Supplementary information for

Bio-based Recyclable Polydithioacetal Covalent Adaptable Networks with Activation Temperature-Tunable Shape Memory Property

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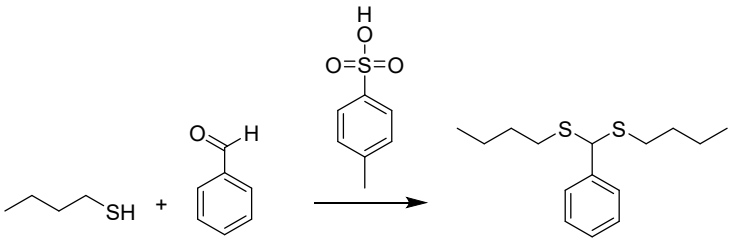
1. Materials

Pentaerythritol tetra(3-mercaptopropionate) (PETMP) and 3,6-dioxa-1,8-octanedithiol were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. *p*-Toluenesulfonic acid (*p*-TSA) was obtained from Shanghai Rhawn chemical reagent. Butanethiol, benzyl mercaptan, trimethylolpropane tris(3-mercaptopropionate) (TMMP), terephthalaldehyde (TPA) and benzaldehyde (BzA) were purchased from Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Chloroform-d was purchased from Merck (Sigma-Aldrich) Co., Ltd.

2. Synthesis of model compounds

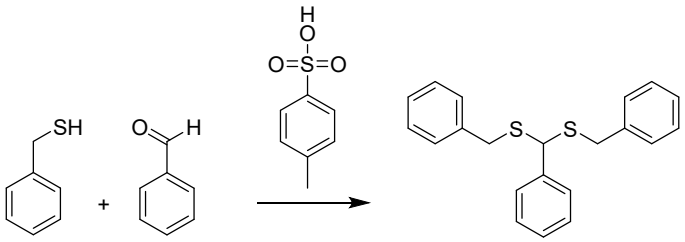
Bis(butylsulfanyl)methylbenzene: BzA (265 mg, 2.5 mmol) and butanethiol (473 mg, 5.25 mmol) were dissolved in dichloromethane (5 mL), *p*-TSA (15 mg, 2 wt%) was added, and the reaction proceeded at room temperature for 4 h. The resulting reaction mixture was washed three times with saturated sodium bicarbonate solution, followed by rotary evaporation to remove the solvent, yielding a colorless liquid. Subsequently, a vacuum distillation was conducted at 70 °C for 1 h to remove butanethiol. The bis(butylsulfanyl)methylbenzene was obtained, appeared as a colorless liquid (509 mg, 76%). Molecular structure was confirmed by ^{1}H NMR (**Fig. S1,** 7.31 (m, 5H), 4.84 (s, 1H), 2.53 (m, 4H), 1.52 (m, 4H), 1.37 (m, 4H), 0.86 (t, J = 7.3 Hz, 6H)).



Scheme S1 Synthetic route of compound bis(butylsulfanyl)methylbenzene.

Bis(benzylsulfanyl)methylbenzene: BzA (265 mg, 2.5 mmol) and benzyl mercaptan (652 mg, 5.25 mmol) were dissolved in dichloromethane (5 mL), *p*-TSA (18 mg, 2 wt%) was added, and the reaction proceeded at room temperature for 4 h. The resulting reaction mixture was washed three times with saturated sodium bicarbonate solution, followed by rotary evaporation to remove the solvent, yielding a colorless liquid. Subsequently, a vacuum distillation was conducted at 120 °C for 1 h to remove benzyl mercaptan. The compound bis(benzylsulfanyl)methylbenzene was obtained,

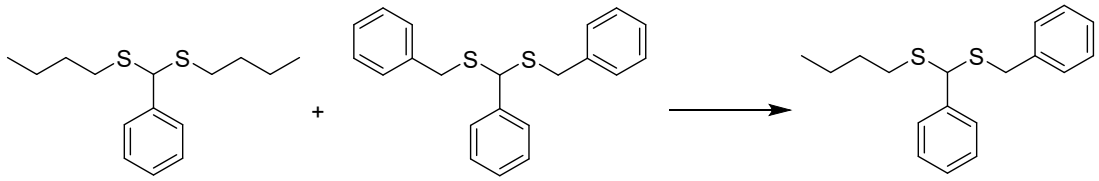
appeared as colorless crystals (592 mg, 65%). Molecular structure was confirmed by ^{1}H NMR (**Fig. S2**, 7.31 (m, 15H), 4.46 (s, 1H), 3.76 (d, J = 13.4, 2H), 3.54 (d, J = 13.4, 2H)).



Scheme S2 Synthetic route of compound bis(benzylsulfanyl)methylbenzene.

3. Dynamic exchange of model compounds

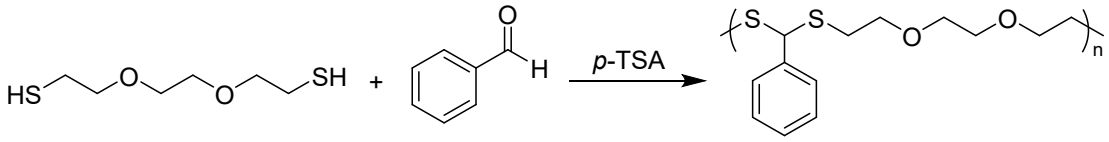
Model compound bis(butylsulfanyl)methylbenzene (268 mg, 1 mmol) and model compound bis(benzylsulfanyl)methylbenzene (336 mg, 1 mmol) were added into a Schlenk flask, which was then evacuated and purged with nitrogen. The Schlenk flask was then placed in a 120 °C oil bath for the dynamic exchange reaction. At intervals of 2 or 3 h, small aliquots of the reaction mixture were taken out for ^{1}H NMR spectroscopy analysis to observe the progress of the exchange reaction (**Fig. S3**).



Scheme S3 Exchange reaction of model compounds.

