

Supplementary Information

Stereocomplexed and Homocrystalline Thermo-Responsive Physical Hydrogels with Tunable Network Structure and Thermo- Responsiveness

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Supplementary Experimental Section

Synthesis of PLLA and PDLA macromonomers. A typical procedure for synthesizing the HEMA-terminated PLLA macromonomer with an expected degree of polymerization (DP) of 30 is shown as follows. L-Lactide (26.6 g, 0.18 mol) was added into a Schlenk flask and then dried in vacuum at 20 °C for 1 h. After purging the flask with dry argon, HEMA (1.6 g, 0.012 mol), Sn(Oct)₂ (141 mg, 0.5 wt%), and toluene (80 mL) were injected into the flask. The mixture was heated up to 110 °C and held at this temperature for 10 h for polymerization. The product was isolated by precipitation into an excess of ethyl ether/*n*-hexane (1/1, v/v) and the precipitate was dried *in vacuo* at 50 °C for 12 h to yield the macromonomer (25.0 g, 89%). PDLA macromonomer was synthesized by the same method using D-lactide as the monomer.

Characterizations. Molecular structures were characterized on a ¹H-NMR spectrometer (400 MHz, Bruker AVANCE II, Bruker BioSpin Co., Switzerland) with the solvents of CDCl₃ for macromonomers and DMSO-*d*₆ for copolymers.

Molecular weights of PLLA and PDLA macromonomers were measured on a gel permeation chromatography (GPC, Waters 1525/2414, Waters Co., USA) with THF as the mobile phase and polystyrene as the standard. Molecular weights of PNIPAM-*g*-PLLA and PNIPAM-*g*-PDLA copolymers were measured on a GPC (Waters 208, Waters Co., USA) with pure DMF as the mobile phase and PMMA as the standard.

TEM observations were made on a HT-7700 microscope operating at an acceleration voltage of 120 kV.

Morphology of HC/SC bilayer hydrogel at the boundary was characterized by a confocal laser scanning microscope (Zeiss LSM700).

Thermal behavior of hydrogels was measured on a differential scanning calorimetry (DSC25, TA Instruments, USA). The sample was heated from 10 to 50 °C at a heating rate of 5 °C/min.

Table S1 Molecular weight and polydispersity of PLLA, PLLA macromonomers and

PNIPAM-*g*-PLLA, PNIPAM-*g*-PDLA copolymers determined by GPC

Sample	M_n (kg/mol)	\bar{D}
HEMA-PLLA	2.98	1.13
HEMA-PDLA	3.01	1.12
L-0.10	156	2.78
D-0.10	165	2.73

Table S2 Yield and composition of synthesized PNIPAM-*g*-PLLA and PNIPAM-*g*-PDLA copolymers

Copolymer	Yield (%)	Mass fraction of PLA macromonomer, M_{PLA}	
		In feed	measured by $^1\text{H-NMR}$
L-0.05	85.5	0.05	0.053
L-0.10	86.0	0.10	0.096
L-0.15	91.9	0.15	0.146
L-0.20	94.0	0.20	0.229
L-0.25	92.0	0.25	0.274
D-0.10	90.0	0.10	0.108
D-0.15	88.3	0.15	0.159

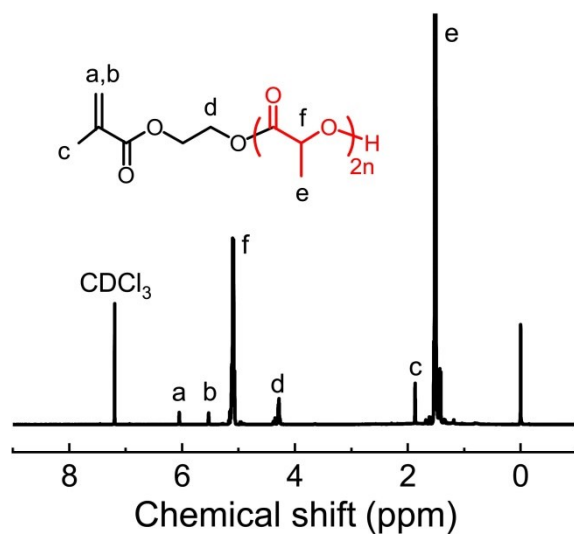


Fig. S1 ¹H-NMR spectrum of PLLA macromonomer (DP = 30).

