

Supporting Information

Stimulus responsive dynamic polymer networks with tuning toughness and elasticity through the regulation of covalent crosslinking and reversible hydrogen bonds

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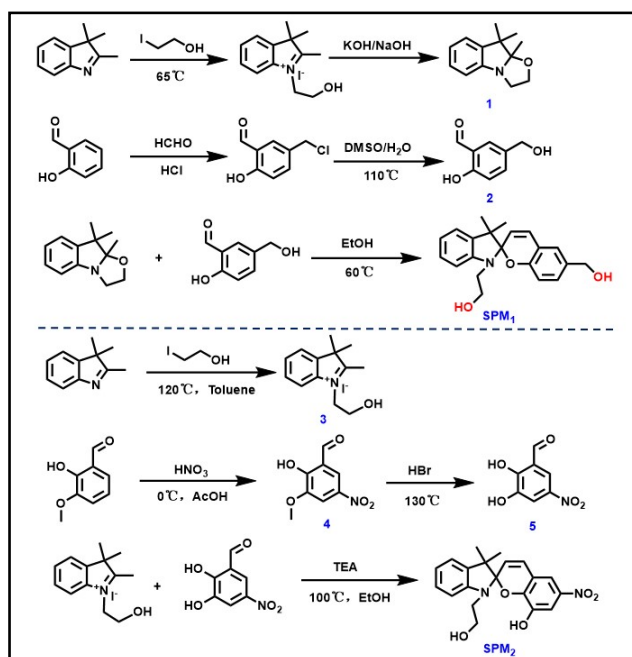
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1. Experimental Section

Commercially purchased reagents were used without further purification unless otherwise specified. m-chloroperoxybenzoic acid (m-CPBA, 85%) and zirconium (IV) chloride ($ZrCl_4$, 99.9%) were purchased from Aladdin Biochemical Technology Co., Ltd. 2,3,3-trimethyl-3H-indole (TCI, 98%), 2-iodoethanol (TCI, 97%), salicylaldehyde (Macklin, 98%), o-vaniline (Macklin, 99%), dibutyltin dilaurate (DBTDL, Alfa Aesar, 95%) and 1,6-diisocyanatohexane (Alfa Aesar, 98%) were used as received. Sodium hydroxide (NaOH), sodium chloride (NaCl), magnesium sulfate ($MgSO_4$), piperidine (AR), formaldehyde (AR), cyclohexane (AR), hexane (AR), tetrahydrofuran (THF, AR), methanol (AR), ethanol (AR), acetonitrile (AR), acetone (AR), ethyl acetate (AR), dichloromethane (AR), chloroform (AR), dimethyl sulfoxide (AR), glacial acetic acid (AR), toluene (AR), triethylamine (AR), N,N-dimethylformamide (DMF), hydrochloric acid (37 wt%), nitric acid (69 wt%) and hydrobromic acid (48 wt%) were purchased from Tianjin Bodi Chemical Co., Ltd. SIS-810 ($M_n=17.8$ kg/mol) was purchased from Jiangsu Shengjie Industrial Co., Ltd. The synthesis step of dynamic 2(6-isocyanatohexylaminocarbon-ylamino)-6-methyl-4[1H]-pyrimidinone (UPy-NCO) referred to our previous work [1].

2. Synthesis and characterizations

The synthetic routes of SPM_1/SPM_2 and its intermediates were shown as **Scheme. S1** and described in detailed as follows.



