

Supporting Information

Achieving Fast Self-Healing and Reprocessing of Supertough Water-Dispersed “Living” Supramolecular Polymers Containing Dynamic Ditelluride Bonds under Visible Light

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Materials. 2-Bromoethanol, tellurium powder (average particle size of 149 μm), 2-acetylbutyrolactone, and guanidine carbonate were purchased from Shanghai Aladdin chemical reagent Co., Ltd. Hydrazine hydrate (85%), potassium hydroxide (KOH), anhydrous MgSO_4 , sodium borohydride, ethanol, ethyl acetate, and dichloromethane were purchased from Chengdu Kelong chemical reagent Co., Ltd. Methyl methacrylate (MMA) was purchased from Shanghai Aladdin chemical reagent Co., Ltd. Polytetrahydrofuran diol (PTMG-3000, $M_n = 3\,000\text{ g/mol}$) was products of Korea PTG Co., Ltd. Isophorone diisocyanate (IPDI) was purchased from Evonik Industries AG. Dimethylolpropionic acid (DMPA) was purchased from Chengdu Huaxia chemical reagent Co., Ltd. Acetone (Ac), 1,4-butanediol (BDO), triethylamine (TEA), dibutyltin dilaurate (DBTDL), and N,N-dimethylformamide (DMF) were purchased from Chengdu Kelong chemical reagent Co., Ltd. PTMG was dried in a vacuum at 120°C and 0.090 MPa for 2 h before use and directly used after drying. DMPA was dried at 120°C for 2 h before use and directly used after drying. TEA, BDO, Ac and DMF were dehydrated with 4A molecular sieves over one week. MMA was washed with 10 wt% NaOH aqueous solution to remove the polymerization inhibitor, and distilled before use. Deionized water was produced in our lab and used directly. All of the reagents above except PTMG and IPDI were analytical grade.

Synthesis of di-(1-hydroxyethyl) ditelluride (DiTe-DiOH). DiTe-DiOH was synthesized according to the previous references with some modification.¹ First, sodium borohydride (1.68g, 44.4 mmol) was dissolved in 50 mL of distilled water at 30°C with nitrogen protection. Then, tellurium powder (5.08 g, 40 mmol) was added in twice to the reactor and reacted at 90°C for 1 h. Subsequently, 1.61 mL hydrazine hydrate (85%) and potassium hydroxide (2.24 g, 40 mmol) dissolved in 10 mL water were added dropwise and reacted for another 3 h to complete the dissolution of the tellurium. After cooling down to ambient temperature, 2-bromoethanol (5.00 g, 40 mmol) was added dropwise and stirred at 50°C for 20 h. After cooled to room temperature, a purplish red solution was obtained after filtered through a layer of diatomite to remove any traces of unreacted tellurium powder. The mixture solution was extracted with ethyl acetate and dried over anhydrous MgSO_4 . The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (dichloromethane: ethyl acetate = 4:1 v/v). The purplish red liquid of DiTe-DiOH was obtained with a yield of 44.5%. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ (ppm): 3.87 (4H, HOCH_2), 3.34 (4H, TeTeCH_2) and 1.25 ppm (2H, HOCH_2) (Figure S1a). ^{125}Te NMR (600 MHz, CDCl_3) δ (ppm): 284.3 ppm (Figure S1b). FTIR (KBr, cm^{-1}): 3321.4 (ν [-OH]), 2924.1 and 2862.4 (ν [CH_2]), 1400.3 (δ [CH_2]), 1033.8 (δ [C-O]), 796.6 (ν [Te-C]), 709.8 (δ [Te-C]) and 615.3 (ν [Te-Te]) (Figure S2).

Synthesis of 5-(2-hydroxyethyl)-6-methyl-2-aminouracil (UPy-OH). A mixture of 2-acetylbutyrolactone (77 mL, 0.51 mol) and guanidine carbonate (52.5 g, 0.58 mol) was refluxed with absolute ethanol (500 mL) in the presence of triethylamine (150 mL, 1.08 mol) for 1 h; the mixture became clear, then a pale yellow solid was precipitated. The reaction was continued for 12 h. The precipitate was filtered, washed with ethanol and dried under vacuum to afford white solid of 5-(2-hydroxyethyl)-6-methyl-2-aminouracil with a yield of 67.0%. ¹H-NMR (300 MHz, *d*₆-DMSO) δ (ppm): 7.42 (H, -NH-(C=O)-NH₂), 6.78 (2H, -NH-(C=O)-NH₂), 4.52 (H, -CH₂CH₂OH), 3.35 (2H, -CH₂CH₂OH), 2.46 (2H, -CH₂CH₂OH), 2.03 (3H, -C=O-C(CH₂-CH₂-OH)=C(CH₃)) (Figure S3). FTIR (KBr, cm⁻¹): 3379.3 (ν [O-H]), 3120.8 (ν [N-H]), 2933.7 (ν [CH₃]), 2945.9 (ν [CH₃]), 1662.6 (ν_{as} [C=O] of UPy), 1600.9 (ν [C=C]), 1556.5 (ν [N-H]), 1236.7 (ν [C-N]), 1047.3 (ν [C-O]) (Figure S4).

