Supporting Information

Near-infrared light-induced shape memory, self-healable and antibacterial elastomers by incorporation of a diketopyrrolopyrrole-based conjugated polymer

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1. Materials and Instruments

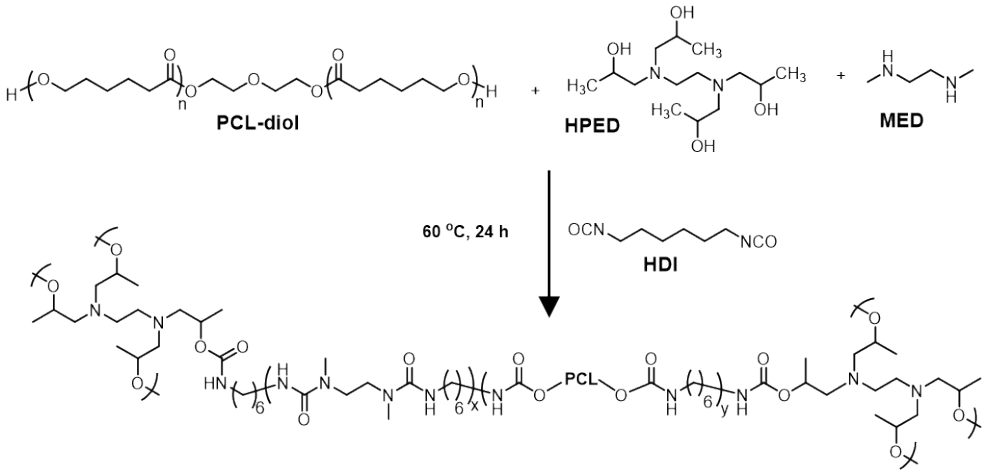
Polycaprolactone diol (PCL-diol, molecular weight Mn ~ 2000), *N,N'*-dimethyl-ethylenediamine (MED, 98%), *N,N'*-di-*tert*-butyl-ethylenediamine (TBED, 98%), *N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine (HPED, 98%) and hexamethylene diisocyanate (HDI, 98%) were purchased from Sigma-Aldrich. Poly{2,2'-[(2,5-bis(2-hexyldecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)dithiophene]-5,5'-diyl-alt-thiophen-2,5-diyl} (PDPP3T, molecular weight Mw > 30,000 by GPC) was purchased from Lumtec. Phosphate buffer saline (PBS, pH 7.4, 10x) was purchased from 1st BASE Singapore and used after dilution by 10 times with ultrapure water and sterilization by autoclave. *Escherichia coli* (*E. coli*, ATCC 25922) bacteria was collected from American Type Culture Collection. Luria-Bertani (LB) agar and LB broth base were both purchased from Thermo Fisher Scientific. Other solvents were purchased from VWR Singapore. All the regents and solvents were used directly unless otherwise mentioned.

Fourier transform infrared (FT IR) spectra were recorded on a Bruker vertex 70 using ATR mode by 40 scans from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. The X-ray diffraction (XRD) patterns of all polymer film samples were collected on a Bruker D8 Advance X-ray diffractometer (Cu Kα X-ray source) operating at a voltage of 40 kV and a current of 30 mA. Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG 60 AH with heating rate 20 ^{o}C/min till 800 ^{o}C under nitrogen. Differential scanning calorimetry (DSC) analysis was performed on a Perkin Elmer DSC 8000. Sample was first heated to 100 ^{o}C and then cooled to 0 ^{o}C to perform the annealing process. Then the temperature was hold at 0 ^{o}C for 4 minutes to induce crystallization of the sample. Afterwards, sample was subjected to heating to 100 ^{o}C at the heating rate of 20 ^{o}C/min and the result was shown. Dynamic mechanical analysis of PCL-PU elastomers with various additions of PDPP3T was performed on a dynamic mechanical analyzer (DMA Q800, TA instruments) under frequency 1.0 Hz and strain 0.5% with sample size ~10.0 × 4.0 ×1.0 mm. Uniaxial tensile tests were performed on an Instron 3345 with the extension rate of 20 mm/min at room temperature (~22 ^{o}C).