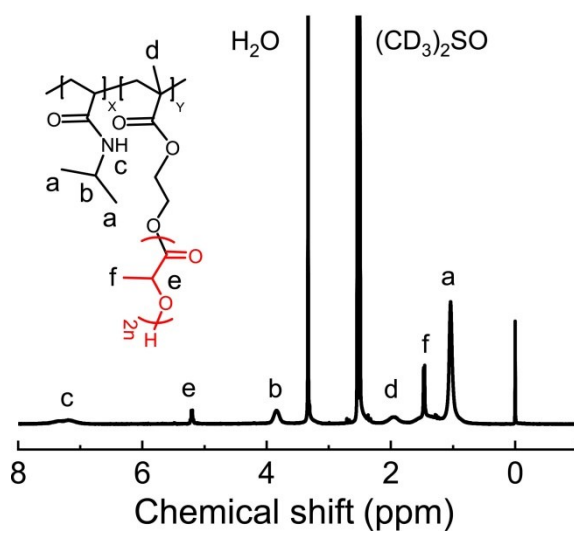


Fig. S2 ¹H-NMR spectrum of PNIPAM-g-PLLA ($M_{PLA} = 0.10$).

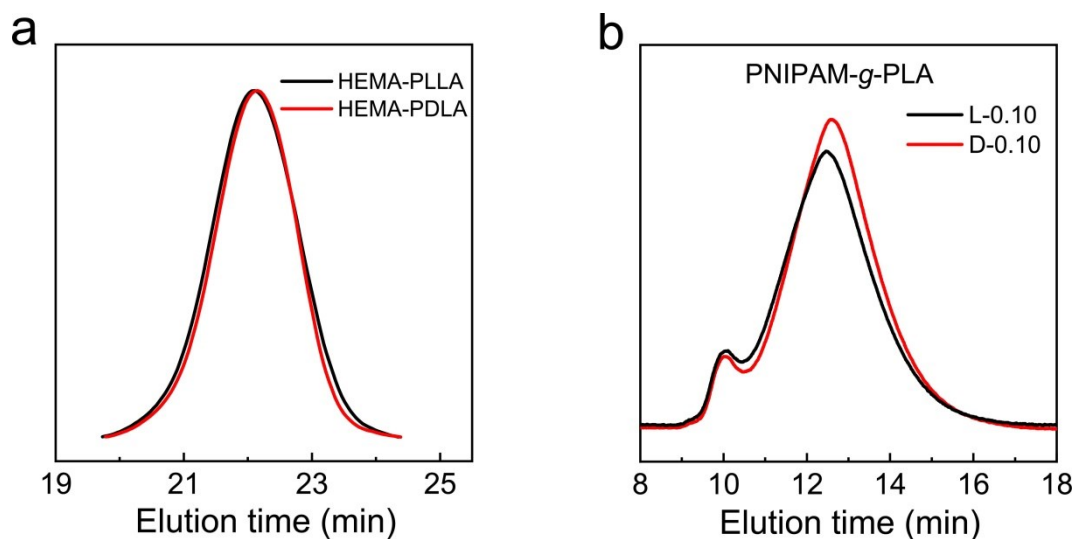


Fig. S3 GPC curves. (a) PLLA and PDLA macromonomers; (b) PNIPAM-*g*-PLLA and PNIPAM-*g*-PDLA copolymers. The small peak at the short elution time in Fig. S3b is likely caused by the aggregation of PNIPAM-*g*-PLA in DMF.