4. Synthesis of dithioacetal based linear polymer

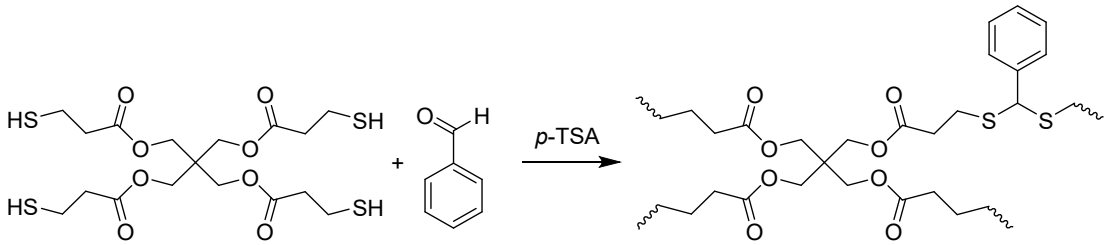
In a 25 mL flask, 3,6-dioxa-1,8-octanedithiol (0.55 g, 3 mmol) and BzA (0.32 g, 3 mmol) were dissolved in 10 mL THF, *p*-TSA (9 mg, 1 wt%) was added into the solution. After stirring for 3 h at room temperature, the polymer was precipitated three times in ethanol and dried. ^{1}H-NMR was applied to verify the structure.



Scheme S4 Synthetic route of dithioacetal based linear polymer.

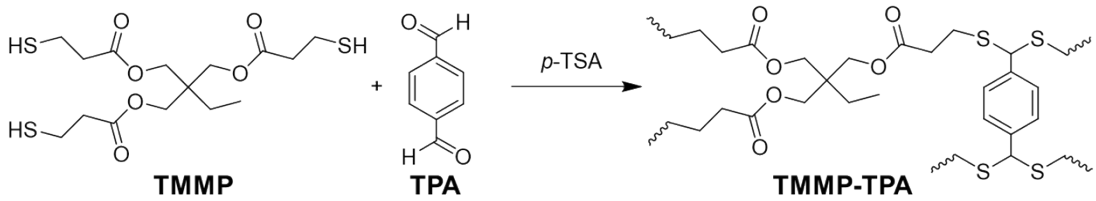
5. Synthesis of crosslinked PDTA

PETMP (48.9 g, 0.1 mol) and BzA (21.2 g, 0.2 mol) were mixed homogenously under vigorous mechanical stirring. To mixture, a solution of *p*-TSA (0.14 g, 0.2 wt%) in THF (0.1 mL) was added. The reaction mixture was stirred at room temperature for 10 min, followed by heating to 70 °C for 1 h, resulting in a white solid containing water. After grinding into powder, the material was dried overnight at 120 °C, yielding a dry white powder, identified as crosslinked PDTA (70.1 g, 100%).



Scheme S5 Synthetic route of crosslinked PDTA.

TMMP (15.9 g, 0.04 mol) and TPA (4.0 g, 0.03 mol) were mixed homogenously under heating. To mixture, a solution of *p*-TSA (40.0 mg, 0.2 wt%) in THF (0.1 mL) was added. The reaction mixture was stirred at room temperature for 30 min, followed by heating to 70 °C for 1 h, resulting in a white solid containing water. After grinding into powder, the material was dried overnight at 120 °C, yielding a dry white powder, identified as crosslinked TMMP-TPA (19.9 g, 100%).

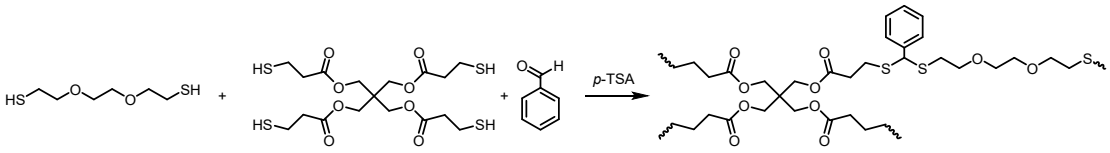


Scheme S6 Synthetic route of TMMP-TPA.

6. Synthesis of crosslinked PDTA with tunable T_g

PDTA with 25 mol% di-thiol: PETMP (14.7 g, 0.03 mol), 3,6-dioxa-1,8-octanedithiol (1.8 g, 0.01 mol) and BzA (7.4 g, 0.07 mol) were mixed homogenously under vigorous mechanical stirring. To mixture, a solution of *p*-TSA (0.05 g, 0.2 wt%) in THF (0.05 mL) was added. The reaction mixture was stirred at room temperature for 10 min, followed by heating to 70 °C for 1 h, resulting in a white solid containing water. After grinding into powder, the material was dried overnight at 120 °C, yielding a dry white powder, identified as $PDTA_{25}$ (23.9 g, 100%).

PDTA with 50 mol% di-thiol: PETMP (9.8 g, 0.02 mol), 3,6-dioxa-1,8-octanedithiol (3.6 g, 0.02 mol) and BzA (6.4 g, 0.06 mol) were mixed homogenously under vigorous mechanical stirring. To mixture, a solution of *p*-TSA (0.04 g, 0.2 wt%) in THF (0.05 mL) was added. The reaction mixture was stirred at room temperature for 10 min, followed by heating to 70 °C for 1 h, resulting in a white solid containing water. After grinding into powder, the material was dried overnight at 120 °C, yielding a dry white powder, identified as crosslinked $PDTA_{50}$ (19.8 g, 100%).



Scheme S7 Synthetic route of crosslinked PDTA with tunable T_g.

7. Characterization and methods

Nuclear magnetic resonance (NMR). NMR proton spectra were performed on the JEOL 400 MHz with tetramethylsilane as an internal standard

Fourier transform infrared (FTIR). FTIR spectra were recorded on the Perkin Elmer 100 serial FTIR spectrophotometer equipped with universal attenuated total reflectance.

Tensile experiments. Tensile experiments were performed on the universal testing machine (CMT 6303, Shenzhen SANS Test Machine Co. Ltd., China). The samples were extended at a speed of 10 mm min^{-1} at 25 ^{o}C. The load was measured via a 5 kN capacity load cell.

Differential scanning calorimetry (DSC). Glass transition temperatures (T_g). was tested by which was performed on the NETZSCH DSC 200PC instrument. The DSC uses nitrogen as the shielding gas. Two thermal cycles were designed. For the first thermal cycle, the heating rate was 10 ^{o}C min^{-1}, and the temperature was in the range of 0 to 100 ^{o}C. For the second thermal cycle, the heating rate was 5 ^{o}C min^{-1}, and the temperature was in the range of 0 to 100 ^{o}C.

