 2 d
3.50	4±0.22 h		

Table S3. The pH value of the precursors with different amino acids and the carboxyl dissociation constant (pK_1) and amino dissociation constant (pK_2) of the corresponding amino acids.[1]

Amino acid (1.0 M)	**pH**	**pK_1**	**pK_2**	**Amino acid (0.2 M)**	**pH**	**pK_1**	**pK_1**
L-serine	6.50	2.19	9.44	L-histidine	7.93	1.81	9.15
glycine	6.92	2.34	9.60	L-cysteine	7.80	1.86	8.35
L-alanine	7.16	2.35	9.87	L-phenylalanine	7.38	2.58	9.24
L-threonine	6.83	2.09	9.10	L-lysine	9.20	2.18	8.95
L-proline	6.95	1.95	10.84	L-valine	7.74	2.29	9.72
D-serine	6.55	2.19	9.44	L-glutamine	7.91	2.13	9.60

Table S4. Calculated m/z of the potential substances in Figure S5.

M	**$[M+H]^+$ m/z**	M	**$[M+H]^+$ m/z**
L-serine	106.0504	DMPO-OH	131.0946
TMEDA	117.1392	DMPO-OSO_3H	211.0514
H_2SO_4	98.9752	DMPO-TMEDA radical	229.2154

Table S5. Comparisons of the PLS-1.0 hydrogel with those reported hydrogels with rapid gelation in terms of the rapid gelation mechanism, preparation conditions, tensile strength, elongation at break and compressive strength, respectively.

Hydrogel name	**Rapid gelation mechanism**	**Preparation condition**	**Tensile strength (MPa)**	**Elongation at break (%)**	**Compressive strength (MPa)**	**Ref.**

DA-PEG/CMC 0.28-2.5%	Amino−yne click reaction	~8 min, 37°C	-	-	0.065, 55%	2
PQB2	Schiff base reaction and photo-crosslinking	a few min, blue light	~0.08	~53	-	3
Silk-HA 20%	Enzymatic crosslinking	~3 min, 37 °C	-	-	~0.003, 30%	4
4P-OPA/4P-NHNH$_2$ 15%	OPA/N-nucleophile condensation	~2 min, 37°C	~0.06	~105	0.41, 70%	5
CS-DMAA	Free radical polymerization induced by a complex of GOx and Fe[Gly]$_2$	~6 s, 37 °C	-	-	0.02, 80%	6
TC-7.5/PSA	Free radical polymerization induced by TC-Zn^{2+}	~6 min, RT	~0.10	~500	1.60, 80%	7
LSN-Fe-2/PAM	Free radical polymerization induced by LSN-Fe^{3+}	60 s, RT	0.20	~950	0.60, 80%	8
PAA-MXene$_{4.29}$	Free radical polymerization induced by MXene	74 s, RT	~0.40	~1700	-	9
PLS-1.0	Free radical polymerization induced by L-serine	75 s, 25 °C	0.45	2060	0.23, 80%	This work

The symbol "-" indicates that information cannot be obtained from the literature. DA-PEG: dipropiolate ester of polyethylene glycol, CMC: carboxymethyl chitosan; PQB: photo-crosslinked hydrogels composed of quaternized methacryloyl chitosan and four-arm benzaldehyde-terminated polyethylene glycol; HA: hyaluronic acid; 4P-OPA: o-phthalaldehyde-terminated four-arm poly(ethylene glycol), 4P-NHNH$_2$: hydrazide-terminated four-arm poly(ethylene glycol); CS: acryloyl-modified chondroitin sulfate, DMAA: N,N-dimethylacrylamide, GOx: glucose oxidase, Fe[Gly]$_2$: ferrous glycinate; PSA: poly([2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)-*co*-acrylic acid); LSN: sulfonated lignin-encapsulated silica nanoparticle.

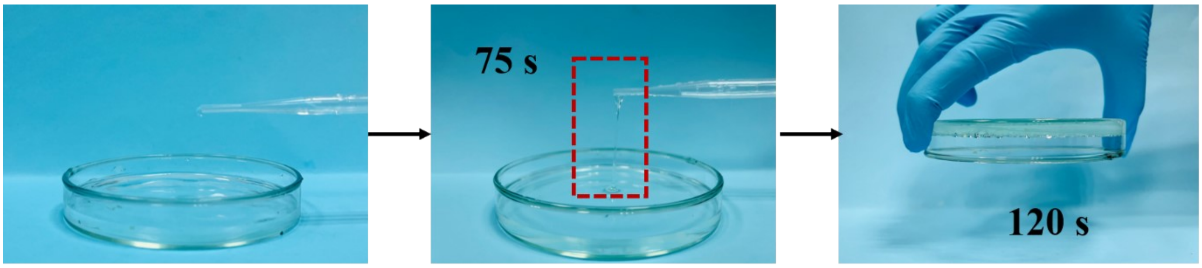
Table S6. Compositions of the PLS-1.0-NaCl$_x$, PAM/0.2 M L-phenylalanine, P(AM-MAA) and P(AM-MAA)/1.0 M L-serine hydrogels.