Characterization. The ¹H-NMR spectra was determined on a JNM-ECA 300 Spectrometer (JEOL, Japan) with CDCl₃ or *d*₆-DMSO as a solvent at 300 MHz. The ¹²⁵Te-NMR spectra was determined on an Avance AV II-600 NMR spectrometer (Bruker, Switzerland) with CDCl₃ as a solvent at 600 MHz. X-ray photoelectron spectroscopy (XPS) was performed using an Escalab 220i spectrometer (Kratos, Japan) with monochromatic Al K α ($h\nu$ = 1100 eV) at 15 kV. The Fourier transform infrared (FTIR) spectra were recorded using an IRAffinity-1 FTIR spectrometer (Shimadzu, Japan) with a resolution of 4 cm⁻¹ over a spectral range of 400 to 4000 cm⁻¹ at 25°C. Gel permeation chromatography (GPC) measurement was conducted on a Breeze2 (Waters, USA) using polystyrene as a standard and tetrahydrofuran as an eluent (flow rate: 1.0 mL/min, at 40 °C). Morphology of emulsion particles was observed using a H7650 transmission electron microscopy (TEM) (Hitachi, Japan) with an accelerating voltage of 75 kV and the sample was stained by 0.2 wt % phosphotungstic acid hydrate before observation. Particle size of emulsion particles was determined using a Nano S90 Dynamic Light Scattering (DLS) analyzer (Malvern, UK) at 25°C, and the results were the mean value of three measurements. Transmittance of film samples with a thickness of \sim 100 μ m was determined by a SP-756P UV/Vis spectrometer (Spectrum, China) in the wavelength range of 380 to 780 nm at 25°C. Dynamic mechanical analysis (DMA) curves were obtained on a DMA 242C (Netzsch, Germany) in the tensile resonant mode, at a heating rate of 5 K/min from -80 °C to 80 °C, and loss factor ($\tan \delta$) was obtained at a frequency of 1 Hz. The strain-stress tests were conducted by a UTM 6203 electronic universal tester (SUNS, China) with a 2 KN load cell at a cross-head speed of 50 mm min⁻¹ at ambient temperature. The tested samples were tailored into an oblong shape with a length of 30 mm, a width of 5 mm and a thickness of \sim 1.5 mm. Mechanical properties including tensile stress and elongation at break were obtained, and the results were

the mean values of five measurements. Toughness, which is defined as the area surrounded by the stress-strain curve, was also calculated by using the software of Origin Pro 9.0 and its values were the mean values of five times. For the loading-unloading tests, the oblong shape samples were tested with 10 mm initial distance between two clamps and the strain speed was constant at 50 mm/min. The samples were initially stretched to a predetermined strain (400%) and then unloaded at the same velocity (50 mm/min). Morphology of the film samples was observed on a VEGA3 scanning electron microscope (SEM) (TESCAN, Czech) with an accelerating voltage of 2 KV, and the samples were sprayed with gold before observation.

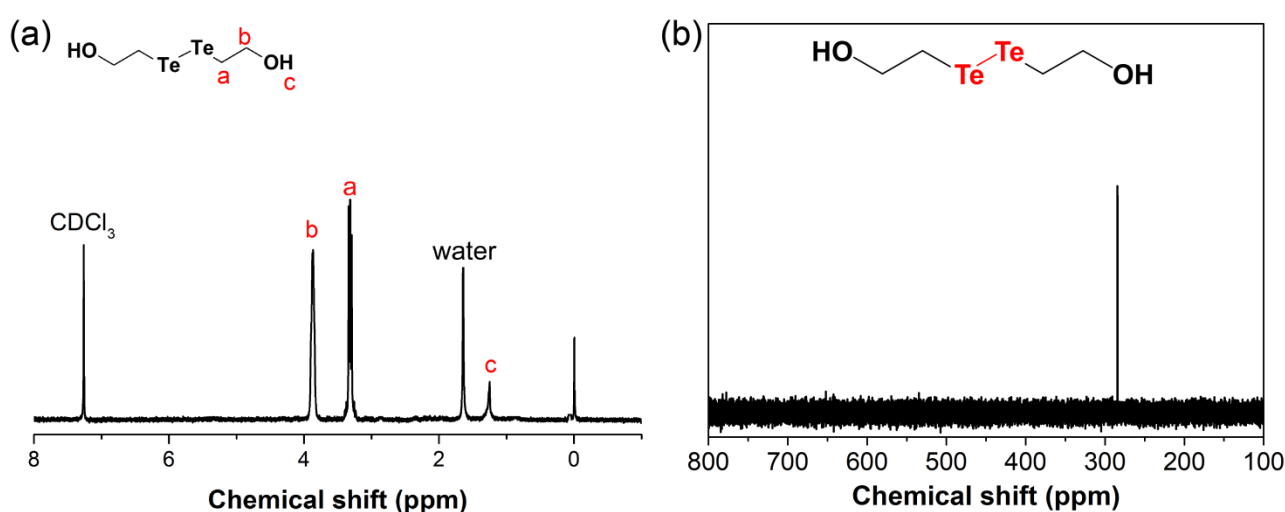


Figure S1. ^1H -NMR (a) and ^{125}Te -NMR (b) spectra of DiTe-DiOH in CDCl_3 .

