

Electronic Supplementary Material (ESI) for Polymer Chemistry.
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Supporting Information

Disulfide Bonds-Embedded Polyurethane Solid Polymer Electrolytes with Self-Healing and Shape-Memory Performance

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1. Experimental section

1.1. Materials

Anhydrous tetrahydrofuran (THF) and *N, N*-Dimethylformamide (DMF) were distilled in the presence of calcium hydride (CaH_2 , >98%, Innochem). Poly(ethylene glycol) methyl ether methacrylate (PEGMA, $M_w = 475 \text{ g mol}^{-1}$, Innochem) was purified by neutral alumina (Al_2O_3). Stannous octoate ($\text{Sn}(\text{Oct})_2$, >97%, Innochem), 2,2'-dithiodiethanol (>90%, Aladdin), Poly(ethylene glycol) (PEG, $M_w = 2000 \text{ g mol}^{-1}$, Innochem), isophorone diisocyanate (IPDI, >99%, Innochem), benzophenone (BP, >98.0%, Aladdin), 2-hydroxyethyl methacrylate (HEMA, >98%, Innochem), 2-

isocyanatoethyl methacrylate (>98%, Innochem), cystamine dihydrochloride (>98.0%, Innochem), dibutyltin dilaurate (DBTDL, >95%, Aladdin) and lithium perchlorate (LiClO_4 , >99.9%, Aladdin) were used as received. Other chemicals, containing *N*-methyl-2-pyrrolidone (NMP), potassium hydroxide (KOH), chloroform-*d* (CDCl_3), poly(vinylidene fluoride) (PVDF), acetonitrile (CH_3CN), ether (Et_2O), dichloromethane (CH_2Cl_2), anhydrous magnesium sulfate (MgSO_4), lithium metal, lithium iron phosphate (LiFePO_4 , LFP), and carbon black (CB) were purchased locally. The areal loading of LFP cathode is $1.25 \pm 0.25 \text{ mg cm}^{-2}$. Li metal anode is $\Phi 15 \text{ mm}$ round pieces with 1 mm thick, and the thickness of the prepared polymer electrolyte membrane is around 300 μm .

1.2. Preparation of cystamine

Cystamine dihydrochloride (2 g, 8.85 mmol) was first dissolved in distilled water before using, then KOH (3 g, 53.5 mmol) was added to the mixed solution to neutralize the hydrochloric acid in the reagent, the mixture was finally extracted four times with CH_2Cl_2 and dried with anhydrous MgSO_4 . The pale yellow oily cystamine was obtained after filtration and evaporation. $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 1.40 (2H, s, $-\text{NH}_2$), 2.76 (2H, s, $-\text{SCH}_2\text{CH}_2$), 3.02 (2H, s, $-\text{CH}_2\text{CH}_2\text{NH}_2$).

1.3. Synthesis of disulfide bond-containing cross-linker (SSDMA)

SSDMA was prepared according to the reported method^[1]: Under argon atmosphere, the THF solution (13 mL) mixed with 2-isocyanatoethyl methacrylate (2.5 g, 16.3 mmol) was added dropwise to the THF solution (50 mL) containing cystamine (1 g, 6.5 mmol). After reacting overnight, a large amount of white solid was precipitated

out of the solution and the crude products was successively purified by evaporating, filtrating, washing with CH₃CN and drying under high vacuum. ¹H NMR (400 MHz, CDCl₃, δ): 1.92 (3H, s, -CH₃), 2.77 (2H, m, -SCH₂CH₂), 3.48 (4H, d, -OCH₂CH₂ & -NHCH₂CH₂), 4.21 (2H, m, -OCH₂CH₂), 5.59 & 6.12 (2H, s, -C=CH₂).

1.4. Synthesis of polyurethane cross-linker (PUDMA)

PUDMA was prepared according to the reported method^[2]: PEG₂₀₀₀ (2 g, 1 mmol) was first depressurized at 120 °C for 2 h to remove the trace amount of water, then 10 mL DMF solution mixed with IPDI (0.445 g, 2 mmol) and 50 μL of DBDTL was added dropwise to the flask and reacted at 75 °C for 2 h. After cooling to 70 °C, the mixture continued to react with 10 mL DMF solution containing HEMA (0.261 g, 2 mmol) for 2 h. PUDMA (GPC: *M_n* ≈ 6300) was successively purified by precipitating with Et₂O and drying under high vacuum. ¹H NMR (400 MHz, CDCl₃, δ): 0.88 (3H, d, -CCH₃), 1.06 (3H, s, -C(CH₃)₂), 1.24 (2H, s, -CCH₂CCH₂), 1.63 (2H, s, -CCH₂CHNHCO), 1.95 (3H, s, =CCH₃), 2.92 (2H, m, -CCH₂NHCO), 3.65 (2H, s, -NHCOOCH₂CH₂), 4.10 & 4.32 (2H, m, -CCOOCH₂CH₂ & -NHCOOCH₂CH₂), 5.59 & 6.14 (2H, s, -C=CH₂).