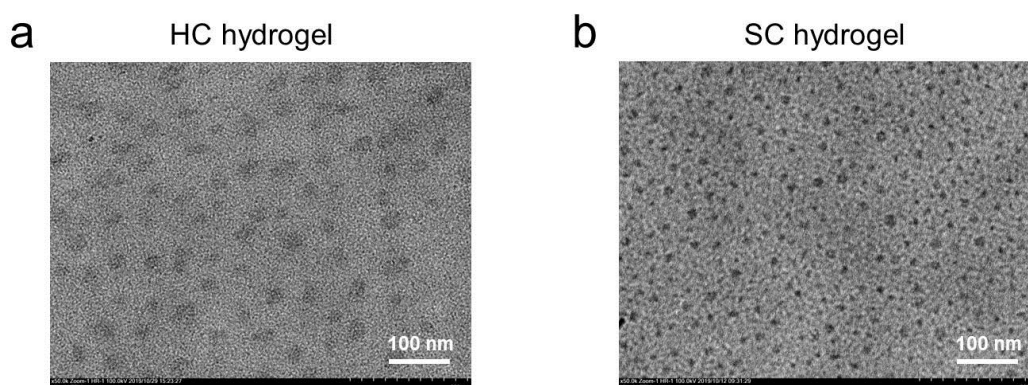


Fig. S4 TEM images of hydrogels ($M_{PLA} = 0.10$). (a) HC hydrogel ($F_D = 0$). (b) SC hydrogel ($F_D = 0.5$).

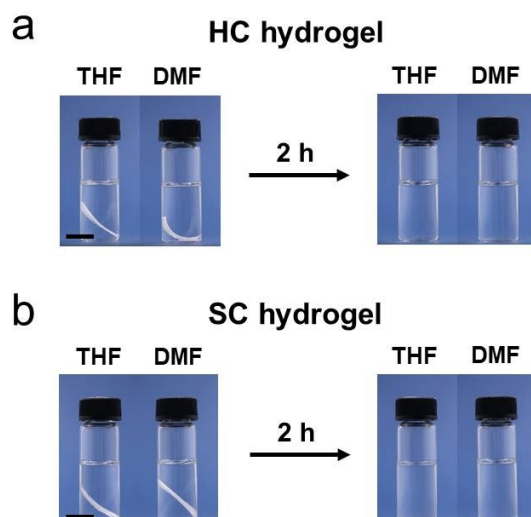


Fig. S5 Images of swollen hydrogels ($M_{PLA} = 0.10$) in different solvents at 20 °C. (a) HC hydrogel ($F_D = 0$). (b) SC hydrogel ($F_D = 0.5$). Scale bar: 1 cm.

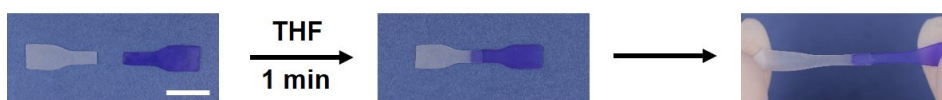


Fig. S6 THF-assisted healing of HC hydrogel ($F_D = 0$) at 20 °C. Scale bar: 1 cm.

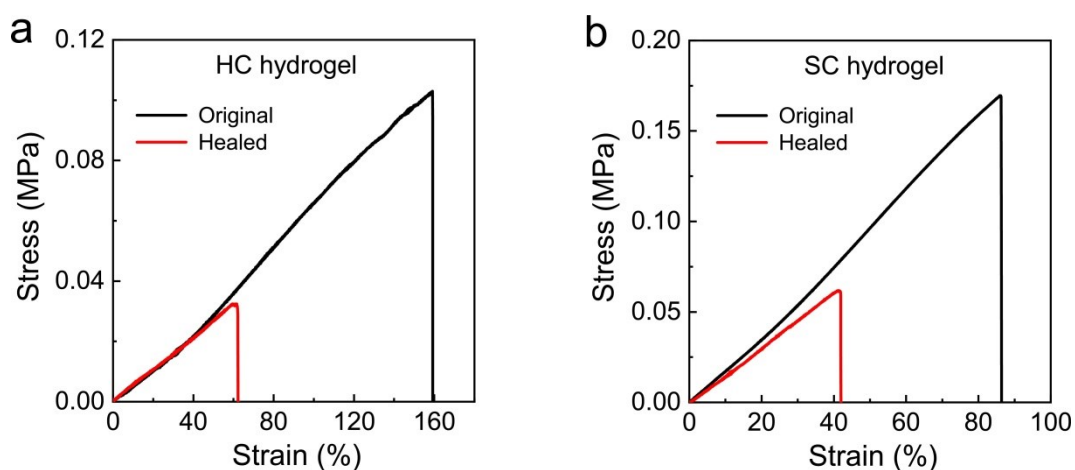


Fig. S7 Stress-strain curves of the original and healed hydrogels ($M_{PLA} = 0.10$). (a) HC hydrogel ($F_D = 0$). (b) SC hydrogel ($F_D = 0.5$).