The sample size was ~40.0 x (2.0 ~ 4.0) x 1.0 mm with a test gauge length of 20 mm. A diode laser (808 nm, Photonitech Pte. Ltd.) was used for photothermal experiments. Infrared (IR) thermographs were obtained by an IR Thermal Camera (FLIR E60). UV-*vis* spectra and optical density at 600 nm (OD_{600}) of bacteria suspension were detected by the Shimadzu 1700 UV-*vis* spectrometer. Dilatometry tests were performed on the DMA from 30 °C to 150 °C by monitoring strain changes under a static force (0.10 N and 0.05 N for MED and TBED based PCL-PU elastomers, respectively).[1,2]

2. Methods

Synthesis of the polycaprolactone-co-poly(urethane/urea) (PCL-PU) elastomers[3,4]



The typical PCL-PU elastomers with PDPP3T polymers were prepared as follows: polycaprolactone diol (PCL-diol, 600.0 mg, 3.0 eqv.) and *N,N,N',N'*-tetrakis(2-hydroxypropyl) ethylenediamine (HPED, 29.2 mg, 2.0 eqv. based on hydroxyl groups) were charged into a vial and dried in an oven of 80 °C for 2 hours. Then the vial was put in an ice bath and added with *N,N'*-dimethyl-ethylenediamine (MED, 8.8 mg, 1.0 eqv.) and chloroform (0.4 mL). For synthesizing PCL-PU elastomers with hindered urea bond, *N,N'*-di-*tert*-butyl-ethylenediamine (TBED, 17.2 mg) was used instead of MED following the same procedure. Then hexamethylene diisocyanate (HDI, 0.1 mL, 6.0 eqv.) was added into the vial drop by drop. Then the vial was kept at room temperature (~ 22 °C). After all the solids were dissolved (~10 min), calculated amounts of PDPP3T chloroform solution (2.5 mg/mL, 150.0 μL for 0.5 wt‰ addition for an

example) was added into the vial. Then the vial was sonicated for 5 min before casting in a hand-made Teflon mould (40.0 x 16.0 x 1.0 mm). The mould was put in an oven (60 ^{o}C, 20 hours) for reaction and followed in a vacuum oven (60 ^{o}C, 4 hours) for drying. The sample was peeled off from the mould and cut into desired size before use.

Photothermal antibacterial experiments of PDPP3T embedded PCL-PU elastomers

Preparation of Solid LB Agar Plate and Bacteria Culture[5,6]

LB agar powder (32.0 g) was dissolved into ultrapure water (1.0 L), then the solution was sterilized by autoclave. The liquid LB agar solution (~ 2.0 mL) at ~50 ^{o}C was dumped into a petri dish (diameter 3.0 cm) with a membrane of PCL-PU elastomer for *in situ* photothermal antibacterial assay. Afterwards, the solution was allowed to cool down in a sterile atmosphere to get the solid LB agar plate. Similarly, liquid LB agar solution (~ 20.0 mL) was dumped into a petri dish (diameter 10.0 cm) to prepare solid LB agar plates for the quantitative assay of colony proliferation of bacteria seeds.

The bacteria seeds of *E. coli* from a colony of solid LB agar plate were picked up and suspended into LB broth medium (20.0 g/L, 5.0 mL). The suspension was incubated at 37 ^{o}C overnight. Then the turbid bacteria suspension was centrifuged (4000 rpm, 5 min) and washed with sterile PBS buffer twice. The fresh bacteria was re-dispersed into PBS buffer and diluted to keep the colony-forming unit (CFU) concentration as ~1×10^{9} CFU/mL by calculation to obatain an OD_{600} = ~1.00.