1.5. Synthesis of disulfide bond-containing polyurethane cross-linker (PUSSDMA)

PEG₂₀₀₀ (2 g, 1 mmol) was first depressurized at 120 °C for 2 h to remove the trace amount of water, then 10 mL DMF solution mixed with IPDI (0.667 g, 3 mmol) and 50 μL of DBDTL was added dropwise to the flask and reacted at 75 °C for 2 h. After cooling to 40 °C, the mixture continued to react with 2,2'-dithiodiethanol (0.154 g, 1 mmol) for 1.5 h to obtain polyurethane prepolymer containing disulfide bonds. DMF solution (10 mL) containing HEMA (0.261 g, 2 mmol) was finally added dropwise to

the mixture and terminated isocyanate group at 70 °C for 2 h. PUSDDMA (GPC: $M_n \approx 12000$) was successively purified by precipitating with Et₂O and drying under high vacuum. ¹H NMR (400 MHz, CDCl₃, δ): 0.90 (3H, d, -CCH₃), 1.06 (3H, s, -C(CH₃)₂), 1.26 (2H, s, -CCH₂CCH₂), 1.60 (2H, s, -CCH₂CHNHCO), 1.98 (3H, s, =CCH₃), 2.91 (2H, m, -CCH₂NHCO & -SCH₂CH₂), 3.65 (2H, s, -NHCOOCH₂CH₂S & -NHCOOCH₂CH₂O), 4.20 (2H, m, -CCOOCH₂CH₂ & -NHCOOCH₂CH₂), 5.60 & 6.14 (2H, s, -C=CH₂).

1.6. Preparation of SSSPEs

(1) Preparation of PU_xSS_yPEG_z

PU_xSS_yPEG_z was obtained by the ultraviolet (UV)-light initiated polymerization of PUDMA, SSDMA, PEGMA₄₇₅ and LiClO₄. Taking PU_{0.5}SS_{0.5}PEG₃ as typical instance, PEGMA (0.143 g, 0.3 mmol), PUDMA (0.315 g, 0.05 mmol), SSDMA (0.232 g, 0.05 mmol), LiClO₄ (0.063 g, 0.590 mmol) and BP (0.022 g) were first dissolved in anhydrous THF (5 mL) (The doping amount of LiClO₄ is calculated according to the content of ethoxy (EO) units in PUDMA and PEGMA₄₇₅, and the formula is EO/Li⁺ = 16:1. The doping amount of BP accounts for 3 wt% of the total monomers. All SSSPEs are implement according to this rule). After stirring 30 min, the mixture was cast into PTFE mold and then irradiated with 12 mW cm⁻² UV-light for 30 min. The membrane prepared was finally dried at 60 °C for 12 h.

(2) Preparation of PUSS_xPEG_y

PUSS_xPEG_y was obtained by the ultraviolet (UV)-light initiated polymerization of PUSDDMA, PEGMA₄₇₅ and LiClO₄. Taking PUSS₁PEG₃ as typical instance, PEGMA

(0.143 g, 0.3 mmol), PUSDDMA (1.2 g, 0.1 mmol), LiClO₄ (0.168 g, 1.575 mmol) and BP (0.041 g) were first dissolved in anhydrous THF (5 mL). After stirring 30 min, the mixture was cast into PTFE mold and then irradiated with 12 mW cm⁻² UV-light for 30 min. The membrane prepared was finally dried at 60 °C for 12 h.

1.7. Characterization of SSSPEs

Nuclear magnetic resonance (NMR) spectra were carried out to evaluate the material's chemical structure on Bruker AV400 NMR spectrometer with CDCl₃ as solvent. The fourier transform infrared (FT-IR) spectroscopy of SSSPEs was measured by EQUINOX 55 spectrometer (Bruker) over the frequency range from 4000-500 cm⁻¹. Mechanical properties were tested by electronic universal testing apparatus with the speed of 10 mm min⁻¹. The thermo-stability of SSSPEs were measured via Thermogravimetric analysis (TGA, 4000 PerkinElmer), which was programmed to heat from 30 to 800 °C at a rate of 10 °C min⁻¹ under N₂. The *T_g* of SSSPEs is characterized by differential scanning calorimetry (DSC, Q2000), which was programmed to heat from -80 to 180 °C at a rate of 10 °C min⁻¹ under N₂.