Samples	Monomer (M)	Amino acid (M)	NaCl (M)	MBA (M)	KPS (M)	TMEDA (M)
PLS-1.0-NaCl$_0$	AM 3.0	L-serine 1.0	0	0.001	0.008	0.016
PLS-1.0-NaCl$_{0.4}$	AM 3.0	L-serine 1.0	0.4	0.001	0.008	0.016
PLS-1.0-NaCl$_{0.8}$	AM 3.0	L-serine 1.0	0.8	0.001	0.008	0.016
PLS-1.0-NaCl$_{1.2}$	AM 3.0	L-serine 1.0	1.2	0.001	0.008	0.016
PLS-1.0-NaCl$_{1.6}$	AM 3.0	L-serine 1.0	1.6	0.001	0.008	0.016
PAM/0.2 M L-phenylalanine	AM 3.0	L-phenylalanine 0.2	0	0.001	0.008	0.016

Table S7. Compositions of PNIPAM, PNHEMAA, PDMAA, PPEGMA, PPEGDA, P(AM-DMAA) and P(AM-HEMA) hydrogels with or without L-serine.

Samples	Monomer (M)	L-serine (M)	MBA (M)	KPS (M)	TMEDA (M)
PNIPAM	NIPAM 2.65	0	0.001	0.008	0.016
PNIPAN/L-serine	NIPAM 2.65	1.0	0.001	0.008	0.016
PNHEMAA	NHEMAA 2.60	0	0.001	0.008	0.016
PNHEMAA/L-serine	NHEMAA 2.60	1.0	0.001	0.008	0.016
PDMAA	DMAA 3.0	0	0.002	0.016	0.032
PDMAA/L-serine	DMAA 3.0	0.75	0.002	0.016	0.032

PPEGMA	PEGMA 1.0	0	0.002	0.016	0.032
PPEGMA/L-serine	PEGMA 1.0	1.0	0.002	0.016	0.032
PPEGDA	PEGDA 0.2	0	0.003	0.024	0.048
PPEGDA/L-serine	PEGDA 0.2	1.25	0.003	0.024	0.048
PNAGA	NAGA 2.0	0	0	0.050	0.160
PNAGA/L-serine	NAGA 2.0	1.0	0	0.050	0.160
P(AM-DMAA)	AM 2.0 DMAA 1.0	0	0.002	0.016	0.032
P(AM-DMAA)/L-serine	AM 2.0 DMAA 1.0	0.75	0.002	0.016	0.032
P(AM-HEMA)	AM 2.0 HEMA 1.0	0	0.002	0.016	0.032
P(AM-HEMA)/L-serine	AM 2.0 HEMA 1.0	0.75	0.002	0.016	0.032



Before gelation Began gelation After gelation

Figure S1. Illustration of the gelation process of the PLS-1.0 hydrogel.

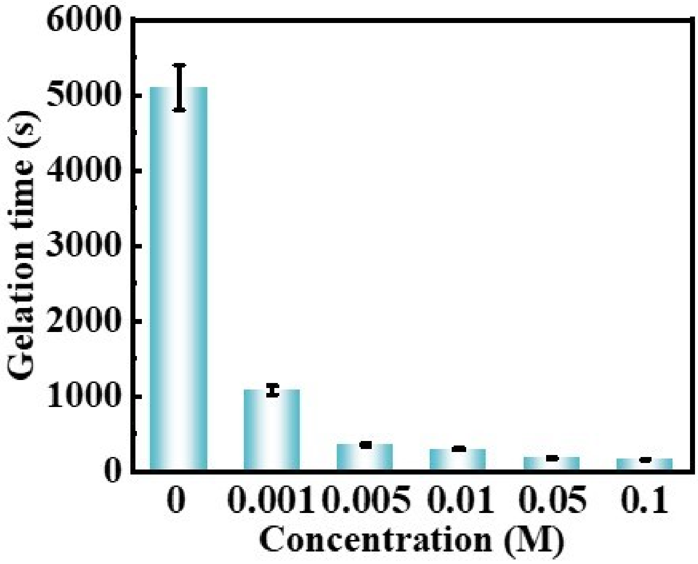


Figure S2. Gelation time of the PLS hydrogels with different L-serine concentrations at 25 °C.