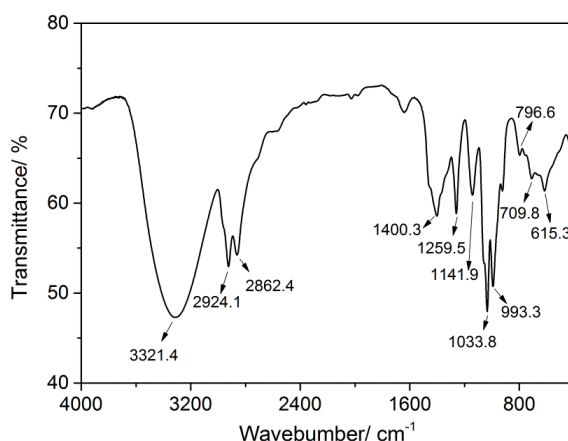


Figure S2. FTIR spectra of DiTe-DiOH.

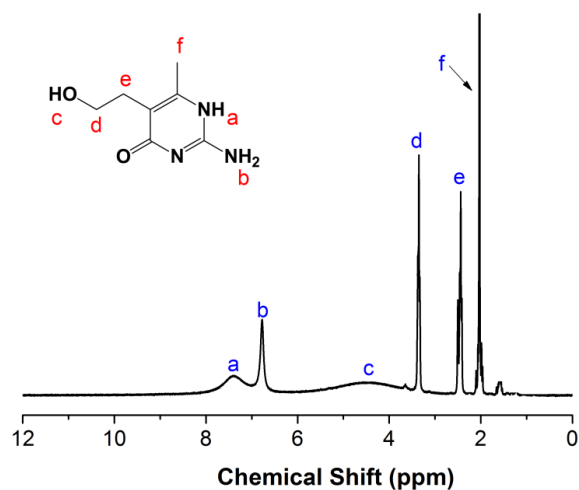


Figure S3. ^1H -NMR spectra of UPy-OH.

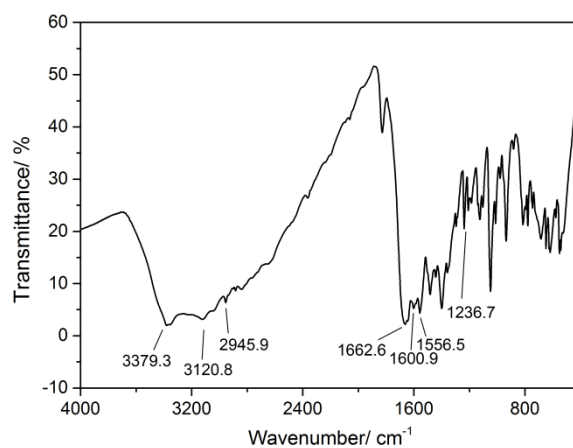


Figure S4. FTIR spectra of UPy-OH.

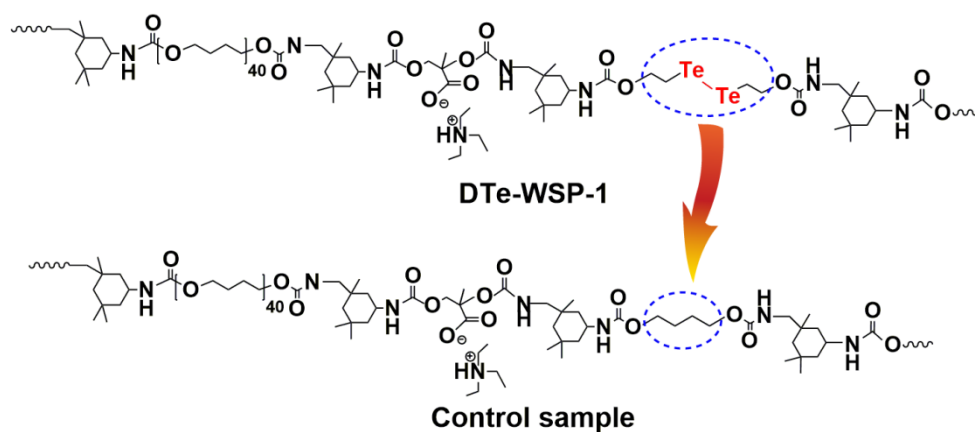


Figure S5. Chemical structure of the control sample.

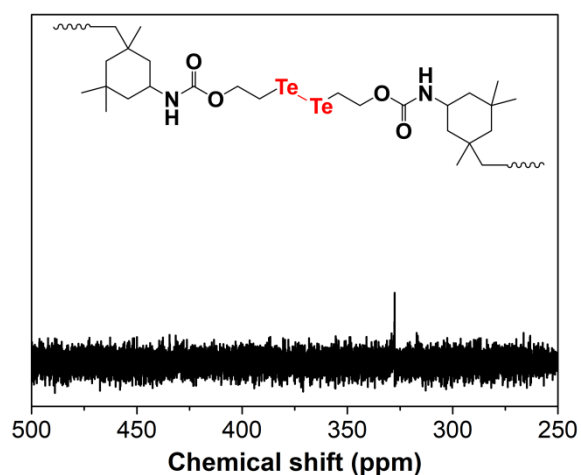


Figure S6. ^{125}Te -NMR spectra of DTe-WSP-3 in CDCl_3 .