Scheme. S1 The synthetic route of SPM_1/SPM_2

2.1 Synthesis of SPM₁

Under an argon atmosphere, 2,3,3-trimethyl-3H-indole (5 g, 0.029 mol) was dissolved in 50 ml acetonitrile and the 2-iodoethanol (5.86 g, 0.03 mol) was slowly dropped into the system. After stirring for 24 h at 65 °C, the reaction mixture was concentrated to obtain solid and 200 ml hexane was added into the mixture with sonicated for 30 min. The solid was added into the NaOH (10 wt.%) aqueous solution after collecting and stirred at R.T. for 2 h, then 80 ml dichloromethane was added into the mixture and keep stirring for 30 min. The mixture was dissolved in 100 ml ethyl acetate and washed with deionized water for three times. The organic phase was concentrated and followed by solvent removal in vacuum to obtain **compound 1** as brownish red oily liquid. (Yield: 45%)

¹H-NMR (400 MHz, CDCl₃) δ (ppm)=7.14 (td, *J*=7.6, 1.3 Hz, 1H, Ar-**H**), 7.08 (dd, *J*=7.4, 1.2 Hz, 1H, Ar-**H**), 6.93 (td, *J*=7.4, 1.0 Hz, 1H, Ar-**H**), 6.76 (d, *J*=7.8 Hz, 1H, Ar-**H**), 3.89-3.67 (m, 2H, -N-CH₂CH₂-O-), 3.63-3.45 (m, 2H, -N-CH₂CH₂-O-), 1.43 (s, 3H, -N-C(CH₃)-O-), 1.39 (s, 3H, -C(CH₃)₂-), 1.18 (s, 3H, -C(CH₃)₂-).

Salicylaldehyde (53 ml, 1.41 mol), formaldehyde (37 wt %, 37 ml) and 50 ml diluted hydro-chloric acid (2 mol/L) were added into the flask and stirred at 25 °C for 24 h. The mixture was concentrated to obtain solid. Dissolved the solid in a mixed solution of 45 ml dimethyl sulfoxide and 20 ml deionized water and the system was stirred at 110 °C for 2 h. After washing with dichloromethane and saturated sodium chloride solution for three times, the organic phase was concentrated under reduced pressure and subsequently purified by flash column chromatography (hexane/ethyl acetate=50:1 (v/v)), followed by solvent removal in vacuum to obtain **compound 2** as white solid. (Yield: 52%)

¹H-NMR (400 MHz, DMSO-*d*₆) δ (ppm)=10.60 (s, 1H, -CHO), 7.61 (d, *J*=2.3 Hz, 1H, Ar-**H**), 7.46 (dd, *J*=8.5, 2.3 Hz, 1H, Ar-**H**), 6.96 (d, *J*=8.4 Hz, 1H, Ar-**H**), 5.17 (t, *J*=5.7 Hz, 1H, -CH₂OH), 4.42 (d, *J*=5.6 Hz, 2H, -CH₂OH).

Under an argon atmosphere, **compound 2** (2 g, 0.013 mol) was dissolved in 50 ml ethanol and piperidine (0.26 ml, 0.026 mol), and **compound 1** dissolved in 50 ml ethanol was slowly dropped into the system. After stirring for 6 h at 60 °C, the reaction mixture was concentrated and the crude product was recrystallized with hot ethanol followed by solvent removal in vacuum to obtain SPM₁ as yellowish gray powder. (Yield: 37%)

¹H-NMR (400 MHz, DMSO-*d*₆) δ (ppm)=7.13-7.04 (m, 3H, Ar-**H**), 7.02 (dd, *J*=8.3, 2.2 Hz, 1H, Ar-

H), 6.97 (d, $J=10.2$ Hz, 1H, $-\text{CH}=\text{CH}-\text{Ar}$), 6.73 (td, $J=7.4, 0.9$ Hz, 1H, Ar-**H**), 6.59 (dd, $J=7.9, 6.1$ Hz, 2H, Ar-**H**), 5.77 (d, $J=10.2$ Hz, 1H, $-\text{C}-\text{CH}=\text{CH}$), 5.02 (t, $J=5.7$ Hz, 1H, $-\text{OH}$), 4.66 (t, $J=5.7$ Hz, 1H, $-\text{OH}$), 4.37 (d, $J=5.7$ Hz, 2H, $-\text{CH}_2\text{OH}$), 3.59-3.38 (m, 2H, $-\text{NHCH}_2\text{CH}_2$), 3.28-3.06 (m, 2H, $-\text{NHCH}_2\text{CH}_2$), 1.19 (s, 3H, $-\text{C}(\text{CH}_3)_2$), 1.07 (s, 3H, $-\text{C}(\text{CH}_3)_2$).

