

*Electronic Supplementary Information*

**Reprocessable and healable room temperature photoactuators based on a main-chain azobenzene liquid crystalline poly(ester-urea)**

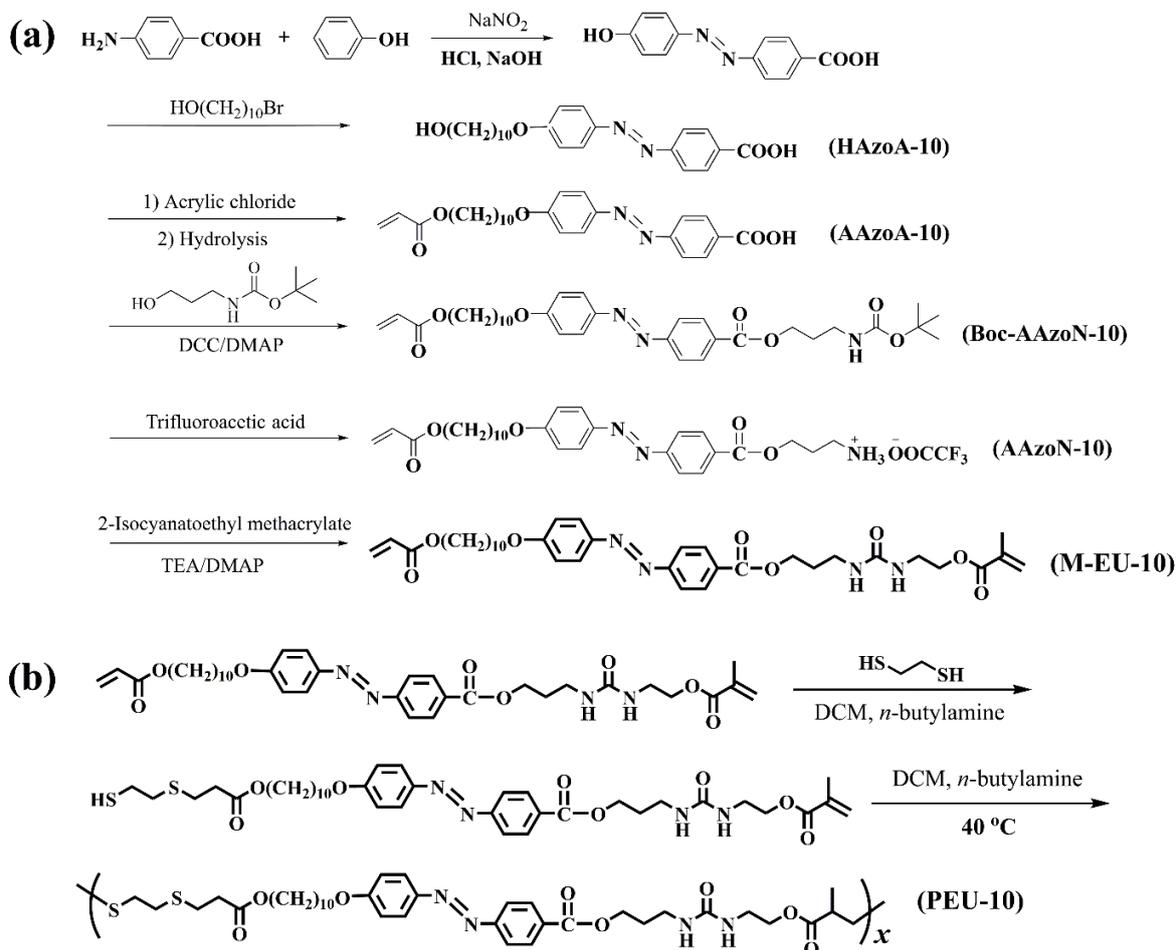
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**Materials**