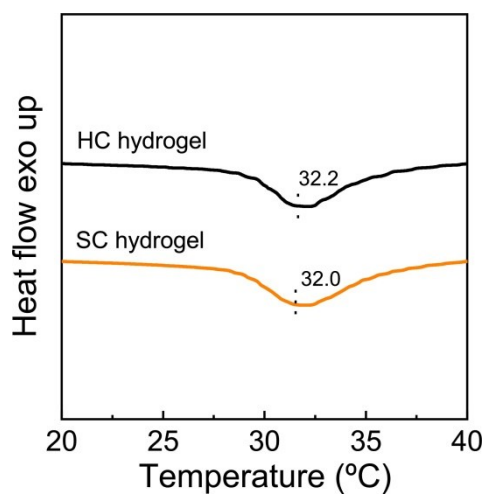


Fig. S8 DSC heating curves of HC ($F_D = 0$) and SC hydrogels ($F_D = 0.5$) with $M_{PLA} = 0.10$. The endothermic peak represents VPTT transition of hydrogel.

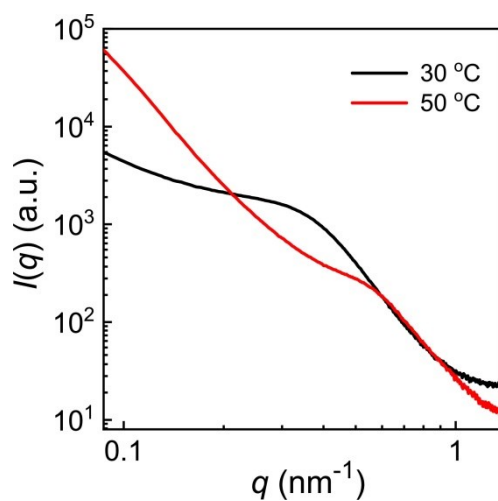


Fig. S9 Temperature-variable SAXS profiles of SC hydrogels ($F_D = 0.5$, $M_{PLA} = 0.10$).

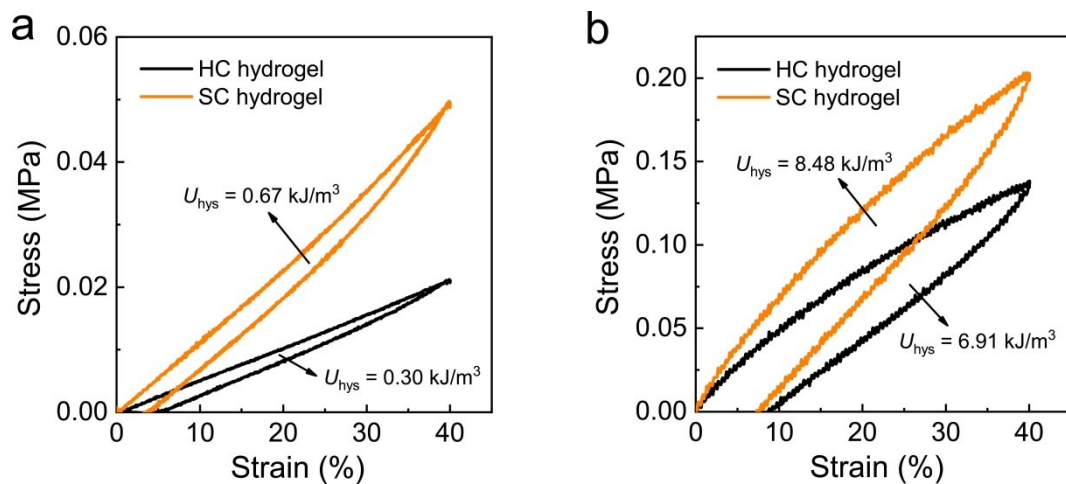


Fig. S10 Tensile loading-unloading curves of HC ($F_D = 0$) and SC hydrogels ($F_D = 0.5$) with $M_{\text{PLA}} = 0.10$ at (a) 20 °C and (b) 50 °C. The tests were conducted under a strain rate of 5 mm/min. Dissipated energy (U_{hys}) was estimated from the area between the loading-unloading curves. SC hydrogel had a larger U_{hys} at both 20 °C and 50 °C, suggesting that the hydrophobic SC domains of SC hydrogel are more effective to dissipate the energy.