Dynamic mechanical analysis (DMA). DMA was also performed to characterize T_g of PDTA. The storage modulus and loss factor of the samples were tested in the DMA tensile mode of the TA Q-800. The size of the samples was 1 mm (T) × 4 mm (W) × 20 mm (L). The samples were first kept at 10 °C for 5 min and then heated up to 100 °C at a rate of 3 °C·min^{-1}.

Thermogravimetric analysis (TGA). Weight loss was performed in the NETZSCH TG209C instrument. The measurements were conducted during heating to 873 K at a rate of 10 K min^{-1} under flowing nitrogen gas.

Ultraviolet-visible (UV-vis) spectrophotometer. The transmittance spectra were performed on an UV-Vis spectrophotometer (PE Lambda950). The PDTA sample and glass for tests were 0.6 mm thickness. The wavelength for testing was set from 800 to 400 nm. The reference for measuring transparency was air.

Swelling tests. PDTA samples (0.6 g) were immersed in variant solvents (10 mL) in glass vials at room temperature. After 24 h, the sample was taken out, and the residual solvent on the surface was wiped. The swelling ratio was calculated by the following equation.

$$\text{Swelling ratio} = \frac{M_w}{M_0} \times 100\%$$

Where M_w is the mass of the swelled sample after swelling and M_0 is the mass of the sample before swelling.

Then the sample was dried in a 120 °C oven until the mass was stable. The soluble fraction was calculated by the following equation.

$$\text{Soluble fraction} = \frac{M_d}{M_0} \times 100\%$$

Where M_d is the mass of the dry samples and M_0 is the mass of the sample before swelling.

Self-healing. Two dumbbell-shaped PDTA samples were put into the dumbbell-shaped mold and molded with a pressure of 6 MPa at 130 °C for 3 h. Stress-strain tests

were performed on the self-healed samples to verify the recovery of the mechanical properties.

Reprocessing. PDTA powder was poured into the dumbbell-shaped mold and molded with a pressure of 6 MPa at 130 °C for 3 h. The resulting samples were subjected to a stress-strain test. Subsequently, the pulled-off samples were reground to a fine powder and remolded with the same hot-pressing procedure.

Stress-relaxation analysis and activation energy (E_a). Stress-relaxation experiments were performed on a TA-Q800 dynamic mechanical analysis (DMA) instrument with DMA controlled force mode. The samples (ca. 1 mm (T) × 4 mm (W) × 40 mm (L)) were allowed to equilibrate at this temperature for approximately 10 minutes, after which samples were subjected to an instantaneous 0.5% strain until the stress relaxation modulus had relaxed to at least 37% (1/e) of its initial value. The characteristic relaxation time (τ^*) was defined as the time required for the stress relaxation modulus to reach 37% (1/e) of its initial value and determined at 90, 100, 110, and 120 °C, respectively. These points were then plotted versus 1000/T and fit the Arrhenius relationship in the following equation.

$$\tau(T) = \tau_0 e^{E^a/RT}$$

Where τ_0 is the characteristic relaxation time at infinite T, E_a is the activation energy (kJ mol^{-1}), R is the universal gas constant and T is the temperature at the stress-relaxation experiments were performed.

Chemical recycling. The crosslinked PDTA sample (0.5 g) was completely immersed in chloroform (10 mL), and the sample was completely dissolved by adding

PETMP (0.9 g, 3 eq.) and *p*-TSA (0.2 g) and heating at 70 °C for 2.5 h. Subsequently, the *p*-TSA precipitated after cooling the solution to room temperature. The *p*-TSA crystals were filtered off to obtain a thiol-terminated oligomer solution. BzA (0.41 g, 3 eq.) was then added and reacted for 10 min at room temperature to form a crosslinked gel, and the crosslinked PDTA powder was obtained by grinding and drying. The chemically recovered crosslinked PDTA was obtained by hot pressing with a pressure of 6 MPa for 3 h at 130 °C, and the mechanical properties of the sample were tested by tensile experiments.

Hot pressing. Hot press processes were using a Shiyan program controlled hot press machine (SY-6210-B) in specific shape steel molds.

Recovery of BzA monomer. The crosslinked PDTA (0.5 g) was immersed in dimethyl sulfoxide (20 mL). After heating at 160 °C for 8 h, PDTA was completely dissolved. After addition the dichloromethane (20 mL), the solution was washed with deionized water (20 mL×3). The remaining organic phase was subjected to reduced pressure distillation with a gradual increase in temperature from room temperature. The fractions between 60 and 65 °C are collected to obtain the renewed BzA.

Shape memory characterization. The shape memory properties were quantitatively characterized by a TA-Q800 DMA apparatus with a film tension clamp under controlled stress. The dimension of the sample was 1 mm (T) × 4 mm (W) × 40 mm (L). The sample was equilibrated at 80 °C (above T_g) for 5 min. The DMA curve was obtained in a “DMA Controlled Force” mode. An external constant force of 0.5 MPa was applied to stretch the sample, and the temperature was decreased to 15 °C (below

T_g) at a cooling rate of 5 K min^{-1}. Once reached 15 °C, the external constant force was removed, and the sample was heated to 80 °C again at a heating rate of 10 K min^{-1}. During the second heating process, the shape recovery of the sample was recorded during the test. The shape memory process was repeated 4 times to verify the robustness of PDTA. The shape fixity rate (R_f) = $\varepsilon_d/\varepsilon_{dload}$ ×100% and shape recovery rate (R_r) = $(\varepsilon_d-\varepsilon_{rec})/(\varepsilon_d-\varepsilon_0)$ ×100%, with ε_0, ε_{dload}, ε_d, and ε_{rec} being the original strain, the maximum strain under load, the fixed strain, and the recovered strain, respectively.