Evaluation of Photothermal Antibacterial Effects of PCL-PU elastomers

A fresh diluted bacteria suspension (1×10^{4} CFU/mL, 50.0 μL) was spread on the solid LB agar plate with a membrane of PCL-PU elastomer in the petri dish (diameter 3.0 cm). For *in situ* photothermal antibacterial assay, the LB agar plate with bacteria seeds was irradiated by 808 nm laser (2.0 W/cm^2, 3 min) over the membrane area. Since diameter of the laser spot was ~ 0.3 cm and area of the elastomer membrane was ~ 1.0 cm^2, irradiation was performed on 9 respective spots. After irradiation, the LB agar

plate was incubated (37 °C, overnight) and observed for the colony proliferation of bacteria seeds.

A quantitative photothermal antibacterial assay was performed by CFU counting method as follows. A fresh bacteria suspension (1×10^9 CFU/mL, 20.0 μL) was dropped on the surface of an elastomer membrane, then the droplet was irradiated by 808 nm laser (2.0 W/cm^2, 2 min). After irradiation, the droplet with the elastomer membrane was immersed into PBS buffer (1.0 mL) to get the bacteria elution. The bacteria suspension was further diluted 2×10^3 fold by PBS buffer, then the diluted bacteria suspension (100.0 μL) was spread on a solid LB agar plate (diameter 10.0 cm). The LB agar plates were incubated (37 °C, overnight) and the colony counts on the plates were calculated to get the bactericidal rates.

3. Supporting Data

Table S1 Properties of PCL-PU elastomers of various component ratios.

no. of samples		1	2	3	4	5
component ratios of the PCL-PU elastomers[a] (eqv.)	HDI	6.0	6.0	6.0	6.0	6.0
	PCL-diol	1.0	2.0	2.0	2.5	3.0
	HPED	2.0	1.0	2.0	2.0	2.0
	MED	3.0	3.0	2.0	1.5	1.0
mechanical property	storage modulus (Mpa)[b]	100	80	30	40	70
shape memory performances	shape fix[c]/recover[d] ratio,	–/–	+/–	+/+	–/+	+/+
	shape recover time[d] (s)	30	45	15	10	25

Abbreviations: Hexamethylene Diisocyanate (HDI), Polycaprolactone Diol (PCL-diol), *N,N,N',N'*-tetrakis(2-hydroxypropyl) ethylenediamine (HPED), *N,N'*-dimethyl-ethylenediamine (MED); [a]: based on functional groups such as hydroxyl, amine and isocyanate groups; [b]: measured at 30 °C, strain 0.5%, frequency 1.0 Hz; [c]: deformed at ~45 °C and fixed at ~22 °C under bending into U shapes; [d]: heated at ~45 °C.

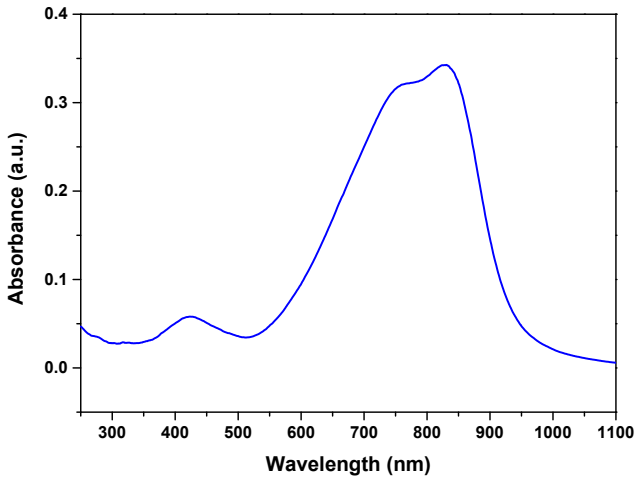


Fig. S1 UV-*vis* absorption spectrum of the PDPP3T polymer thin film.

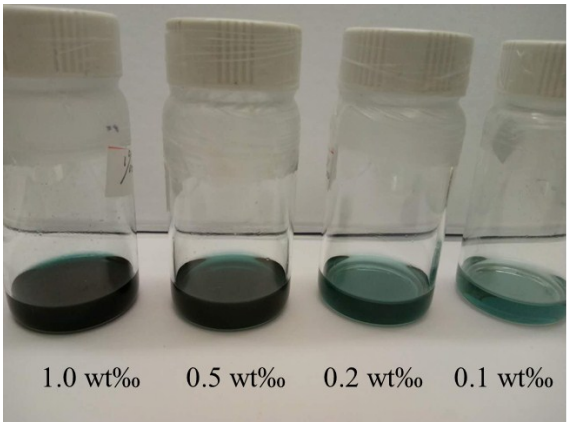


Fig. S2 Photos of PCL-PU elastomer precursor solutions with PDPP3T.