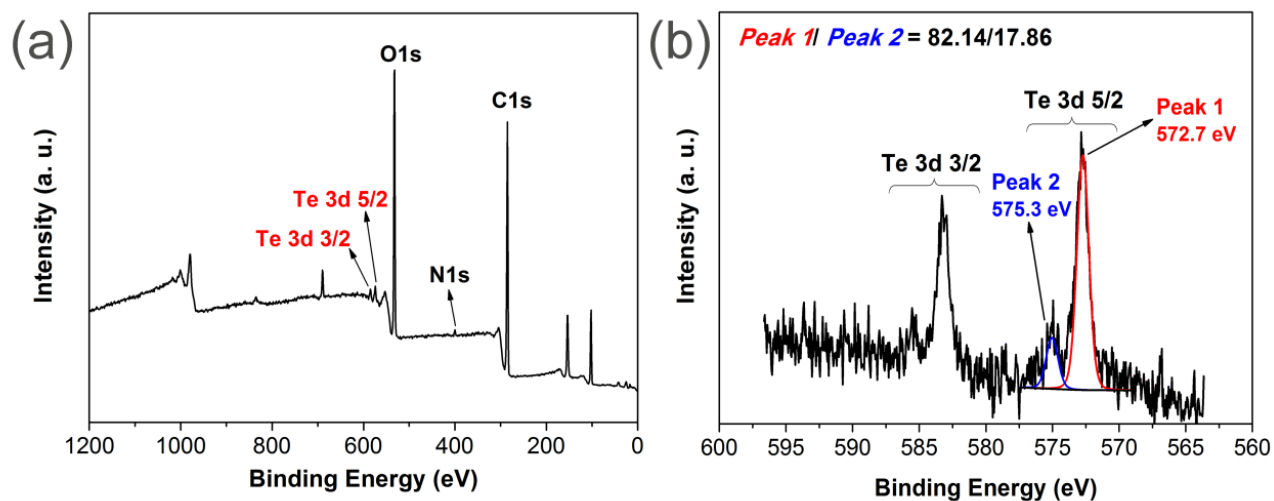


Figure S7. XPS curve of DTe-WSP-3 (a) and Core level XPS spectra of Te 3d (b).

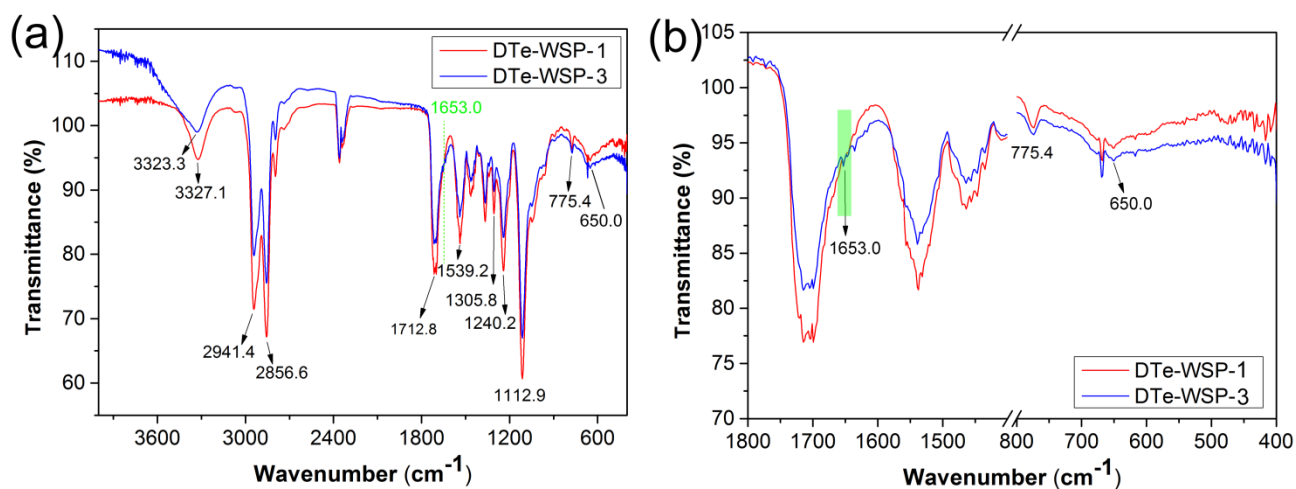


Figure S8. FTIR spectra of DTe-WSP-1 and DTe-WSP-3 with the following characteristic peaks demonstrating its chemical structure in the wavenumber ranges from 400 to 4 000 cm^{-1} (a) and 400 to 1 800 cm^{-1} (b): 3327.1 cm^{-1} ($\nu(\text{-NH-})$), 2941.4, and 2856.6 cm^{-1} ($\nu(\text{CH}_3, \text{CH}_2)$), 1712.8 cm^{-1} ($\nu_{\text{as}}(\text{C=O})$), 1653.0 ($\nu_{\text{as}}[\text{C=O}]$ of UPy), 1539.2 cm^{-1}

($\delta(\text{C-N-H})$), 1305.8 cm^{-1} ($\delta(\text{C}(\text{C=O})\text{-N-H})$), 1240.2 and 1112.9 cm^{-1} ($\nu(\text{C-O-C})$), 775.4 ($\nu[\text{Te-C}]$) and 650.0 ($\nu[\text{Te-Te}]$).