Cut the electrolyte membrane in half with a knife in order to study the self-healing process of SSSPEs, and the self-healing efficiency of SSSPEs was estimated through electronic universal testing apparatus and obtained by eq 1

$$\text{SH efficiency} = \frac{\text{self - healing}}{\text{original}} \times 100\% \quad (1)$$

According to the *T_{g,1}* obtained from the above DSC test, shape-memory test is performed by the following steps: Under the condition of *T_{g,1}* + 40 °C, a certain external force was applied to the cut SSSPEs to deform them, and then they were rapidly cooled

to $T_{g,1} - 50$ °C to fix the temporary shape. Subsequently, the temperature was raised again to $T_{g,1} + 40$ °C to restore it to its original shape and the recovery time was recorded.

The ionic conductivities of SSSPEs were examined via Autolab PGSTAR302N and performed by a program with temperatures ranging from 30 to 80 °C at 10 °C interval, the ionic conductivities of SSSPEs were calculated according to equation $\sigma = L/(SR_b)$, where L , S , R_b refer to the SSSPEs thickness, contact area between SSSPEs film and stainless-steel electrodes, bulk SSSPEs film resistance, respectively. Linear sweep voltammetry (LSV) test is carried out to detect the electrochemical stability of Li|SSSPEs|SS cell with a program of 0 to 7 V with a scan rate of 1 mV s⁻¹. Li||Li symmetrical cells were assembled to estimate lithium-ion transference number (t_{Li^+}) of SSSPEs according to the equation $t_{Li^+} = I_s (\Delta V - I_0 R_0) / I_0 (\Delta V - I_s R_s)$, where the value of ΔV is 10 mV and I_s , I_0 , R_0 and R_s respectively represent the initial current, the steady-state current, resistance before and after polarization.

Stability of the interface between electrolyte and Lithium electrodes and battery performance were detected by LANHE CT2001A cell test systems. Li||Li symmetric cells were assembled and the interfacial stability was evaluated at current densities ranging from 0.0125 to 0.1 mA cm⁻² at 60 °C, and the cells were alternately charged and discharged every 1 h. Scanning electron microscope (Nova Nano SEM 450) and X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA DLD-600 W) were carried out to further analyze the morphology and chemical composition of SEI layer on Li metal anode after battery cycling.

70% LiFePO₄ (1.12 g), 10% CB (0.16 g), 20% PVDF (0.32 g) were dissolved in NMP to make a LiFePO₄ electrode slurry (LFP), then it was coated on the aluminum sheet and dried at 80 °C for 24 h to obtain LFP positive electrode sheet, the charge-discharge cycling performance was examined via Li|SSSPEs|LiFeO₄ coin cell, and the potential of the charge and discharge test is from 2.5 to 4.2 V at 60 °C.

Table S1. Composition of SSSPEs.

Entry	SSSPEs	PUDMA (mmol)	SSDMA (mmol)	PUSSDMA (mmol)	PEGMA (mmol)	LiClO ₄ (mmol)	BP (wt %)
1	PU _{0.8} SS _{0.2} PEG ₃	0.16	0.04	0	0.60	1.686	3 %
2	PU _{0.5} SS _{0.5} PEG ₃	0.10	0.10	0	0.60	1.181	3 %
3	PU _{0.2} SS _{0.8} PEG ₃	0.04	0.16	0	0.60	0.675	3 %
4	PU ₁ PEG ₃	0.2	0	0	0.60	1.744	3 %
5	SS ₁ PEG ₃	0	0.20	0	0.60	0.388	3 %
6	PUSS ₁ PEG ₃	0	0	0.20	0.60	2.137	3 %