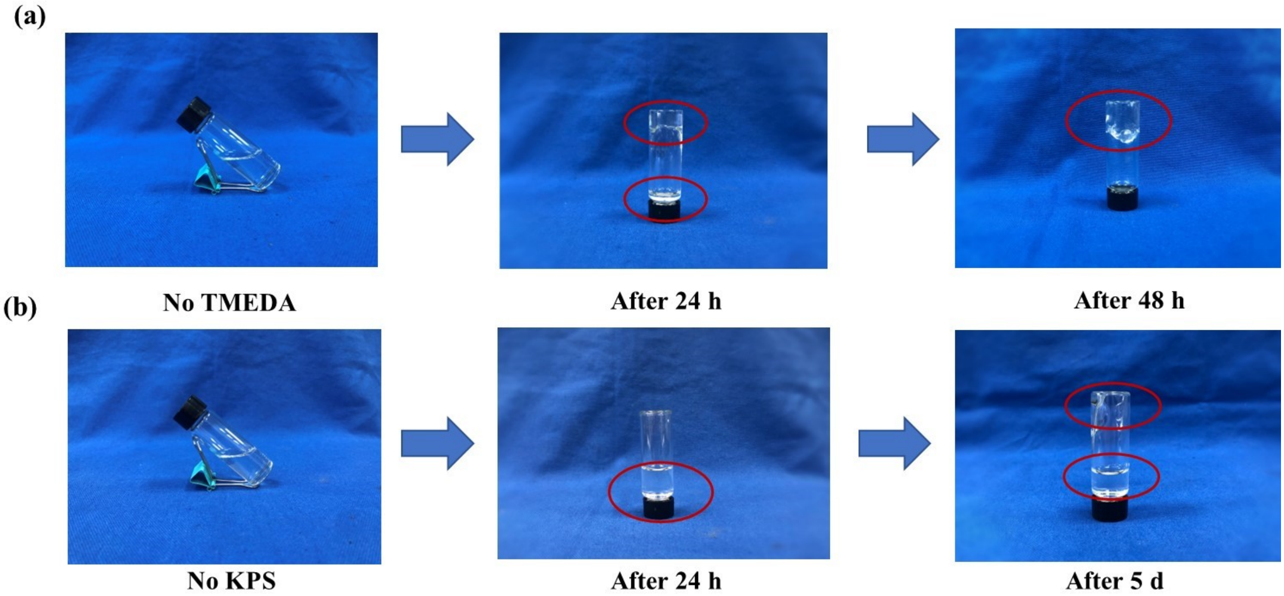


Figure S3. (a) Gelation process of the precursor without TMEDA at 24 h and 48 h. (b) Gelation process of the precursor without KPS at 24 h and 5 d.

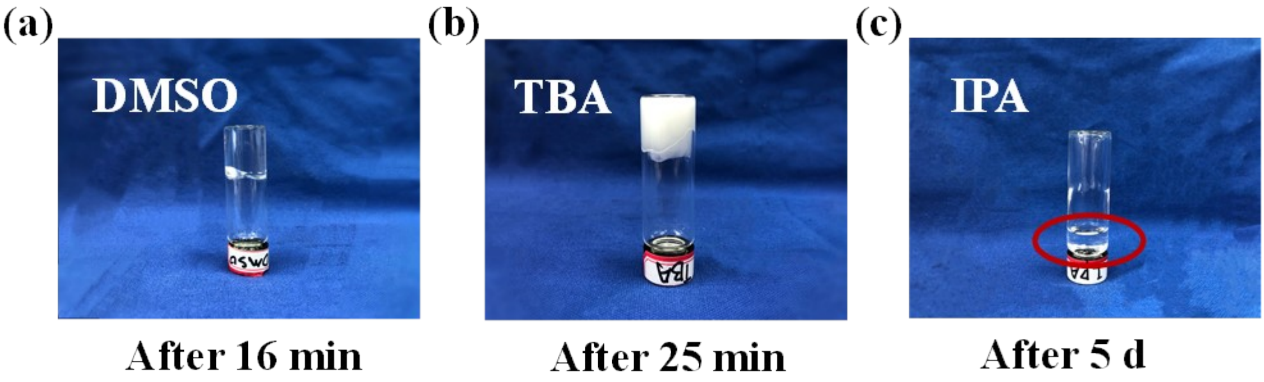


Figure S4. The influence of (a) DMSO, (b) TBA and (c) IPA as free radical scavengers on the gelation processes of the PLS hydrogels.

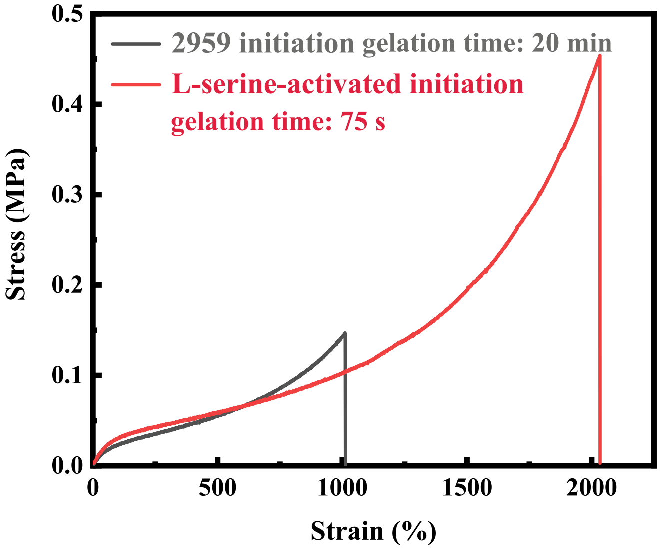


Figure S5. Gelation time and tensile stress–strain curves of the PLS hydrogels initiated by L-serine-activated KPS-TMEDA initiation system and photoinitiator 2959 initiation system under the same water content.