Cytocompatibility of PDTA. End1/E6E7 human cervical epithelial cells and HCerEpic human cervical epithelial cells were incubated at 37 °C with 5% CO_2. The End1/E6E7 cells were maintained in Dulbecco's modified Eagle medium (DMEM, Gibco) and the HCerEpic cells were cultured in Roswell Park Memorial Institute (RPMI) 1640 medium (Gibco). All media were supplemented with 10% FBS and 1% penicillin-streptomycin (Hyclone). End1/E6E7 cells and HCerEpic cells were seeded in a 96-well plate at a density of 5000 cells/well. After the cells adhered to the plate for 24 h, the culture medium was replaced with 100 μL PDTA extract (12.5 mg/mL). After 24, 48, or 72 h of incubation, the media were replaced with fresh media containing 10% CCK-8 solution (Beyotime). The absorbance at 450 nm was determined with a microplate reader (Bio-Rad, Hercules, CA, USA). The relative cell viability was expressed as Abst/Absc×100%, where Abst and Absc represent the relative absorbance intensity of the test sample and control group, respectively. The cultural medium served as a control.

Then, Live/Dead staining was conducted with cells which were plated into a 96-well plate with a density of 5000 cells/well. After cultured for 24 h, the medium was replaced with fresh PDTA extract and the cells were incubated for another 24, 48, or 72 h. After staining with 100 μL calcein-AM/propidium iodide dye (Beyotime) for 30 min, cells were observed under a fluorescent microscope (DM505, Nikon Co., Ltd., Otawara, Tochigi, Japan). All Experiments were performed in triplicate.

Fabrication of artificial blood vessel. The artificial blood vessel was fabricated by using silicone elastomer kit (Sylgard 184, Dow Inc.). The two components of the silicone elastomer were mixed and evenly applied to the outer wall of the glass tube. The silicone elastomer was cured at 50 °C for 10 h and then carefully peeled off to obtain the artificial blood vessel.

8. Data

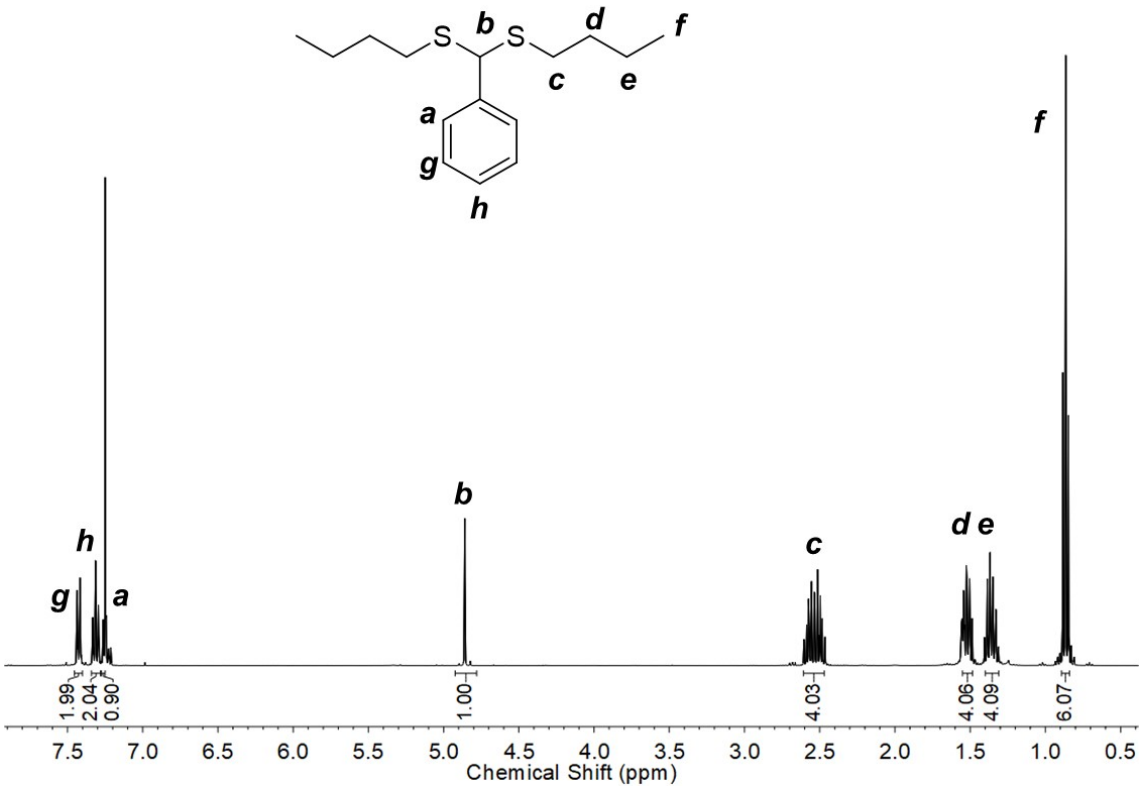


Fig. S1 ^{1}H-NMR spectrum of compound bis(butylsulfanyl)methylbenzene.