2.2 Synthesis of SPM₂

Under an argon atmosphere, 2,3,3-trimethyl-3H-indole (10 g, 0.063 mol) and 2-iodoethanol (7.34 ml, 0.094 mol) was dissolved in 105 ml toluene and stirred at 110 °C for 18 h. The solid was filtered following by washing with deionized water and ethyl acetate. The organic phase was concentrated under reduced pressure and dried in vacuum to obtain **compound 3** as yellow powder. (Yield: 66%)
¹H-NMR (400 MHz, DMSO-*d*₆) δ (ppm)=7.95 (dd, $J=5.9, 3.3$ Hz, 1H, Ar-**H**), 7.85 (dd, $J=5.5, 3.2$ Hz, 1H, Ar-**H**), 7.62 (dd, $J=5.8, 3.1$ Hz, 2H, Ar-**H**), 4.60 (t, $J=5.1$ Hz, 2H, $-\text{NCH}_2\text{CH}_2-\text{O}$), 3.88 (t, $J=5.1$ Hz, 2H, $-\text{N}-\text{CH}_2\text{CH}_2-\text{O}$), 2.82 (s, 3H, $-\text{CH}_3$), 1.55 (s, 6H, $-\text{C}(\text{CH}_3)_2$).

o-vaniline (20.0 g, 0.13 mol) was dissolved in the mixture of 126 ml glacial acetic acid and 6 ml deionized water. The system was cooled to 0 °C and the nitric acid (9.21 ml, 0.15 mol) was slowly dropped into the mixture followed by stirring for 1.5 h. After diluting by 150 ml deionized water, the solid was filtered and washed with deionized water for three times, then dried in vacuum to obtain **compound 4** as yellow powder. (Yield: 70%)

¹H-NMR (400 MHz, DMSO-*d*₆) δ (ppm)=11.72 (s, 1H, $-\text{OH}$), 10.33 (d, $J=1.1$ Hz, 1H, $-\text{CHO}$), 8.10 (d, $J=2.6$ Hz, 1H, Ar-**H**), 7.93 (d, $J=2.6$ Hz, 1H, Ar-**H**), 3.99 (s, 3H, $-\text{CH}_3$).

compound 4 (24 g, 0.12 mol) and 400 ml hydrobromic acid were added into the flash and stirred at 120 °C for 4 h. The mixture was diluted by 450 ml deionized water and the solid was filtered following by washing with deionized water, ethyl acetate and activated carbon. The crude product was recrystallized with hot ethanol followed by solvent removal in vacuum to obtain **compound 5** as yellow solid. (Yield: 75%)

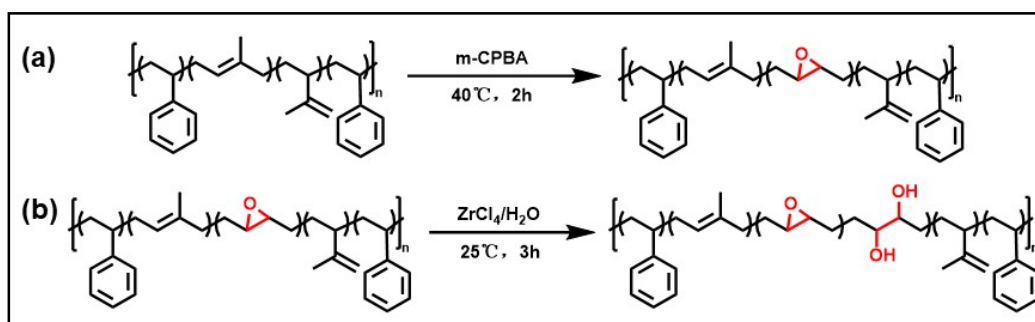
¹H-NMR (400 MHz, DMSO-*d*₆) δ (ppm)=11.15 (s, 1H, $-\text{OH}$), 10.30 (d, $J=1.2$ Hz, 1H, $-\text{OH}$), 7.99 (dd, $J=2.9, 1.2$ Hz, 1H, Ar-**H**), 7.78 (d, $J=2.8$ Hz, 1H, Ar-**H**).