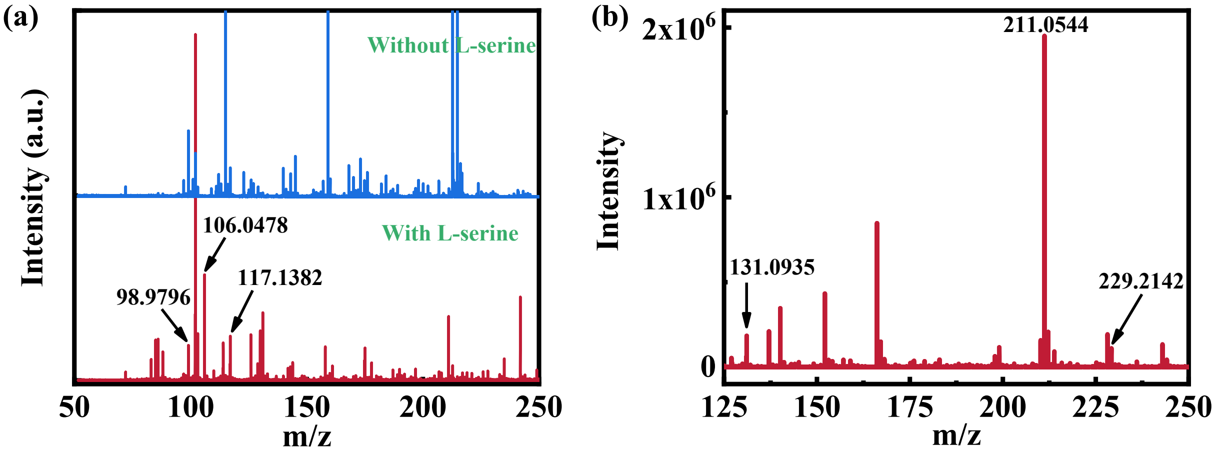


Figure S6. (a) High resolution mass spectra of the product in KPS-TMEDA initiating system without L-serine (0.008 M KPS and 0.016 M TMEDA) or with L-serine (1.0 M L-serine, 0.008 M KPS and 0.016 M TMEDA). (b) High resolution mass spectrum of the product in L-serine-KPS-TMEDA initiating system with DMPO (1.0 M L-serine, 0.008 M KPS, 0.016 M TMEDA and 1 μL DMPO).

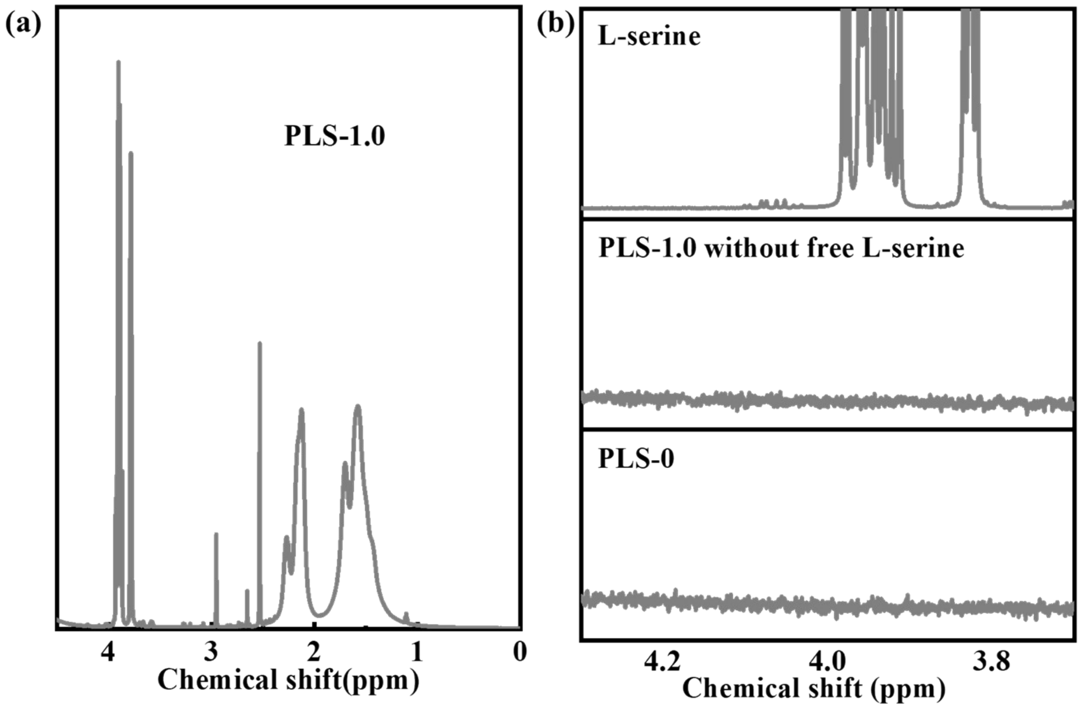


Figure S7. (a) ^{1}H NMR spectrum of the polymer of the PLS-1.0 hydrogel. (b) Enlarged image of the corresponding ^{1}H NMR spectra in Figure 2b.