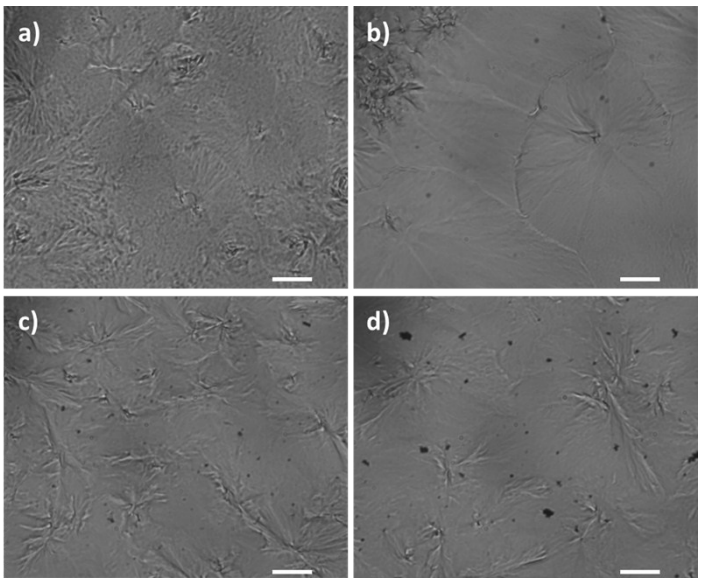


Fig. S3 Photos of PCL-PU elastomer precursor thin films with various additions of a) 0, b) 0.1, c) 0.2 and d) 0.5 wt‰ PDPP3T under microscope (400 ×, scale bar 100 μm).

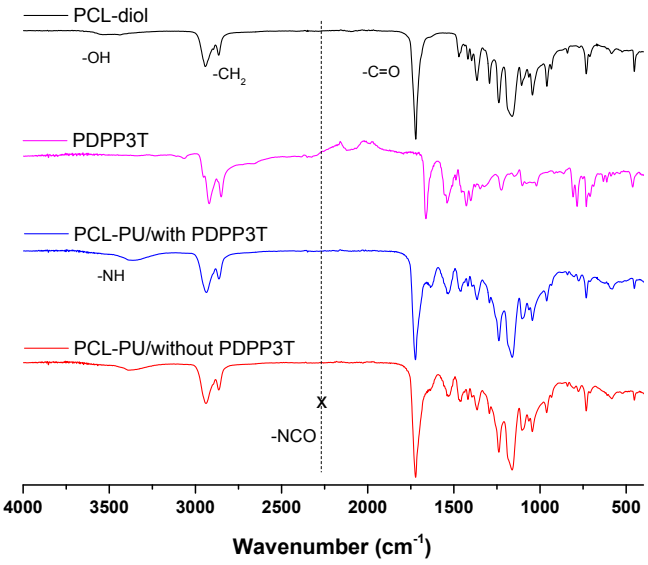


Fig. S4 FT IR spectra of the different polymers.

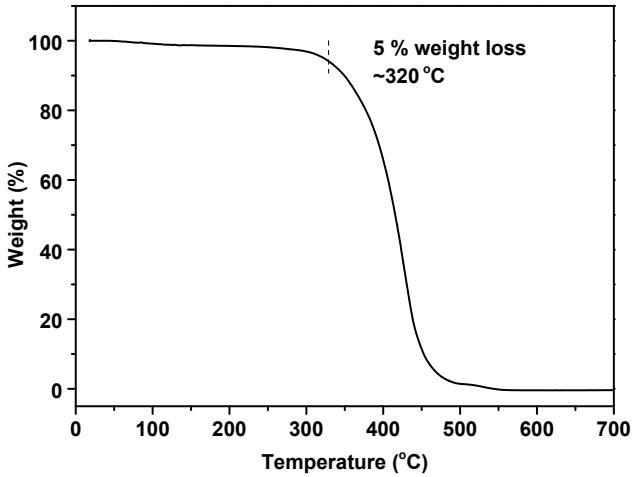


Fig. S5 TGA result of the PCL-PU elastomer with 0.5 wt‰ addition of PDPP3T.