Under an argon atmosphere, **compound 3** (5.17 g, 0.016 mol) and **compound 5** (2.86g, 0.016 mol) dissolved in 150 ml ethanol and triethylamine (4.37 ml, 0.031 mol) were added into the flash and stirred at 60 °C for 2 h. The mixture was filtered following by washing with cool ethanol and dried in vacuum to obtain SPM₂ as green solid. (Yield: 48%)

$^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, HCl) δ (ppm)=8.49 (s, 1H, Ar-**H**), 7.89 (dd, $J=21.0, 13.0$ Hz, 4H, Ar-**H**), 7.59 (d, $J=6.1$ Hz, 2H, Ar-**H**), 4.77 (s, 2H, $-\text{CH}_2\text{CH}_2\text{OH}$), 3.87 (s, 2H, $-\text{CH}_2\text{CH}_2\text{OH}$), 1.75 (s, 6H, $-\text{C}(\text{CH}_3)_2-$).

2.3 Synthesis of ESIS and SIS-OH

The synthetic route of ESIS and SIS-OH were shown as **Scheme. S2**. The mixture of SIS and m-CPBA was dissolved in dichloromethane (controlling the feeding mole ratio of m-CPBA and C=C in 1,4-*Ip* to achieve the designed epoxidation degree). The reaction was conducted at 40 °C for 2 h. The resulting mixture was concentrated under reduced pressure and ESIS was obtained upon purification by using THF/ethanol for several times. The mixture of ESIS, deionized water and ZrCl_4 was dissolved in THF (feeding mole ratio [epoxy: H_2O : ZrCl_4] =1:15:0.5) and the reaction was conducted at 25 °C for 3 h. The resulting mixture was concentrated under reduced pressure and SIS-OH was obtained upon purification by using THF/ethanol for several times and dried in vacuum.



Scheme. S2 The synthetic route of ESIS and SIS-OH.

2.4 Synthesis of SIS-SP₁/SP₂-UPy

Firstly, under an argon atmosphere, $\text{SPM}_1/\text{SPM}_2$, excessive 1,6-diisocyanatohexane and DBTDL (2-3 drops) were added into the flash and the reaction was conducted at 25 °C for 1 h to obtain $\text{SPM}_1/\text{SPM}_2\text{-NCO}$ as the covalent crosslinker. Subsequently, SIS-OH and UPy-NCO dissolved in dry chloroform was added into the above system and the reaction continued for 24 hours at 60 °C. The **SIS-SP₁/SP₂-UPy** was obtained upon purification by using ethanol and dried in vacuum. The dynamic polymer networks with variable content of crosslinkers can be synthesized by regulating the feed ratio of SIS-OH, $\text{SPM}_1/\text{SPM}_2\text{-NCO}$ and UPy-NCO.

3. Results and Discussion

The characteristic peak assignments of the SIS, ESIS and SIS-OH in **Fig. S1** have been summarized in **Tab S1**. The mass fraction of St and Ip, the St block mole fraction and the molar content of 3,4-*Ip* in SIS can be calculated according to the integrated area as summarized in **Tab. S2**.