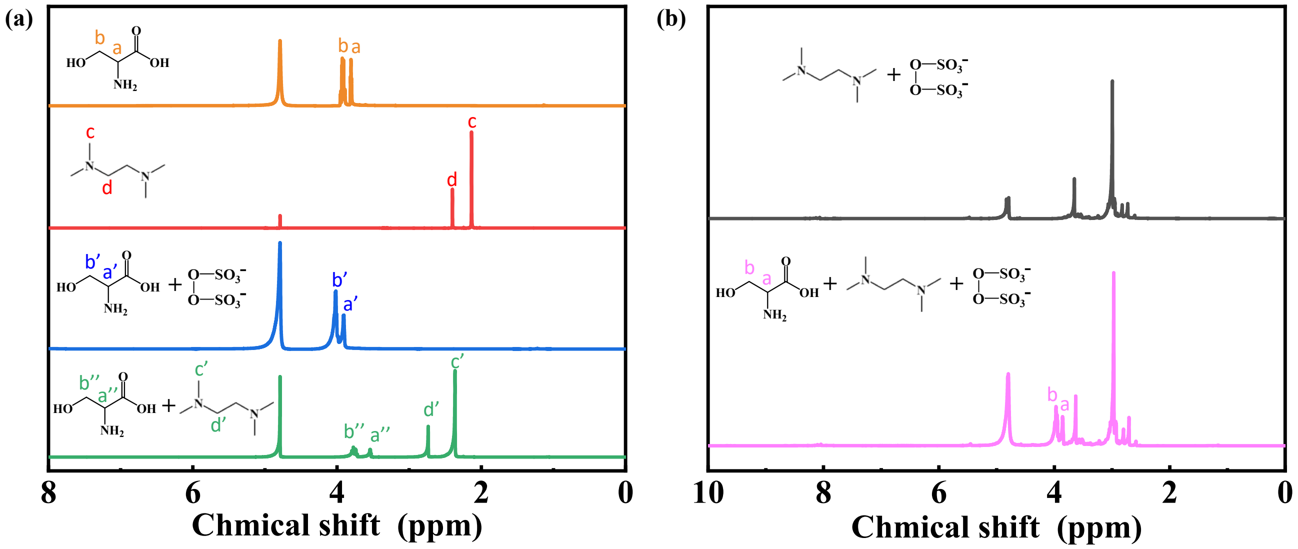


Figure S8. (a) ^{1}H NMR spectra of 0.6 M L-serine, 0.3 M TMEDA, the mixture of 0.6 M L-serine and 0.3 M KPS, and the mixture of 0.6 M L-serine and 0.3 M TMEDA recorded in D_2O after placing for one day, respectively. (b) ^{1}H NMR spectra of the mixture of 0.3 M KPS and 0.3 M TMEDA, and the mixture of 0.6 M L-serine, 0.3 M KPS and 0.3 M TMEDA recorded in D_2O after placing for one day, respectively.

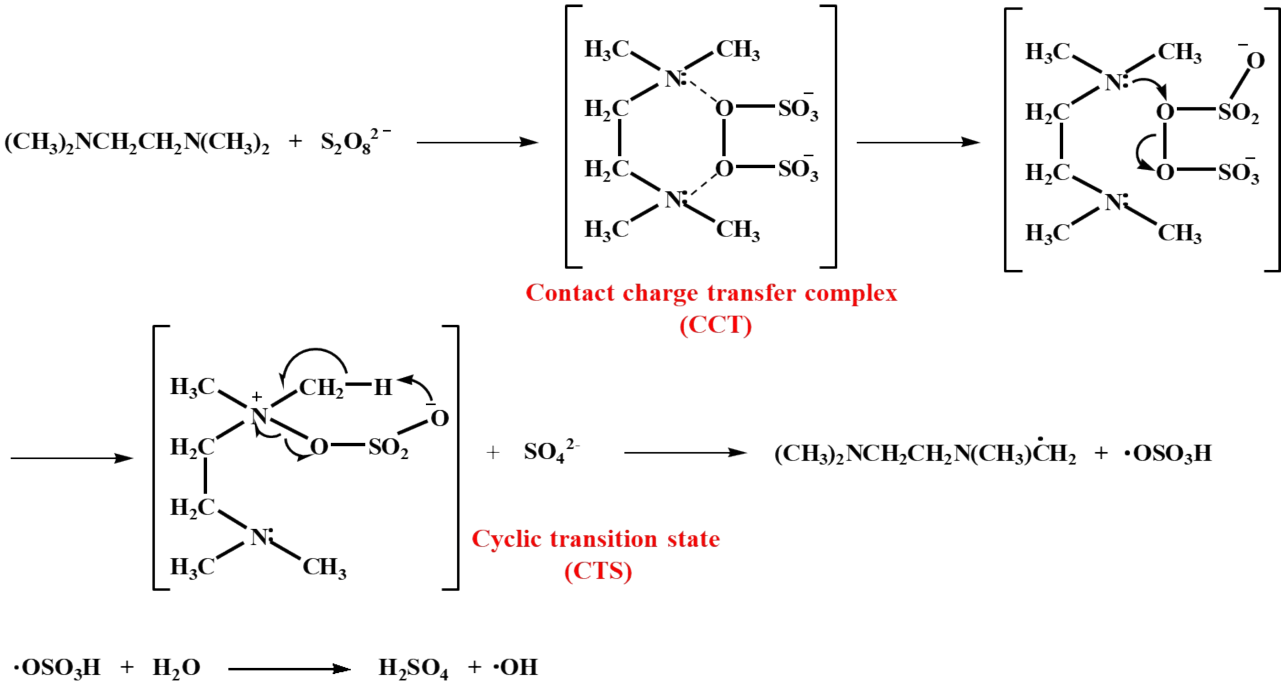


Figure S9. The reaction mechanism of the redox initiation system KPS-TMEDA.[10]

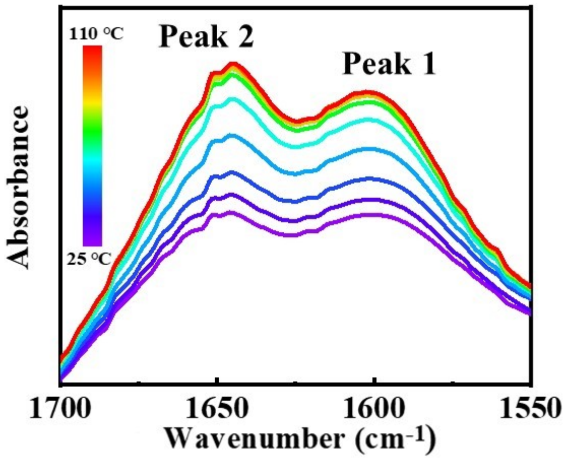


Figure S10. Temperature-dependent FTIR spectra of the PLS-0 hydrogel upon heating from 25 to 110 °C.