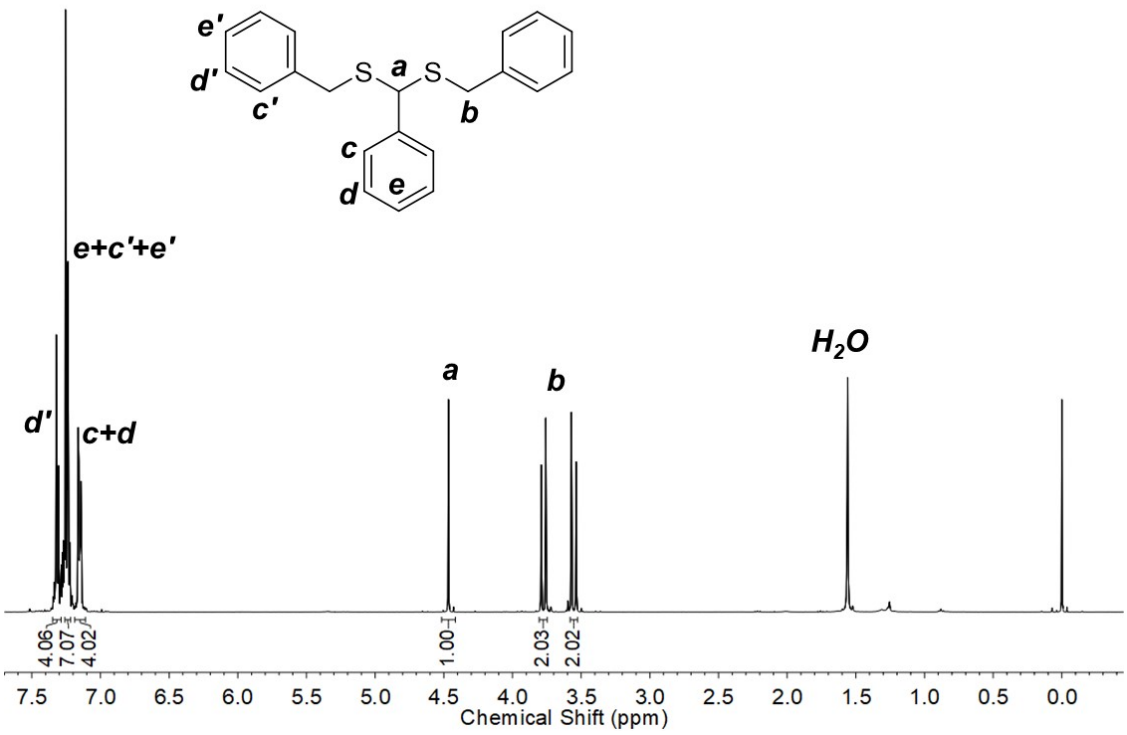


Fig. S2 ^{1}H-NMR spectrum of compound bis(benzylsulfanyl)methylbenzene.

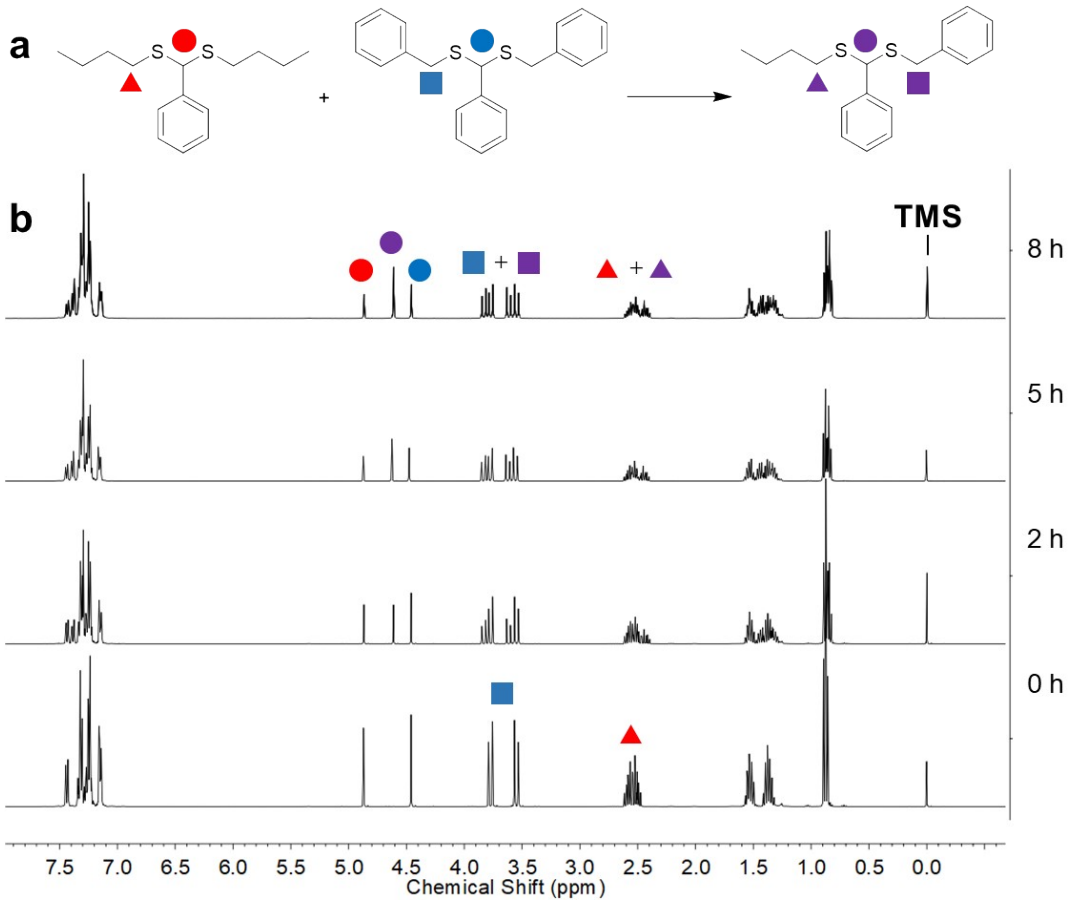


Fig. S3 (a) The dynamic exchange reaction equation of model compounds. (b) ^{1}H-NMR spectrum of reaction mixture during exchange reaction of model compounds.

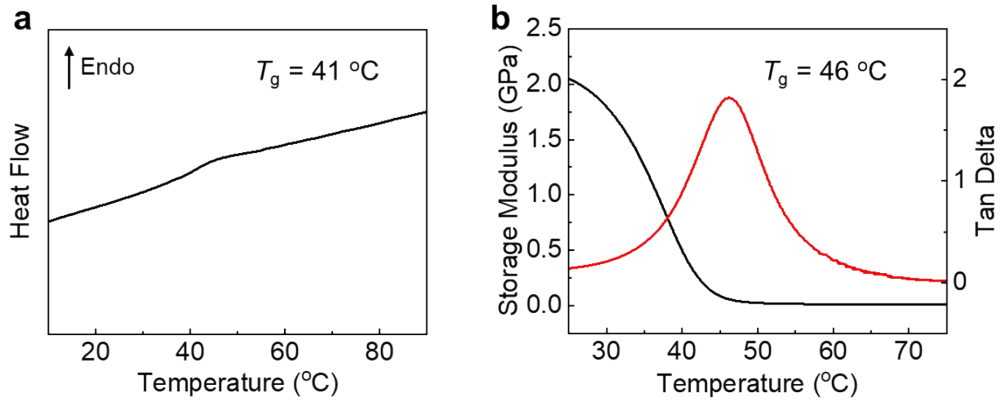


Fig. S4 The T_g of crosslinked PDTA. (a) DSC curve of crosslinked PDTA. (b) Storage modulus and Tan delta curves of crosslinked PDTA.