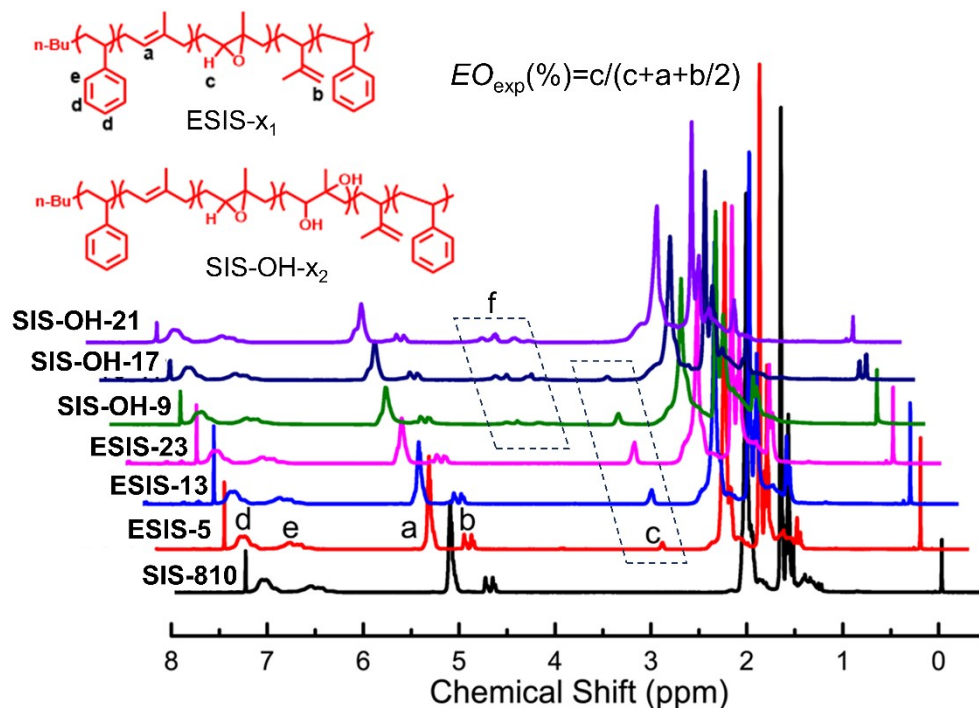


Fig. S1. $^1\text{H-NMR}$ spectrum of SIS, ESIS and SIS-OH

Tab. S1. Assignment of characteristic peaks in $^1\text{H-NMR}$ spectrum of SIS, ESIS and SIS-OH

NO.	δ (ppm)	Spectra attribution
a	5.25-4.85	=CH- of 1,4- <i>Ip</i> ,
b	5.85-4.25	=CH ₂ of 3,4- <i>Ip</i> ,
c	2.80-2.60	-CH- of epoxy group
d	7.25-6.86	H of benzene ring (St. random); para- and meta-H of benzene ring (St. block)
e	6.86-6.20	ortho-H of benzene ring (St. block)
f	4.20-3.30	-CH(OH)-CH(OH) of hydroxylated <i>Ip</i>

Tab. S2. The microstructure analysis of SIS

Sample	M_n^a (kg/mol)	PDI ^b	Microcompositions			
			St (wt.%) ^c	Ip (wt.%) ^d	St _{block} (mol%) ^e	Vinyl (mol%) ^f
SIS	17.8	1.03	18.2	81.8	99.2	9.5

^a number-average molecular weight (M_n , kg/mol); ^b poly-dispersity index ($\text{PDI} = M_w/M_n$), all determined by GPC; ^{c,d} the weight percentage of St and Ip (wt.%) in SIS, calculated by $^1\text{H-NMR}$; ^e the St block mole fraction (mol%) in the total St units, calculated by $^1\text{H-NMR}$; ^f 1,2-vinyl mole fraction (mol %) occupied in the total Ip units, calculated by $^1\text{H-NMR}$.