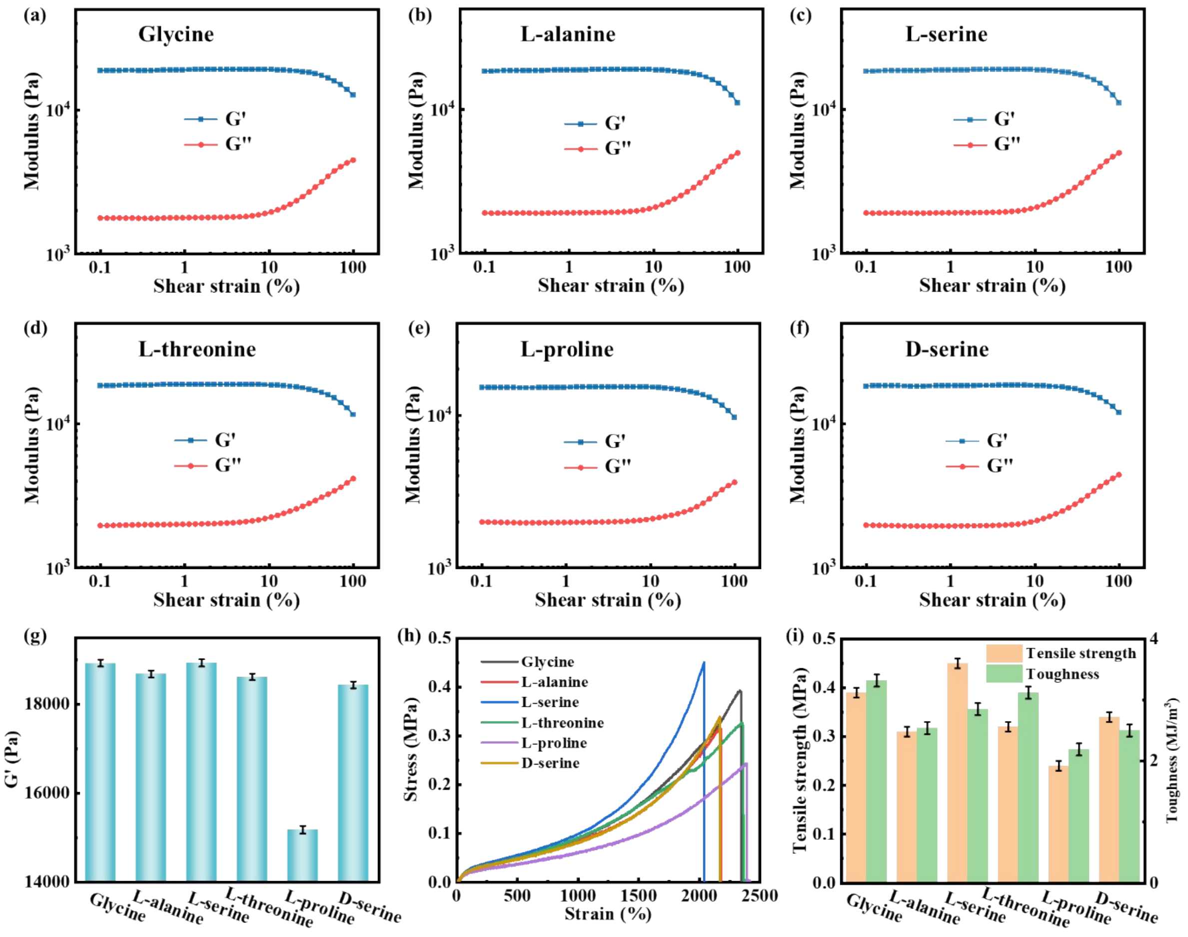


Figure S11. (a-f) Variation of storage modulus (G’) and loss modulus (G’’) with shear strain changing from 0. 1% to 100% and (g) the corresponding average storage modulus (G’) in the linear region.

The value of G’ of the glycine-induced hydrogel and L-serine-induced hydrogel is larger than that of L-alanine-induced hydrogel and L-threonine, indicating that hydrophilic groups will increase network crosslinking density while hydrophobic groups will reduce the cross-linking density of the network. Among the six kinds of amino acid-induced hydrogels, the L-proline-induced hydrogel possesses the smallest value of G’, displaying that groups with high steric hindrance will significantly decrease the cross-linking density of the network. In addition, the value of G’ of the D-serine-induced hydrogel is smaller than that of the L-serine-induced hydrogel, implying that L- amino acids will form stronger hydrogen bonding networks with the hydrogel matrix. Different degrees of gelation will lead to different mechanical properties of the hydrogels. As shown in Figures h and i, the overall tensile strength and toughness of the glycine-induced hydrogel and L-serine-induced hydrogel are larger than those of other hydrogels, which is consistent with the trend of the influence of amino acid structure on the degree of gelation. Compared with the glycine-induced hydrogel, the L-serine-induced hydrogel possesses larger tensile strength, indicating that the additional hydroxyl groups further improve hydrogen bonding interactions.