Tetrahydrofuran (THF, Tianjin Jiangtian Chemicals, 99%) was refluxed over sodium and distilled. Dichloromethane (DCM, Tianjin Jiangtian Chemicals, 99%) was refluxed over calcium hydride and distilled. *N,N*-Dimethylformamide (DMF, Tianjin Jiangtian Chemicals, 99.5%) was dried with anhydrous magnesium sulfate and distilled under vacuum. Triethylamine (TEA, Tianjin Jiangtian Chemicals, 99%) was dried with anhydrous sodium sulfate and distilled. 4-((4-Hydroxy)phenylazo)benzoic acid (HAzoA-10), 4-((4-( $\omega$ -hydroxydecanyloxy)phenylazo)benzoic acid (AAzoA-10), 3-(*tert*-butoxycarbonylamino)-1-propyl 4-((4-( $\omega$ -acryloyloxydecanyloxy))phenylazo)benzoate (Boc-AAzoN-10), and trifluoroacetate salt of 3-amino-1-propyl 4-((4-( $\omega$ -acryloyloxydecanyloxy))phenylazo)benzoate (AAzoN-10) were synthesized according to our previously reported procedures (Scheme S1).<sup>1,2</sup> 3-(*tert*-Butoxycarbonylamino)-1-propanol was prepared following a literature method.<sup>3</sup> 1,2-Ethanedithiol (Shanghai Macklin Biochemical Co., Ltd., 97%), *n*-butylamine (Shanghai Aladdin Biochemical Technology Co., Ltd., 99%), 4-(dimethylamino)pyridine (DMAP, Merck, analytical grade (AR)), *N,N'*-dicyclohexylcarbodiimide (DCC, Tianjin Jiangtian Chemicals, AR), 2-isocyanatoethyl methacrylate [Meryer (Shanghai) Chemical Technology Co., Ltd., 98%], 2,6-di-*tert*-butyl-4-methylphenol (BHT, Tianjin Fine Chemical Co., Ltd., AR), 4-chlorobutanoyl

chloride (Tianjin Heowns Biochem Technologies, 98%), sodium polyacrylate (PAANa, Shanghai Xian-Dinn Biotech Co., Ltd., 50% aqueous solution, weight-average molecular weight: 3000-5000 g/mol) and all the other chemicals were commercially available and used without further purification.



**Scheme S1** (a) Chemical structure and synthetic procedure of the azo monomer M-EU-10. (b) Synthetic procedure for the main-chain azo PEU (PEU-10) via Michael addition polymerization of M-EU-10 and 1,2-ethanedithiol with *n*-butylamine as the catalyst.

### Synthesis of an ester and urea unit-containing azo monomer with both acrylate and methacrylate end-groups (i.e., M-EU-10, Scheme S1a)

To a one-neck round-bottom flask (50 mL) were added AAzoN-10 (537 mg, 0.86 mmol) and dried THF (20 mL). After the solution was bubbled with argon for 15 min in an ice-water bath, TEA (120  $\mu$ L, 0.86 mmol), DMAP (21.1 mg, 0.17 mmol), BHT (15.2 mg, 0.07 mmol; as the polymerization inhibitor) and 2-isocyanatoethyl methacrylate (144.4 mg, 0.93 mmol) were added successively under magnetic stirring. The above solution

was purged with argon for another 15 min in an ice-water bath, sealed, immersed into a water bath at 25 °C, and stirred for 24 h. The mixed solution was then added dropwise into ethyl ether under stirring. The precipitate was collected by centrifugation, washed thoroughly with ethyl ether and distilled water, and then dried at 40 °C under vacuum to the constant weight, leading to orange M-EU-10 (yield: 96%). UV-Vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{L mol}^{-1} \text{ cm}^{-1}$ ) = 361 (24660), around 450 nm (not available due to the overlap of the absorption bands). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.20 (d, 2H, Ar-H), 8.02-7.92 (m, 4H, Ar-H), 7.06 (d, 2H, Ar-H), 6.45 (dd, 1H, CH=C-COO-), 6.22-6.13 [m, 2H, C=CH-COO-, CH=C(CH<sub>3</sub>)-COO-], 5.87 (dd, 1H, CH=C-COO-), 5.67-5.61 [m, 1H, CH=C(CH<sub>3</sub>)-COO-], 4.83 (t, 1H, -NH-CO-), 4.73 (t, 1H, -CO-NH-), 4.50 (t, 2H, -CH<sub>2</sub>-O-CO-), 4.30 (t, 2H, -COO-CH<sub>2</sub>-), 4.21 (t, 2H, -CH<sub>2</sub>-O-Ph-), 4.11 (t, 2H, -COO-CH<sub>2</sub>-), 3.57 (dd, 2H, -CH<sub>2</sub>-N-), 3.41 (dd, 2H, -N-CH<sub>2</sub>-), 2.10- 2.01 (m, 2H, -C-CH<sub>2</sub>-C-), 1.99 (s, 3H, -CH<sub>3</sub>), 1.93-1.33 [m, 16H, -(CH<sub>2</sub>)<sub>8</sub>-].