Tab. S3. The mole ratio of crosslinkers relative to -OH groups the in the synthetic SIS-UPy and DPNs

Samples	UPy-NCO ^{a)}	SPM ₁ -NCO or SPM ₂ -NCO ^{b)}
SIS-UPy-2%	2 mol%	-
SIS-UPy-5%	5 mol%	-
SIS-UPy-10%	10 mol%	-
SIS-UPy-20%	20 mol%	-
SIS-SP ₁ /SP ₂ -UPy-[0,5%]	5 mol%	0
SIS-SP ₁ /SP ₂ -UPy-[0.5%,5%]	5 mol%	0.5 mol%
SIS-SP ₁ /SP ₂ -UPy-[1%,5%]	5 mol%	1 mol%
SIS-SP ₁ /SP ₂ -UPy-[10%,5%]	5 mol%	10 mol%

^{a)} The mole ratio of UPy-NCO relative to -OH groups; ^{b)} the mole ratio of UPy-NCO and SPM₁-NCO (or SPM₂-NCO) relative to -OH groups.

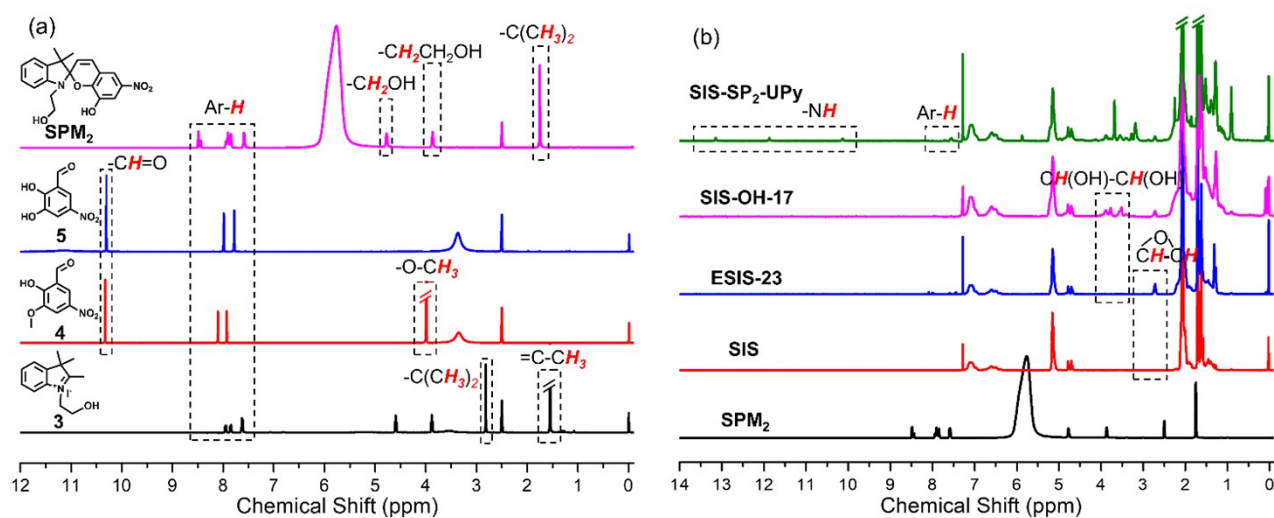


Fig. S2. The synthetic (a) SPM₂ monomer and (b) SIS-SP₂-UPy network tracked by ¹H-NMR.