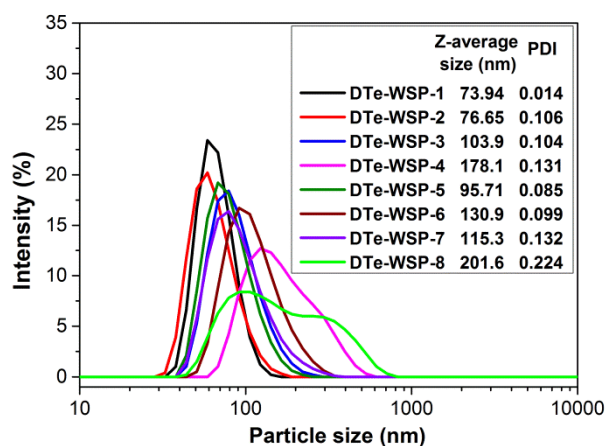


Figure S9. Intensity and particle size of DTe-WSPs emulsion particles.

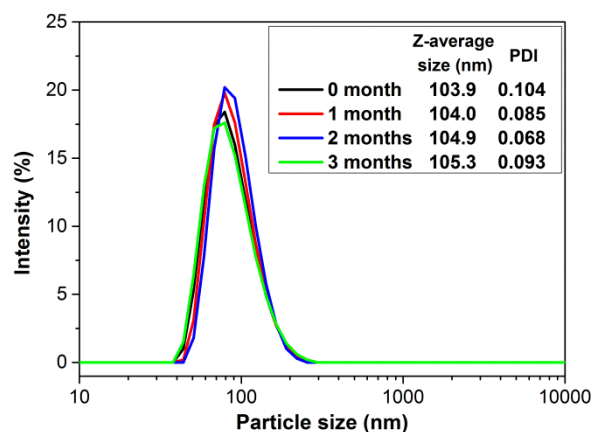


Figure S10. Particle size of DTe-WSP-3 emulsion particles with different storage time.

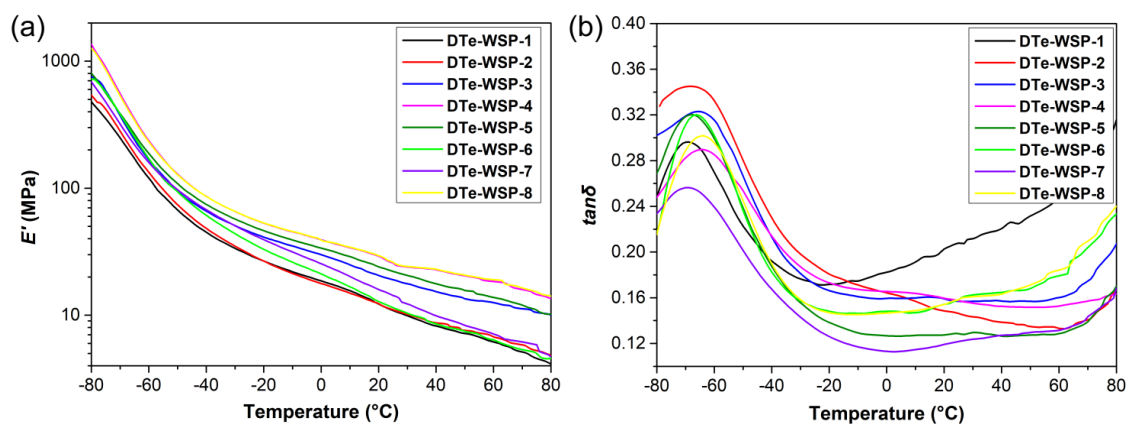


Figure S11. The storage modulus (E') (a) and loss factor ($\tan\delta$) (b) curves of DTe-WSPs recorded from DMA tests.

Table S1. Thermal Characteristics of DTe-WSPs Recorded from DMA Tests

sample	E'_{-80} ^a (MPa)	E'_{25} ^a (MPa)	E'_{80} ^a (MPa)	T_g (°C)
DTe-WSP-1	478.4	10.9	4.1	-69.2
DTe-WSP-2	540.3	11.0	4.8	-68.2
DTe-WSP-3	756.5	19.0	10.0	-65.3
DTe-WSP-4	1361.1	25.8	13.5	-64.3
DTe-WSP-5	802.5	22.1	10.4	-67.9
DTe-WSP-6	722.0	11.5	4.6	-64.6
DTe-WSP-7	690.1	14.3	4.7	-65.7
DTe-WSP-8	1261.8	24.2	14.1	-64.0

^a E'_{-80} , E'_{25} , and E'_{80} are the storage modulus of DTe-WSPs at temperature of -80°C, 25°C and 80°C, respectively.