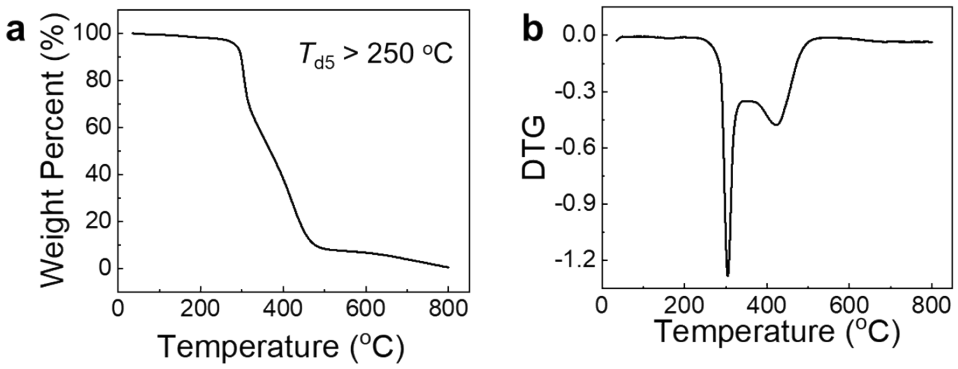


Fig. S5 The TGA test of crosslinked PDTA. (a) The thermal weight loss curve of crosslinked PDTA. (b) The derivative thermogravimetric (DTG) curve of crosslinked PDTA.

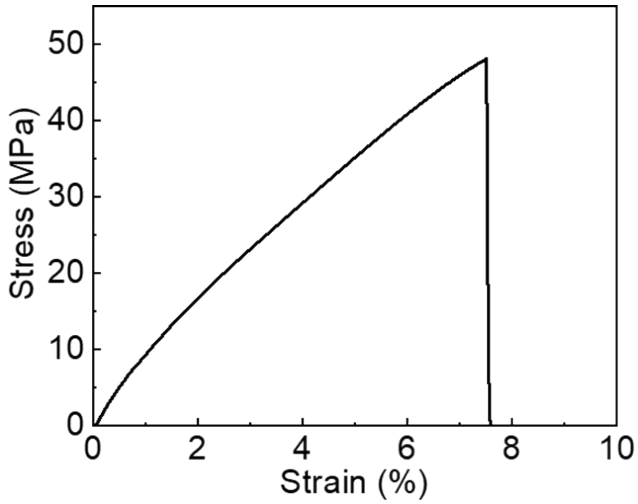


Fig. S6 The stress-strain curve of crosslinked PDTA.

Entry	Young's Modulus (MPa)	Tensile Strength (MPa)	Breaking Elongation (%)
Pristine	680.8 ± 89.7	50.3 ± 9.4	7.9 ± 0.4
2nd Reprocessed	631.2 ± 57.2	46.6 ± 8.9	7.4 ± 0.9
3rd Reprocessed	603.2 ± 47.3	46.6 ± 5.1	6.9 ± 0.4
4th Reprocessed	609.9 ± 33.0	42.2 ± 0.7	8.6 ± 1.6
Healed	622.6 ± 82.7	45.7 ± 6.2	8.6 ± 0.8
Recycled	623.8 ± 91.3	48.5 ± 4.7	9.0 ± 1.5
Renewed	675.9 ± 95.7	51.8 ± 7.9	7.5 ± 1.3

Table S1 The mechanical property of crosslinked PDTA.

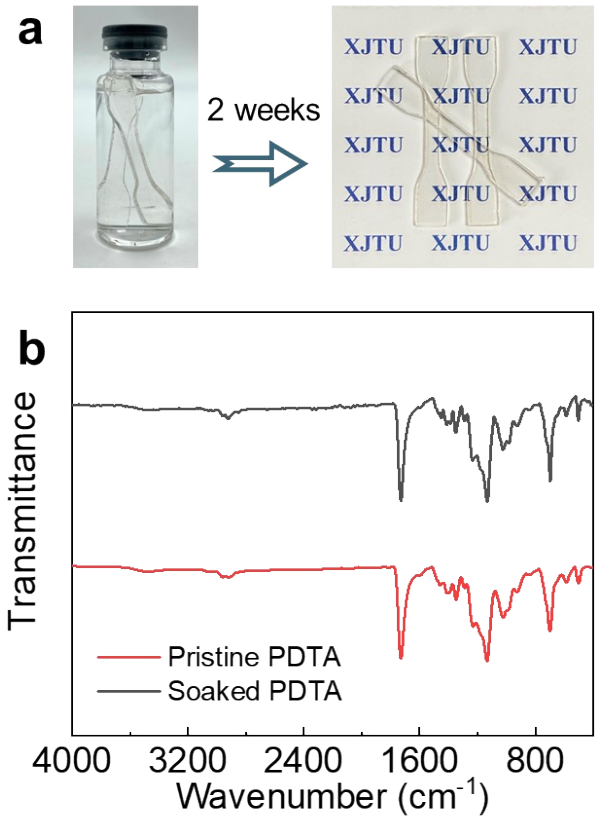


Fig. S7 (a) The PDTA after soaking in deionized water for 2 weeks at room temperature. (b) FTIR spectra of pristine PDTA and soaked PDTA.