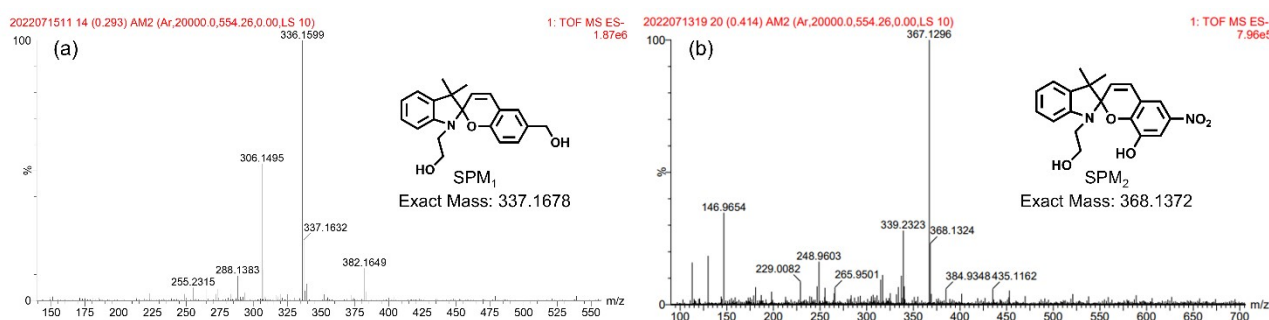


Fig. S3 HDMS spectrum of (a) SPM₁ and (b) SPM₂.

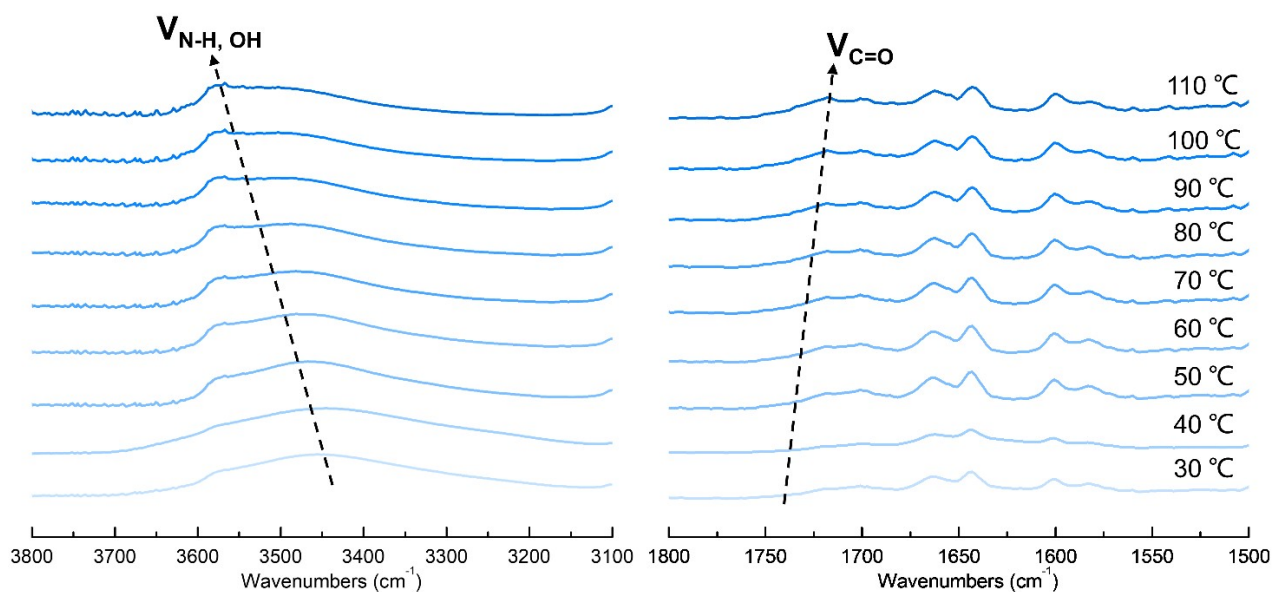


Fig. S4. The temperature-dependent FT-IR spectra of SIS-SP₁-UPy.