Conditions: n_(EO:Li⁺)=16:1; UV intensity: 12 mW cm⁻²; UV time: 30 min

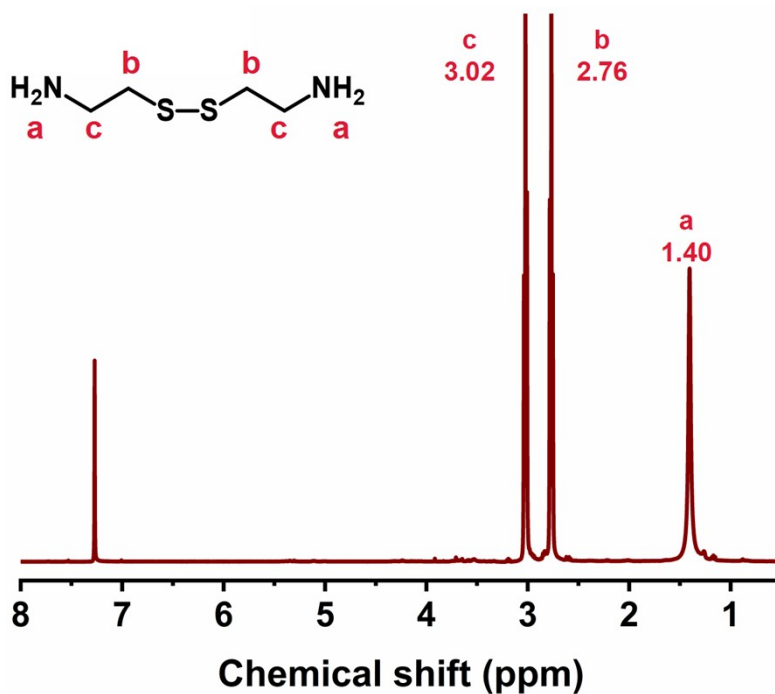
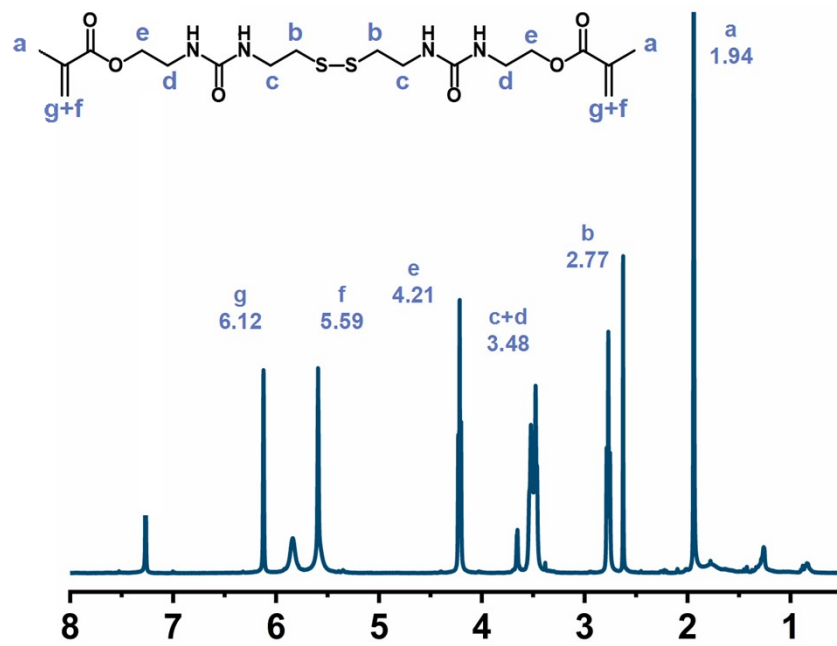
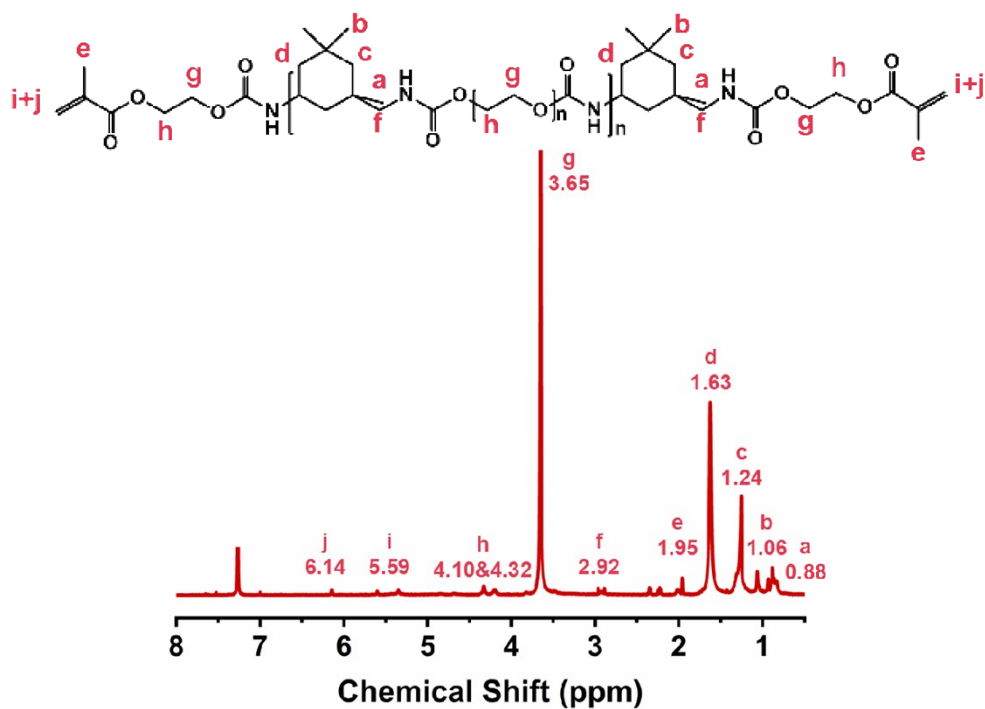


Figure S1. ¹H NMR spectrum of cystamine.