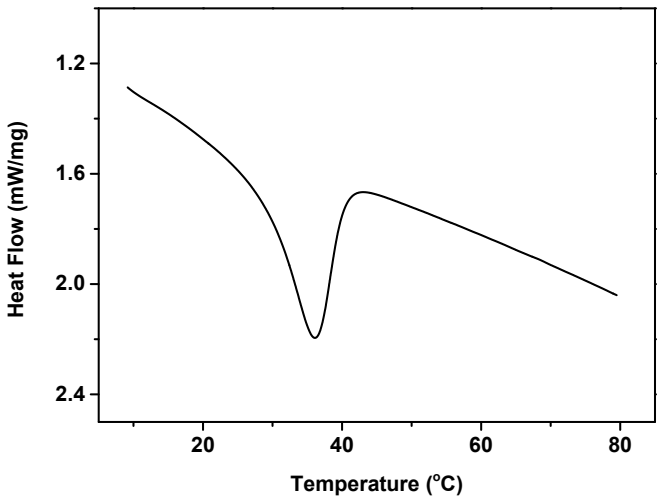


Fig. S6 DSC result of the PCL-PU elastomer with 0.5 wt‰ addition of PDPP3T.

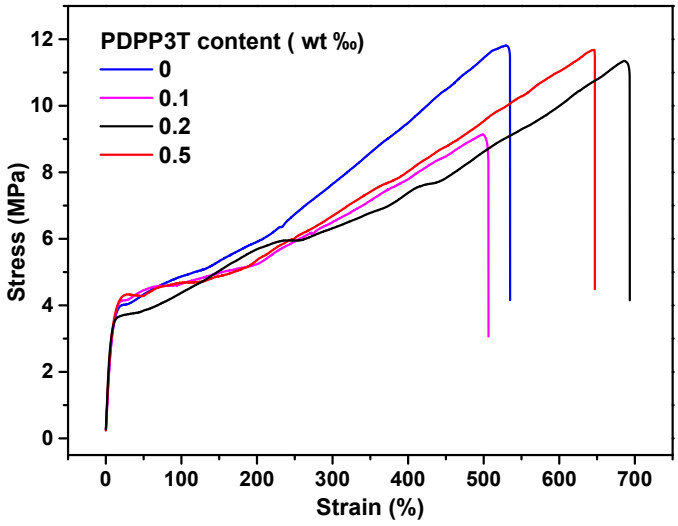


Fig. S7 Tensile curves of PCL-PU elastomers with various additions of PDPP3T.

Table S2 Tensile properties of PCL-PU elastomers with PDPP3T.

PDPP3T (wt‰)	Young's Modulus (MPa)	Stress of Break (σ_b, MPa)	Strain of Break (ε_b, %)
0	34.5±2.5	11.8±0.8	530±30
0.1	38.2±2.5	8.4±1.2	500±20
0.2	43.5±2.0	12.4±1.0	700±30
0.5	41.5±1.5	12.8±1.0	650±30