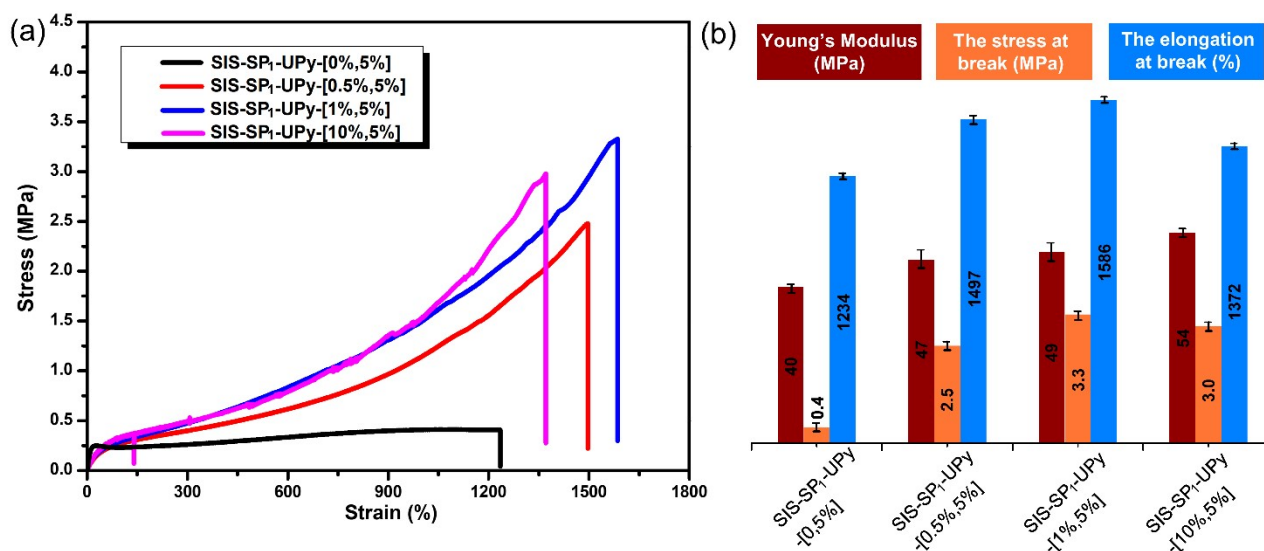


Fig. S5 Stress-strain curves (10 mm/min) and bar graph of Young's modulus, the stress and elongation at break of SIS-SP₁-UPy film.

Tab. S4 Mechanical properties of SIS-SP₁-UPy

Samples	Young's modulus (MPa)	The stress at break (MPa)	The elongation at break (%)	Toughness (MJ·m ⁻³)
SIS-SP ₁ -UPy-[0,5%]	40±2.2	0.4±0.1	1234±14	3.8
SIS-SP ₁ -UPy-[0.5%,5%]	47±1.8	2.5±0.1	1497±25	12.7
SIS-SP ₁ -UPy-[1%,5%]	49±2.0	3.3±0.2	1586±12	18.5
SIS-SP ₁ -UPy-[10%,5%]	54±1.3	3.0±0.1	1372±16	13.7

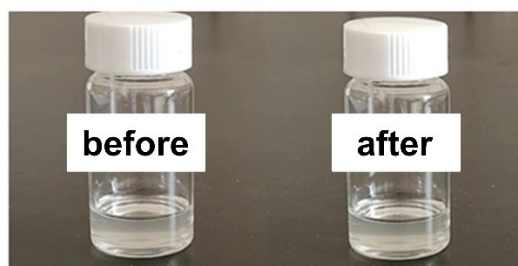


Fig. S6 The images of SIS-SP₁-UPy solution (0.6 mg/ml in DMF) before and after ultrasound treatment

As seen in **Fig. S7**, the tensile test was performed to study the mechanochromic property of the SIS-SP_{1/2}-UPy films through uniformly applied mechanical force. The films were continuously stretched but no significant color change was observed even when stretched to the maximum length, which could be attributed to the restricted molecular mobility in such solid system.



Fig. S7 Stretching changes of (a) SIS-SPM₁-UPy and (b) SIS-SPM₂-UPy

Reference

[1] L. Lan, L. Han, H. Ma, et al. Well-Tailored Dynamic Liquid Crystal Networks with Anionically Polymerized Styrene-Butadiene Rubbers toward Modulating Shape Memory and Self-Healing Capacity. *Macromolecules*, 2021, **54**, 2691-2702.