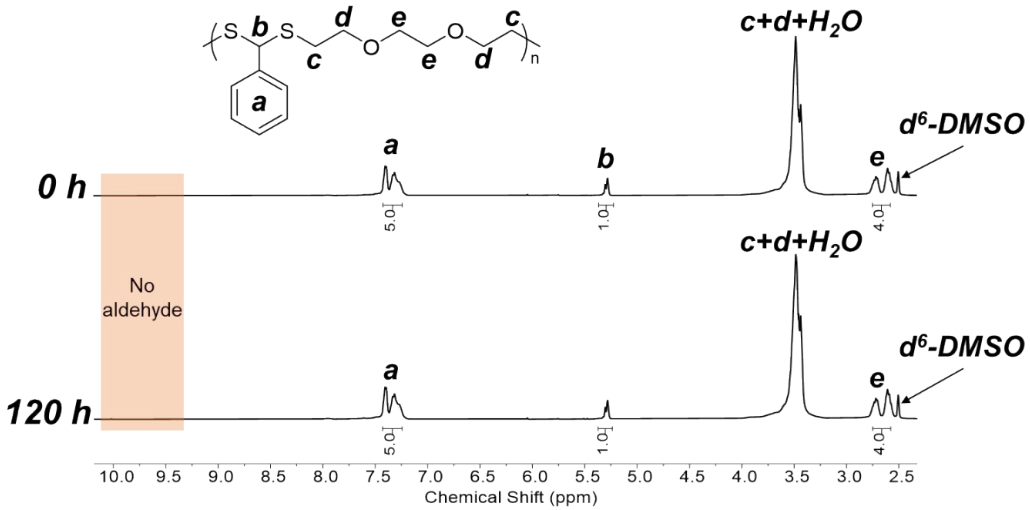


Fig. S8 The overlay of ^{1}H NMR spectrums of the freshly prepared dithioacetal-based linear polymer (10.0 mg) solution in d^{6}-DMSO (0.5 mL) containing deionized water (5 mg, 1% in DMSO) taken at t = 0 and the same solution retaken 120 h later at room temperature.

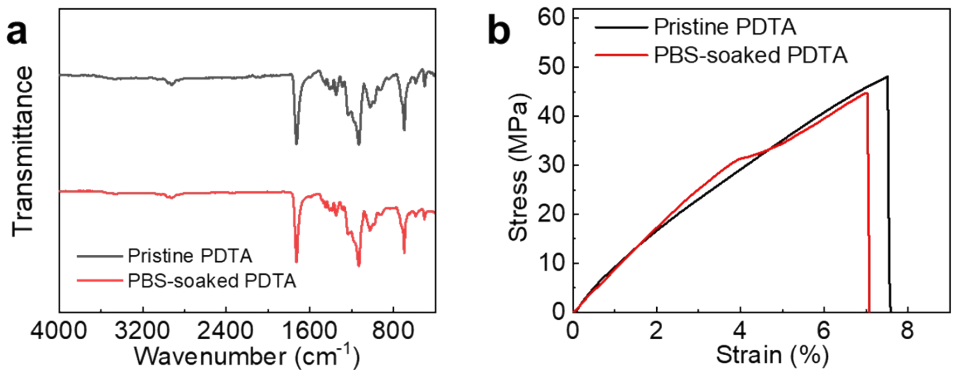


Fig. S9 (a) FITR spectra of pristine and PBS-soaked PDTA. (b) The stress-strain curves of pristine and PBS-soaked PDTA.

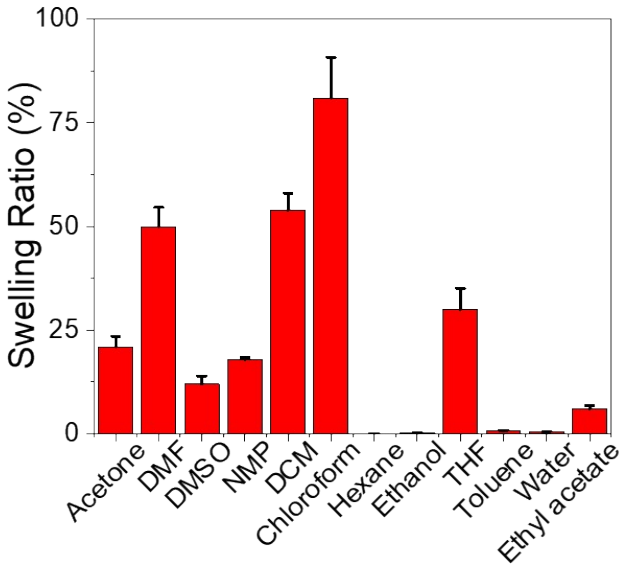


Fig. S10 Swelling ratios of PDTA in various solvents.

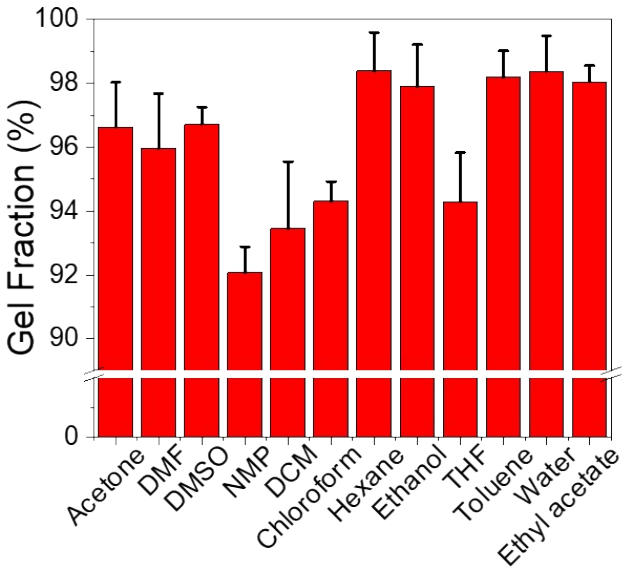


Fig. S11 Gel fractions of PDTA after swelling in various solvents.