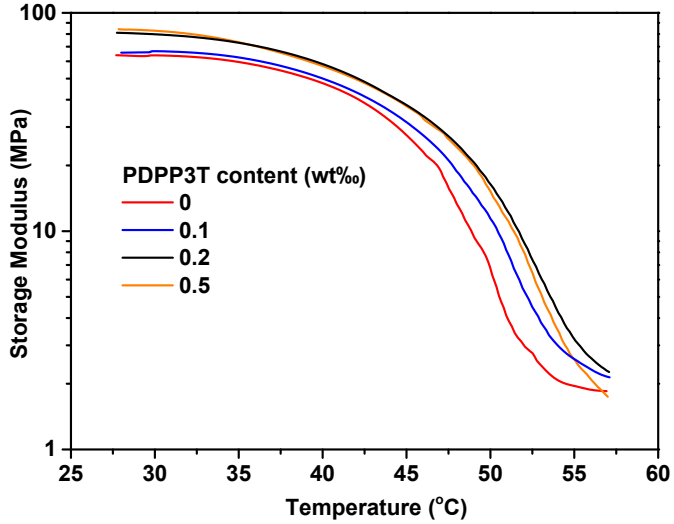


Fig. S8 Dynamic mechanical analysis of PCL-PU elastomers with various additions of PDPP3T polymer under strain 0.5% and frequency 1.0 Hz.

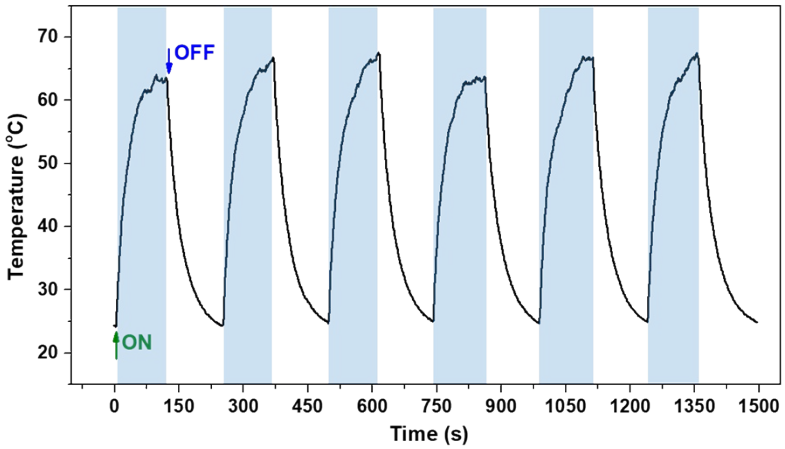


Fig. S9 Cyclic photothermal effect of the PCL-PU elastomer with 0.5 wt‰ addition of PDPP3T under on-off cycles of laser irradiation (808 nm, 0.5 W/cm^2).

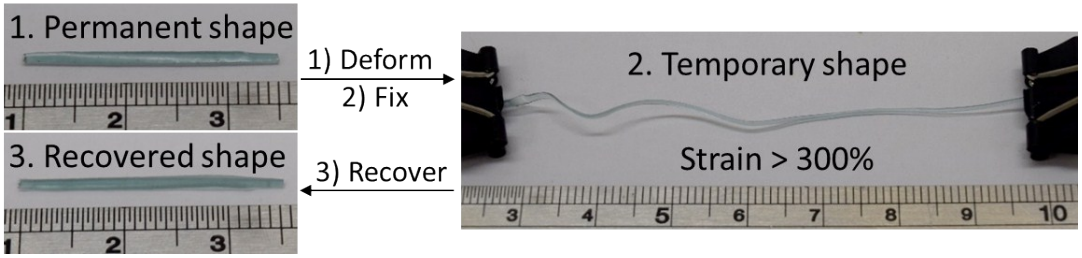


Fig. S10 Shape memory performance of the PCL-PU elastomer with 0.2 wt‰ addition of PDPP3T under laser irradiation; 1) deform at ~45 °C, 2) fix at ~20 °C and 3) recover by laser irradiation (0.5 w/cm^2, 1 min).