Chemical shift (ppm)
Figure S2. ¹H NMR spectrum of SSDMA.



Chemical Shift (ppm)
Figure S3. ¹H NMR spectrum of PUDMA.

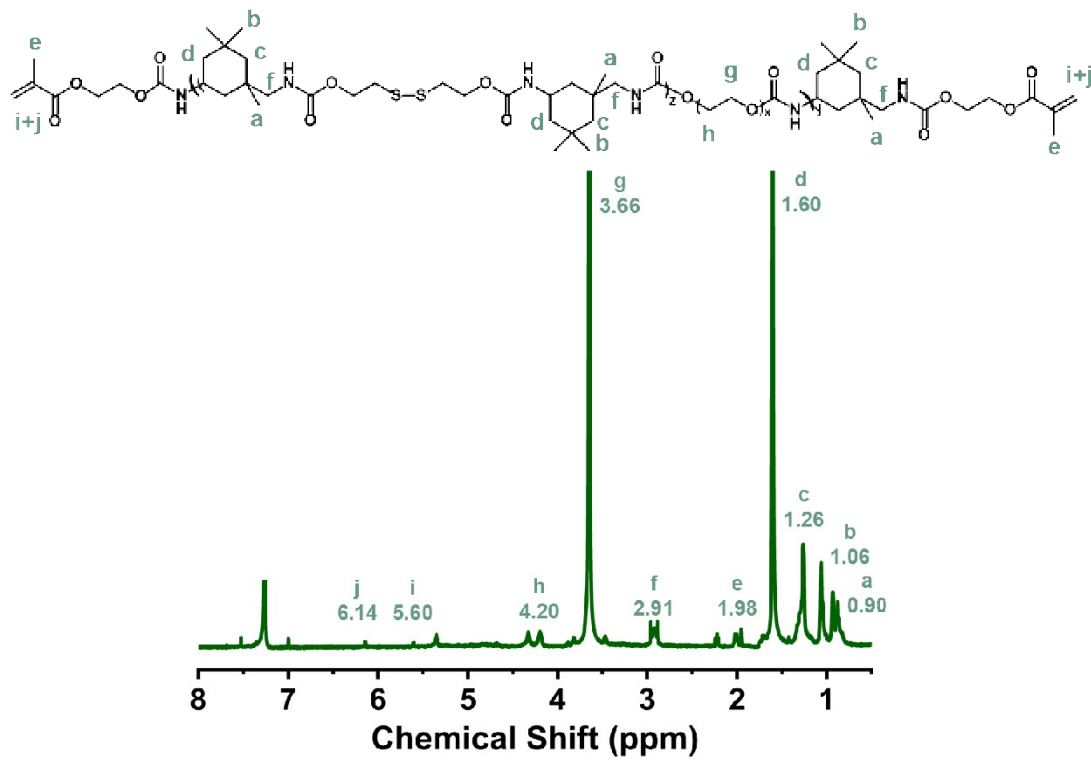


Figure S4. ¹H NMR spectrum of PUSSDMA.