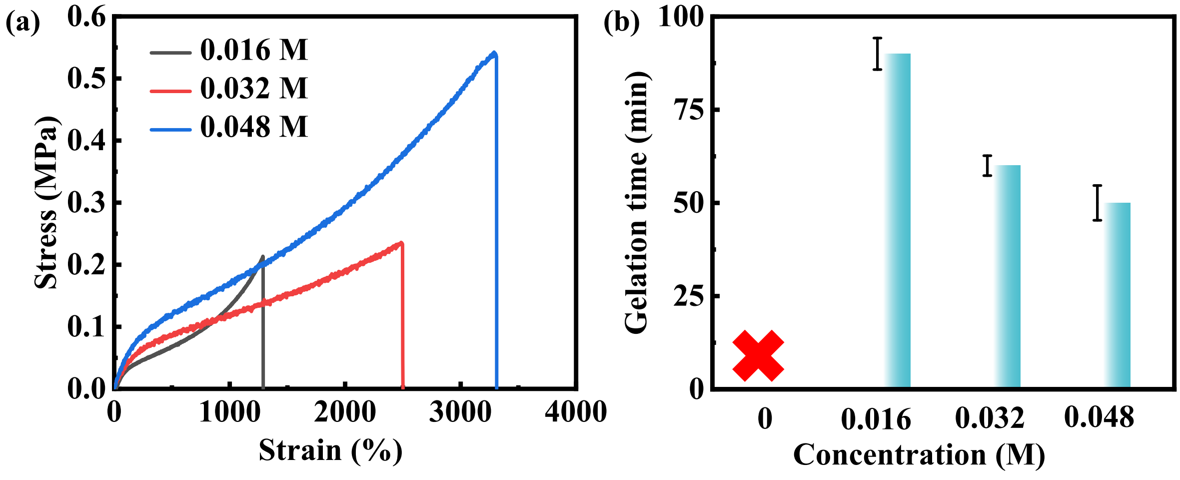


Figure S12. (a) Tensile stress−strain curves of the PLS-1.0 hydrogels with different TMEDA concentrations and (b) corresponding gelation time.

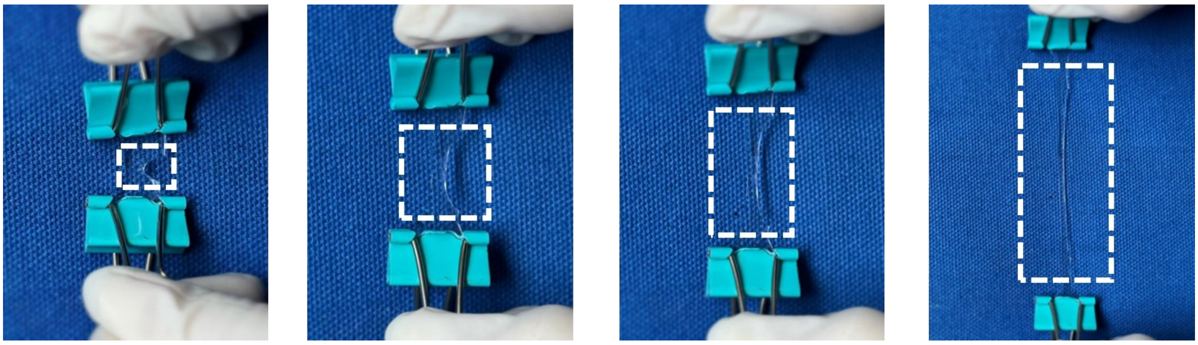


Figure S13. Demonstration of notch-resistant stretching of the PLS-1.0 hydrogel.