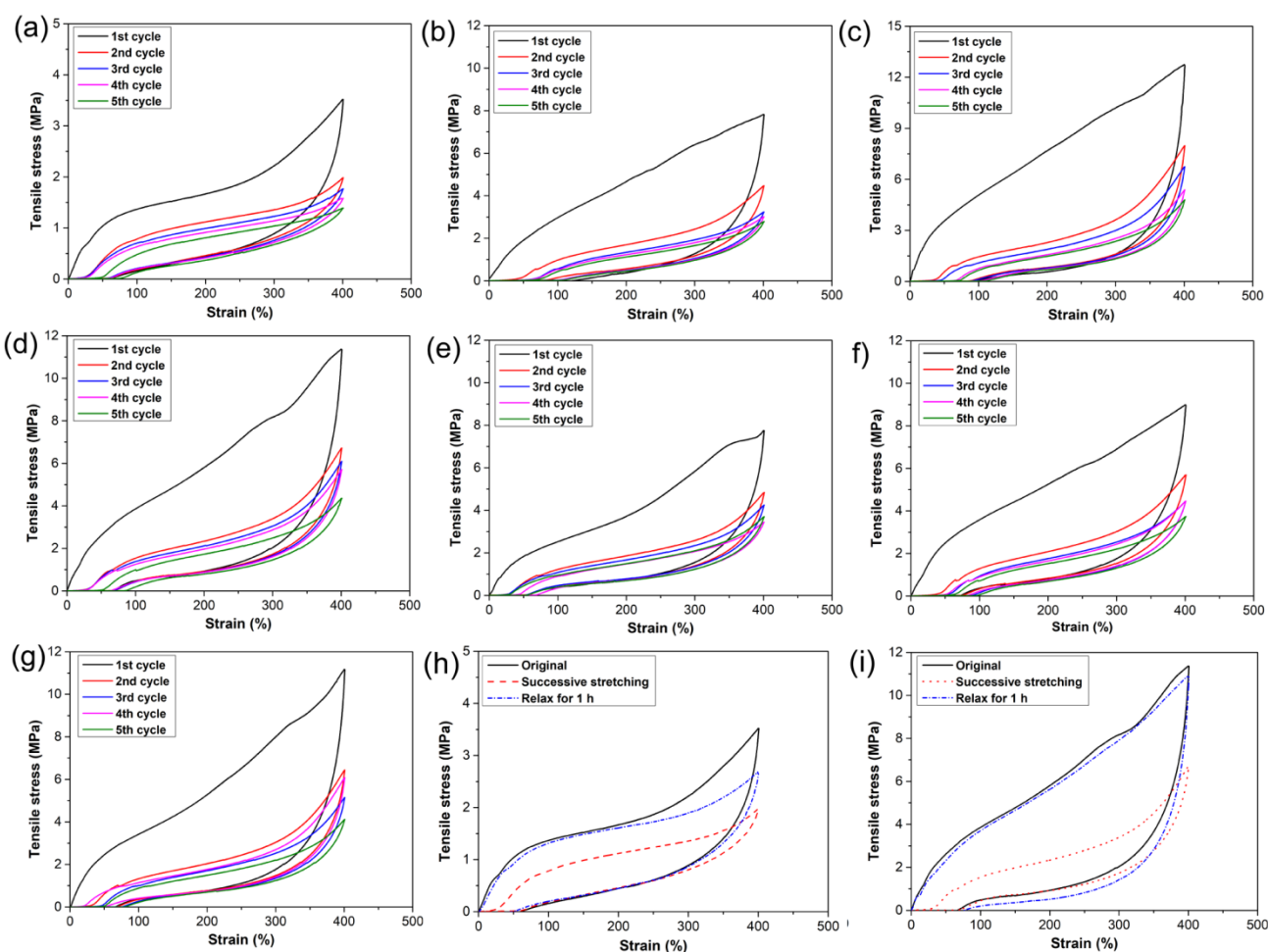


Figure S12. Cyclic stress-strain curves (up to 400% strain with five cycles) of DTe-WSP-1 (a), DTe-WSP-2 (b), DTe-WSP-4 (c), DTe-WSP-5 (d), DTe-WSP-6 (e), DTe-WSP-7 (f) and DTe-WSP-8 (g); (h) Cyclic stress-strain curves of DTe-WSP-7 (up to 400% strain) at first loading (black), second loading (red) successively and third loading (blue) after 1 h rest, respectively; (i) Cyclic stress-strain curves of DTe-WSP-5 (up to 400% strain) at first

loading (black), second loading (red) successively and third loading (blue) after 1 h rest, respectively.

Table S2. Hysteresis of DTe-WSPs with Different Loading-Unloading Cycles at a Strain of 400%

sample	hysteresis (MJ m ⁻³)				
	1 st cycle	2 nd cycle	3 th cycle	4 th cycle	5 th cycle
DTe-WSP-7	4.64	1.98	1.67	1.47	1.18
DTe-WSP-5	17.41	4.96	4.22	3.75	2.89
DTe-WSP-3	15.72	3.70	2.77	2.60	2.11

Table S3. Hysteresis of DTe-WSPs at the First Loading-Unloading Cycle at a Strain of 400%

sample	hysteresis of the first cycle (MJ m ⁻³)
DTe-WSP-1	4.64
DTe-WSP-2	14.47
DTe-WSP-3	15.72
DTe-WSP-4	24.73
DTe-WSP-5	17.41
DTe-WSP-6	11.56
DTe-WSP-7	12.23
DTe-WSP-8	18.69

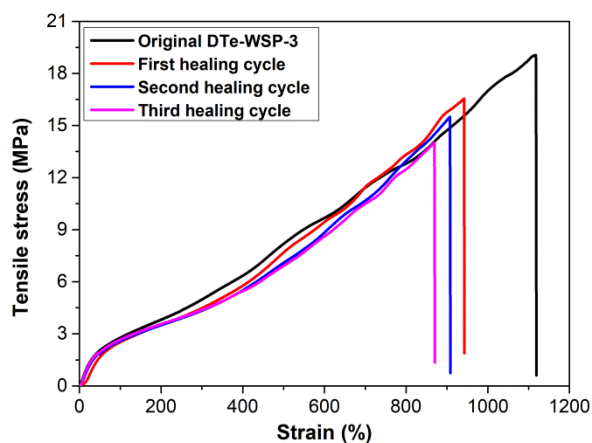


Figure S13. Stress-strain curves of the fractured DTe-WSP-3 sample with different healing cycles.