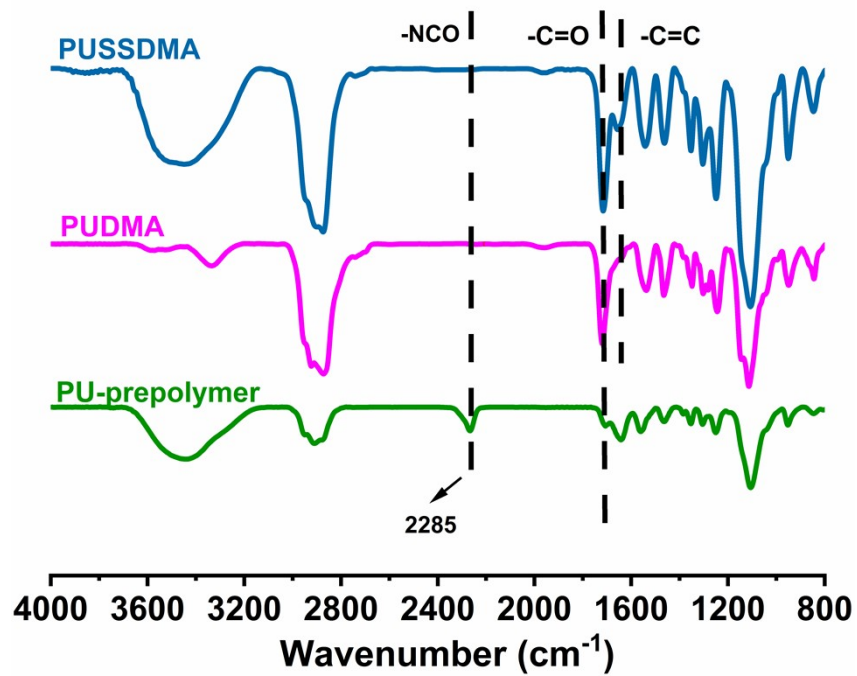


Figure S5. FT-IR spectra of PU-prepolymer, PUDMA and PUSSDMA.

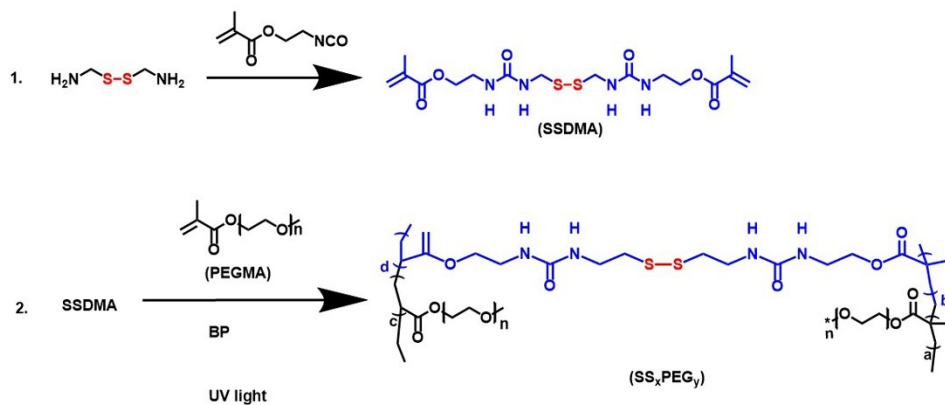


Figure S6. Synthetic routes of SS_xPEG_y.

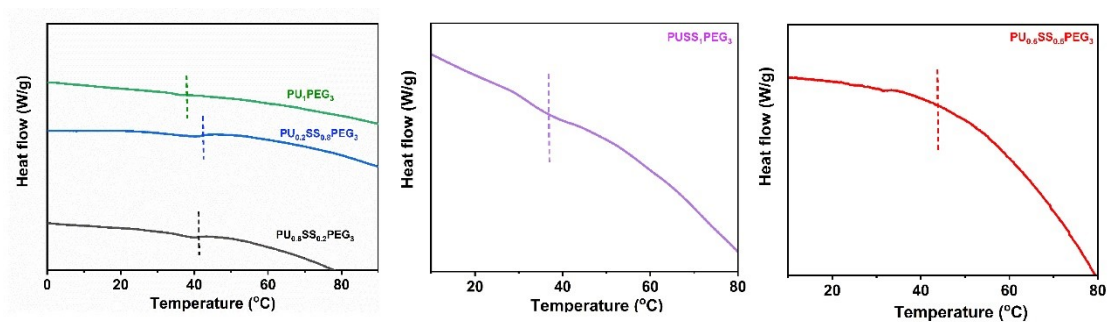


Figure S7. Enlarged DSC curves of SSSPEs ($T_{g,1}$).

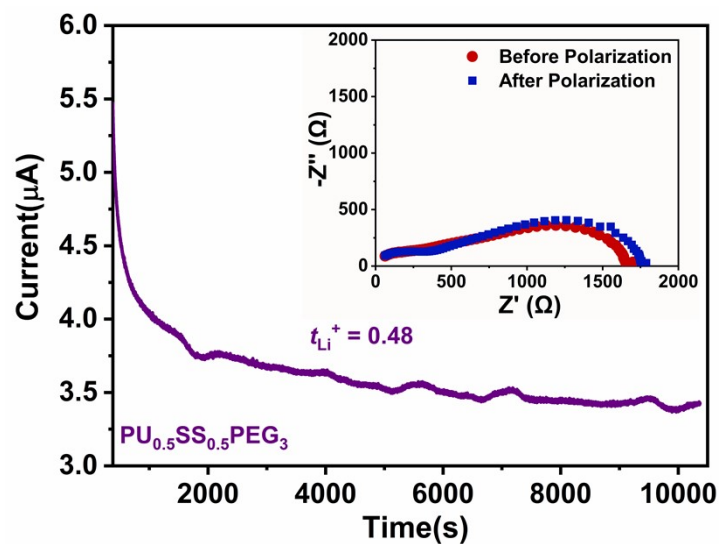


Figure S8. Chronoamperometry of the Li|PU_{0.5}SS_{0.5}PEG₃|Li cell and the inset shows the AC impedance before and after polarization at 60 °C.