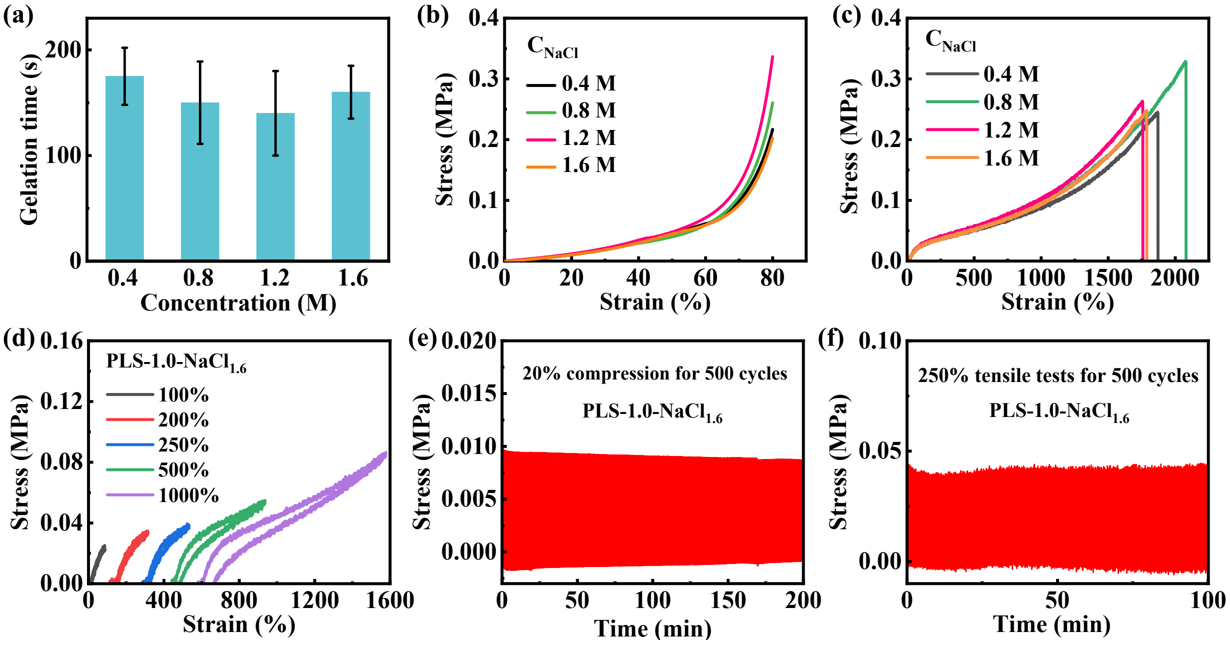


Figure S14. (a) Gelation time of PLS-1.0-NaCl$_x$ hydrogels with different NaCl concentrations. (b) Compression and (c) tensile stress–strain curves of the PLS-1.0-NaCl$_x$ hydrogels with different NaCl concentrations. (d) Loading–unloading tensile curves at different strains of the PLS-1.0-NaCl$_{1.6}$ hydrogel. (e, f) Loading–unloading curves of 500 successive compression and tensile cycles of the PLS-1.0-NaCl$_{1.6}$ hydrogel.

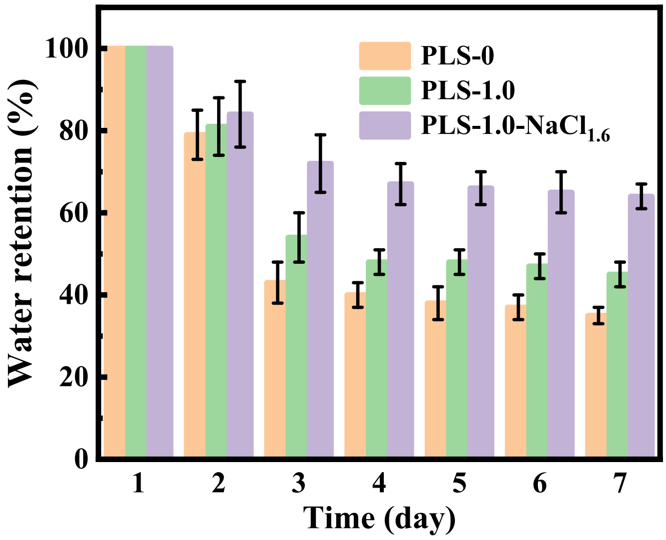


Figure S15. Water retention of the PLS-0, PLS-1.0 and PLS-1.0-NaCl$_{1.6}$ hydrogels after storage at 25 °C and 65% RH for 7 days.

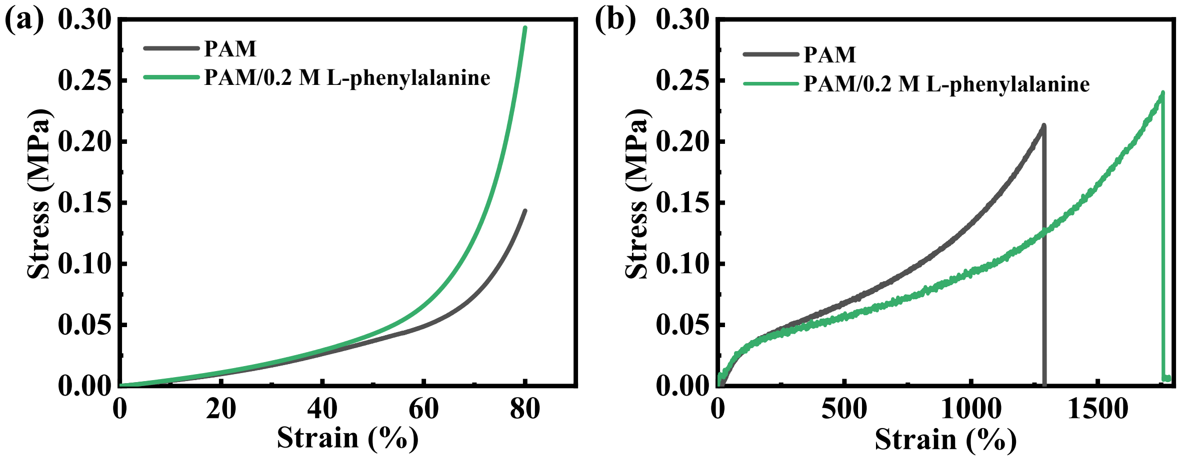


Figure S16. (a) Compression and (b) tensile stress−strain curves of PAM and PAM/0.2 M L-phenylalanine hydrogels.

Figure S17. Demonstration of the PAM/0.2 M L-phenylalanine hydrogel for high transparency to visible light.

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