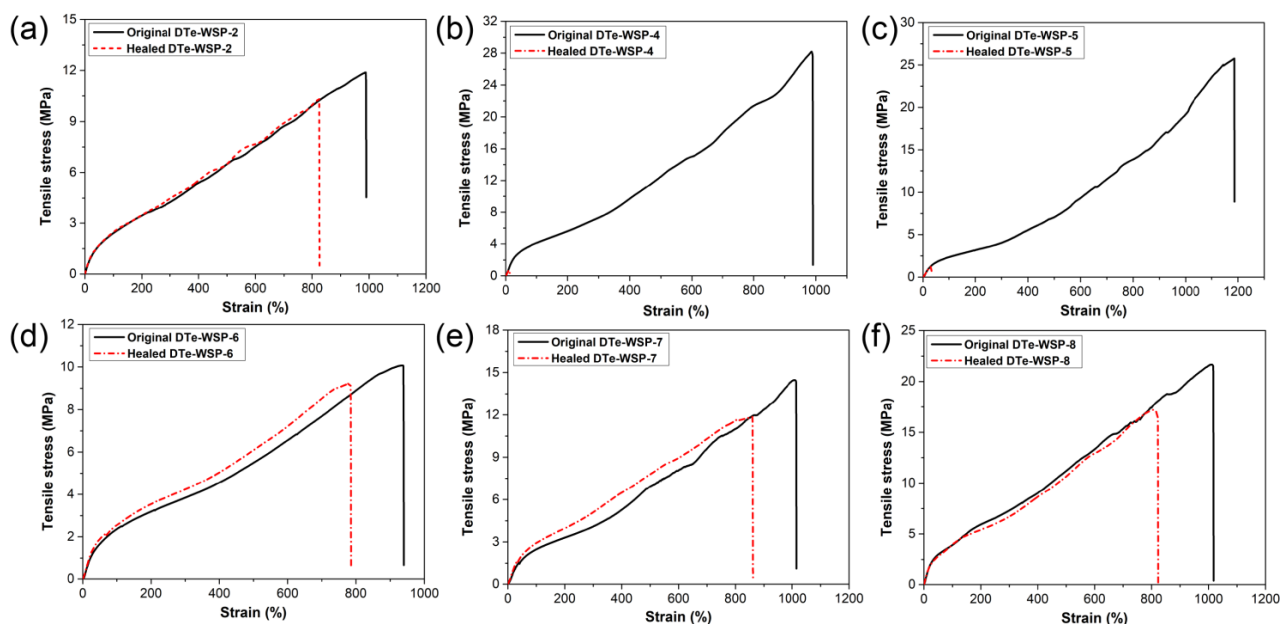


Figure S14. Stress-strain curves of the healed sample: (a) DTTe-WSP-2, (b) DTTe-WSP-4, (c) DTTe-WSP-5, (d) DTTe-WSP-6, (e) DTTe-WSP-7, and (f) DTTe-WSP-8.

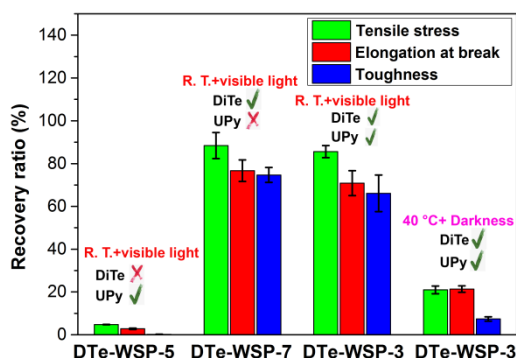


Figure S15. The recovery ratios of mechanical properties for DTTe-WSP-3 and its reference samples.

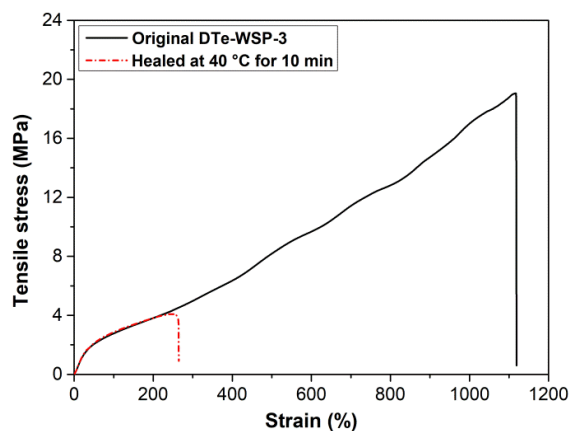


Figure S16. Representative tensile stress-strain curves of the fractured DTTe-WSP-3 sample after healed at 40 °C for 10 min.