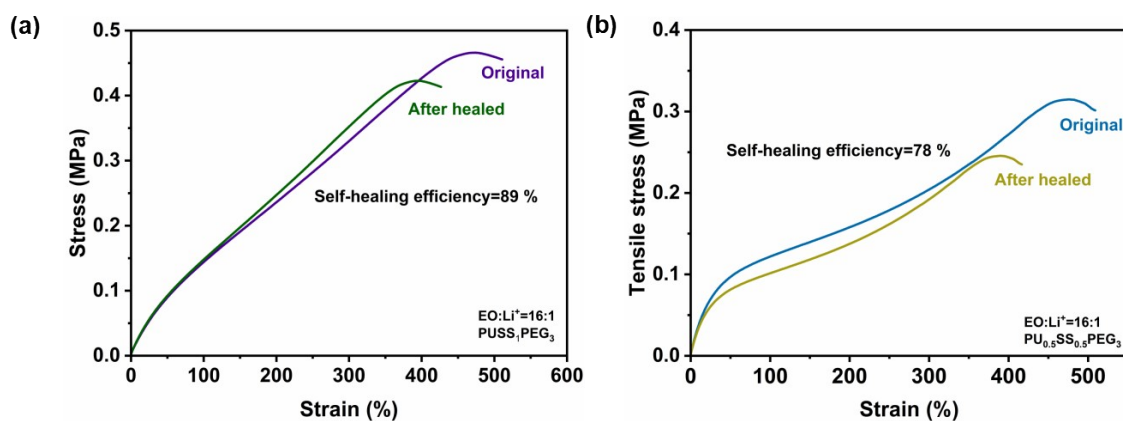


Figure S9. Stress-strain curves of original and healed (a) $\text{PUSS}_1\text{PEG}_3$. (b) $\text{PU}_{0.5}\text{SS}_{0.5}\text{PEG}_3$ films.

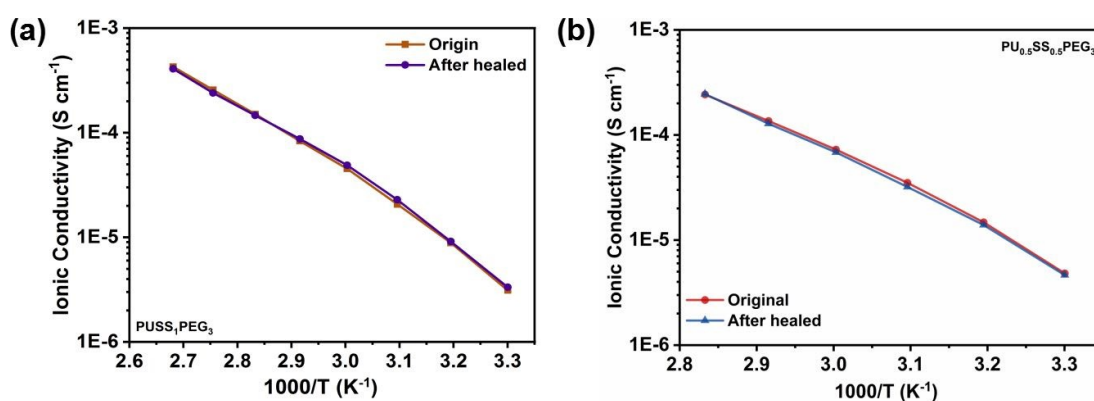


Figure S10. Temperature dependence of ionic conductivities for original and healed (a) $\text{PUSS}_1\text{PEG}_3$. (b) $\text{PU}_{0.5}\text{SS}_{0.5}\text{PEG}_3$ films.