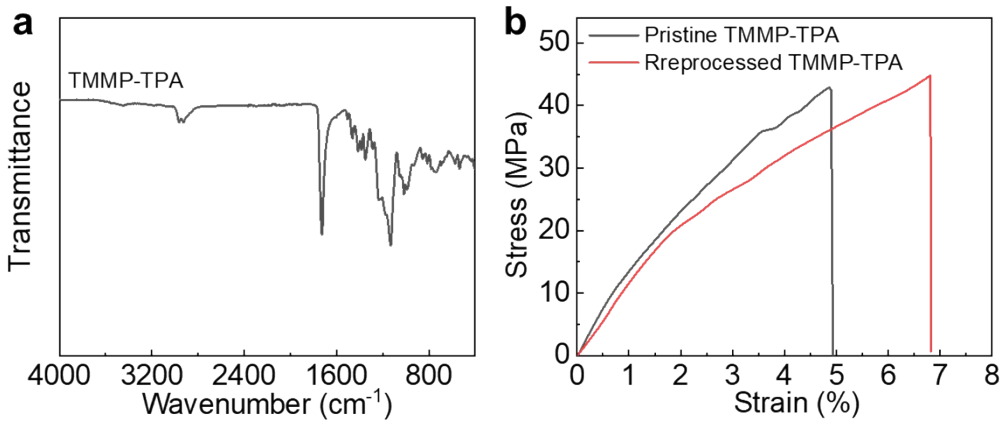


Fig. S12 (a) FITR spectrum of as-synthesized TMMP-TPA. (b) The stress-strain curves of pristine and reprocessed TMMP-TPA (Reprocess condition: 6 MPa, 130 ^{o}C, 3h).

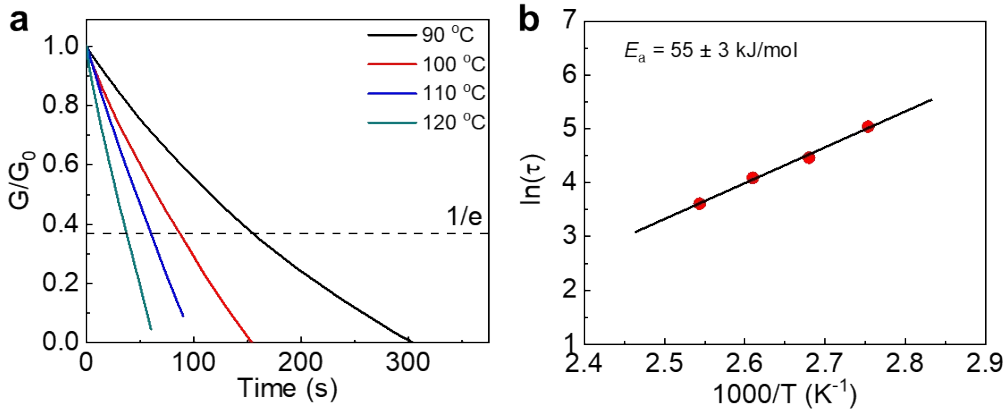


Fig. S13 Stress relaxation of crosslinked PDTA samples. (a) Normalized relaxation modulus curves of PDTA samples at 90, 100, 110, and 120 °C. (b) Arrhenius fitting analysis for crosslinked PDTA samples.

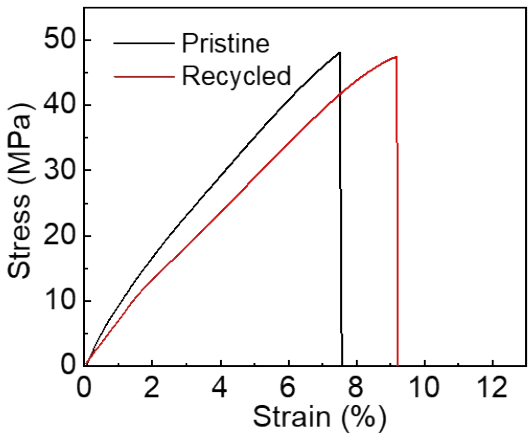


Fig. S14 The stress-strain curve of pristine and recycled PDTA.

	1st	2nd	3rd	4th
Fixity ratio (%)	99.46	99.48	99.50	99.36
Recovery ratio (%)	99.23	94.14	94.24	94.18

Table S2 R_f and R_r of PDTA during the four cycles of shape memory process.

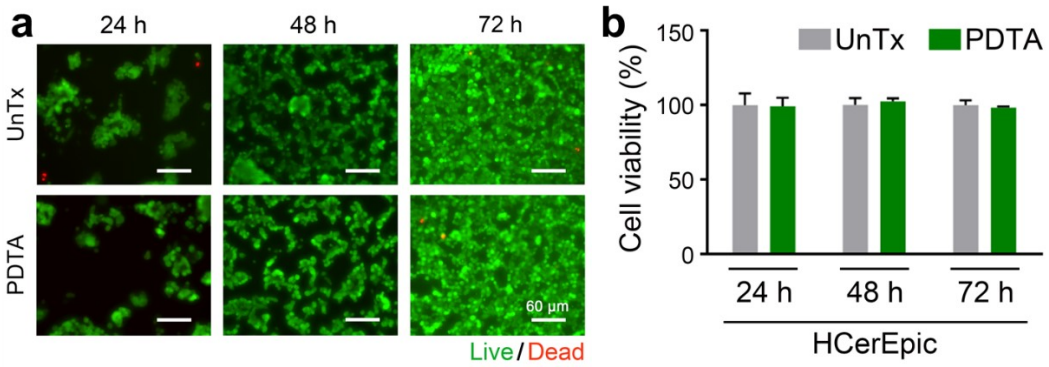


Fig. S15 (a) Relative cell viability of HCerEpic cells incubated in PDTA extract for 1, 2, and 3 days, respectively. (b) Live/Dead staining of HCerEpic cells incubated in PDTA extract for 1, 2, and 3 days, respectively.

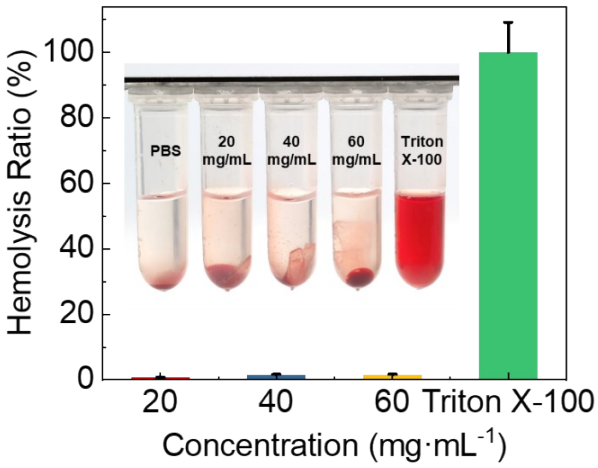


Fig. S16 Hemolysis of the $PDTA_{25}$ with different concentrations.