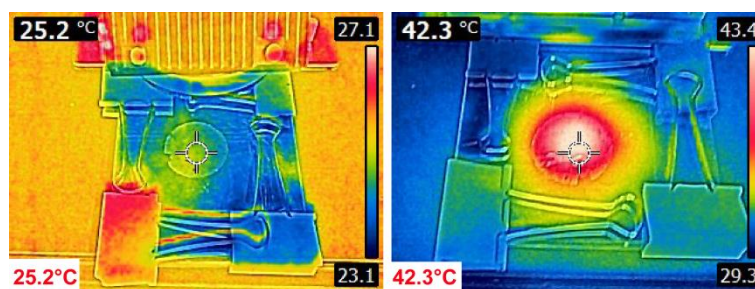


Figure S17. Surface temperature of the compressed DTe-WSP-3 polymer sheet before (left) and after (right) irradiated in the photoreactor for 30 min.

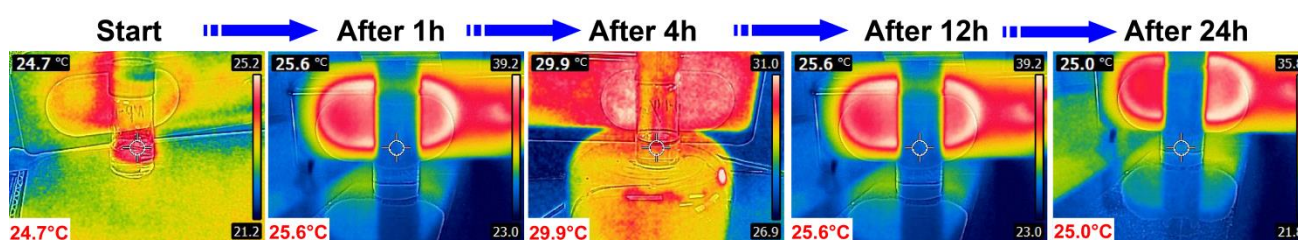


Figure S18. Surface temperature of the photoinitiated polymerization process of MMA using DTe-WSP-3 polymer as a macroinitiator with different irradiation time at room temperature.

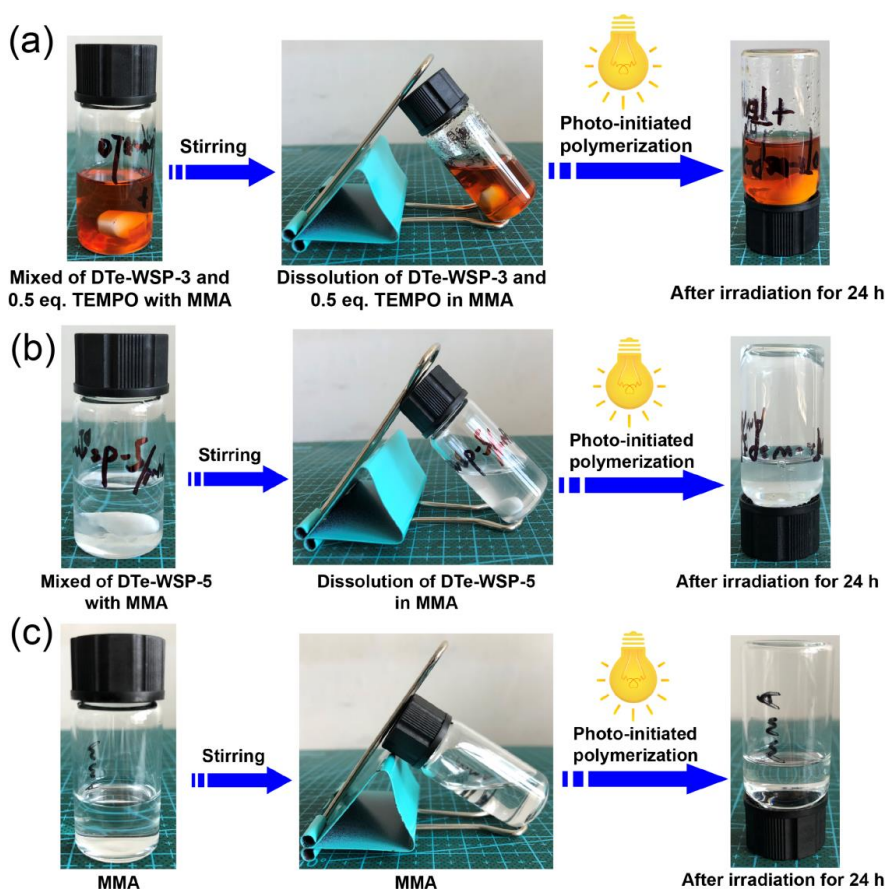


Figure S19. Photographs of the mixture of DTe-WSP-3, MMA and TEMPO (DTe-WSP-3/MMA mass ratio of 1/20, and 5 eq. TEMPO to ditelluride bonds) (a), pure MMA (b), and the mixture of DTe-WSP-5 and MMA (c) after

irradiated under visible light for 24 h.

References

- (1) Wang, Y.; Zhu, L.; Wang, Y.; Li, L.; Lu, Y.; Shen, L.; Zhang, L. W. Ultrasensitive GSH-Responsive Ditelluride-Containing Poly(ether-urethane) Nanoparticles for Controlled Drug Release. *ACS Appl. Mater. Interfaces* **2016**, 8, 35106–35113.