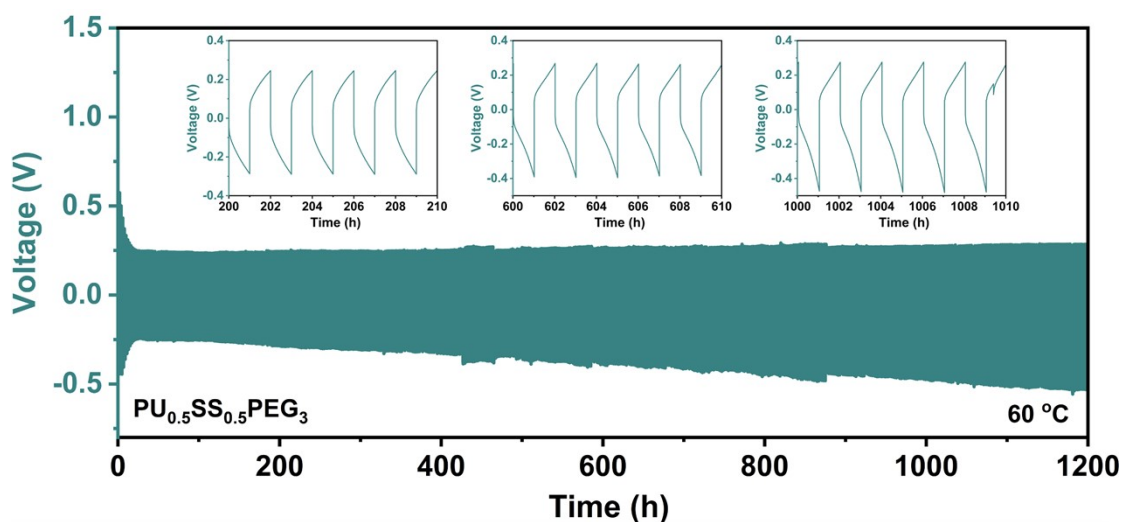


Figure S11. Galvanostatic cycling profile of $\text{Li}|\text{PU}_{0.5}\text{SS}_{0.5}\text{PEG}_3|\text{Li}$ cell at 0.05 mA cm^{-2} at 60°C .

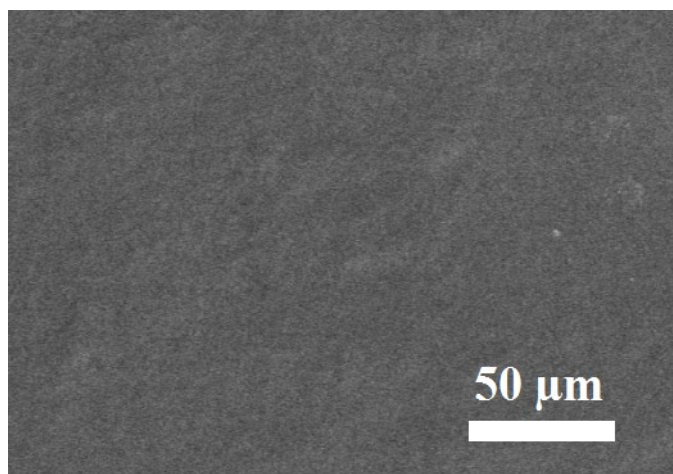


Figure S12. SEM image of cycled Li anode in Li|PUSS₁PEG₃|Li cell.

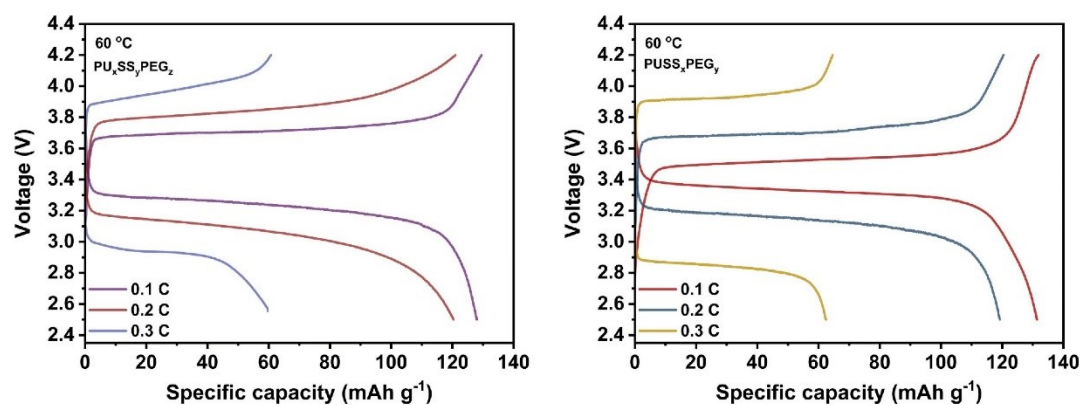


Figure S13. Charge-discharge curves of Li|PU_{0.5}SS_{0.5}PEG₃|LFP (left) and Li|PUSS₁PEG₃|LFP (right) cells at different rates.



Figure S14. Photographs of the lamps lightened by the flat, folded and cut Li|PUSS₁PEG₃|LFP pouch cell.

[1] Y. H. Jo, S. Li, C. Zuo, Y. Zhang, H. Gan, S. Li, L. Yu, D. He, X. Xie, Z. Xue, *Macromolecules* **2020**, *53*, 1024-1032.

[2] Y. Lin, G. Li, *J Mater. Chem. B* **2014**, *2*, 6878-6885.