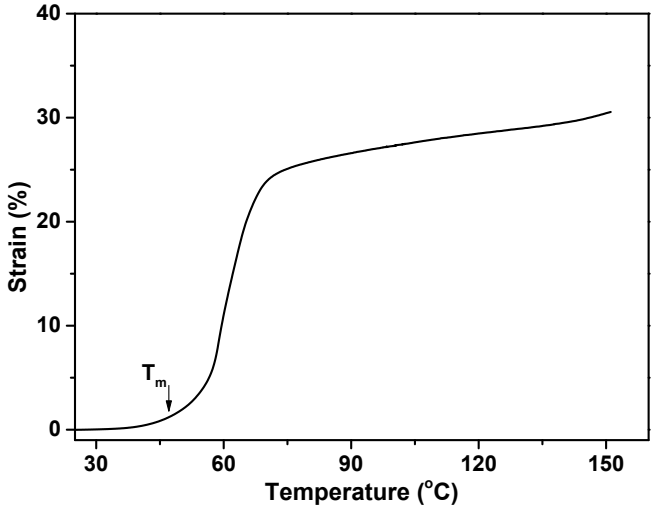


Fig. S11 Dilatometry test of the MED based PCL-PU elastomer with 0.5 wt‰ addition of PDPP3T polymer.

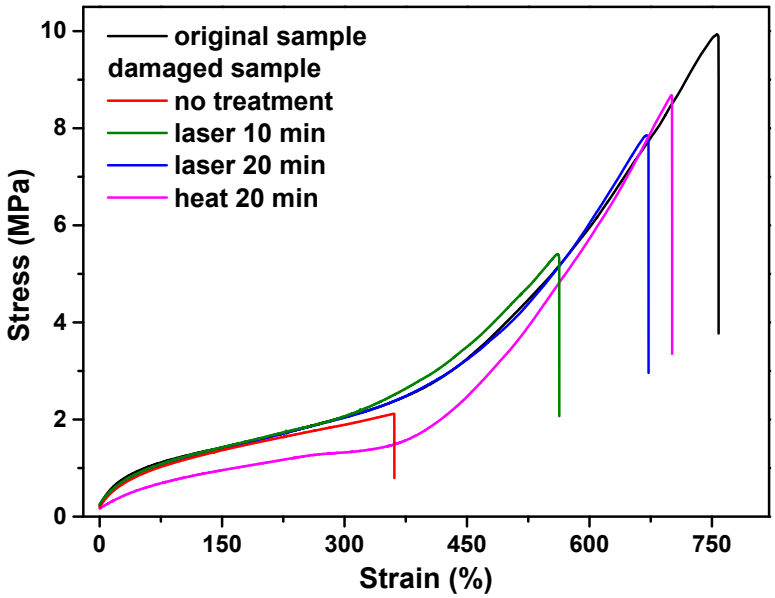


Fig. S12 Tensile curves of the TBED based PCL-PU elastomers with 0.5 wt‰ addition of PDPP3T after self-healing tests under various conditions.

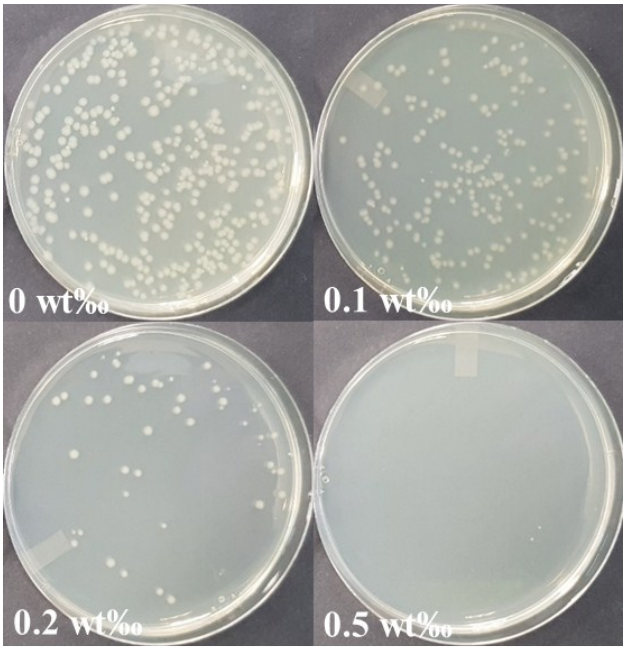


Fig. S13 LB agar plates of *E. coli* seeds which were from surfaces of elastomers with various additions of PDPP3T after laser irradiation (2.0 W/cm^2, 2 min).

4. References

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