## Characterization

<sup>1</sup>H NMR spectra of the samples were recorded on a Bruker Avance III 400 MHz NMR spectrometer.

Thermogravimetric analyses (TGA) were performed on a Netzsch TG 209 instrument under nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>.

Differential scanning calorimetry (DSC, Netzsch 200 F3) was used to study thermal transitions of PEU-10 at a heating/cooling rate of 10 °C min<sup>-1</sup> under nitrogen. The temperature and heat flow scale were calibrated with standard materials including indium (70-190 °C), tin (150-270 °C), zinc (350-450 °C), bismuth (190-310 °C) and mercury (-100 to 0 °C) in different temperature ranges. The glass transition temperatures ( $T_g$ ) of the polymer were determined as the midpoints of the step changes of the heat capacities, while the phase transition temperatures were measured from the maximum/minimum of the endothermic/exothermic peaks.

The liquid crystalline texture of PEU-10 and the alignment states of PEU-10 fibers and films were observed by using an Olympus BX51 polarizing optical microscope (POM, with crossed polarizer and analyzer) equipped with a Linksys 32 THMSE600 hot stage and a digital camera (micropublisher 5.0 RTV).

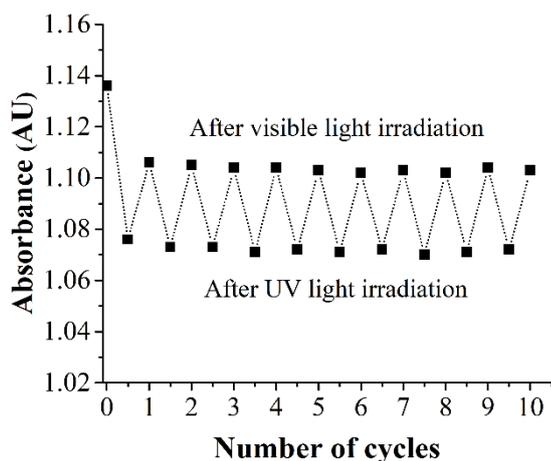
X-ray diffraction (XRD) pattern of PEU-10 was recorded on a Rigaku SmartLab 9 kW X-ray diffractometer with Cu K $\alpha$  radiation (1.5406 Å) at room temperature. The measured  $2\theta$  ranged from 0.7° to 40° and the scanning rate was 2° min<sup>-1</sup>. PEU-10 sample for XRD measurement was prepared through first heating it to 180 °C at a heating rate of 10 °C min<sup>-1</sup>, then cooling it to 81 °C at a cooling rate of 10 °C min<sup>-1</sup>, annealing it at 81 °C for 1 h, and finally cooling it in liquid nitrogen.

The molecular weights and molar-mass dispersities ( $D$ ) of PEU-10 and PEE-10 were characterized with a gel permeation chromatography (GPC) equipped with an Agilent 1200 series manual injector, an Agilent 1200 HPLC pump, an Agilent 1200 refractive index detector, and three Agilent PLgel columns (Mixed-C, 10<sup>4</sup> Å and 500 Å) with 200-3 M, 4-400 K, and 500-20 K molecular ranges. DMF (containing 0.1 % LiBr) was used as the mobile phase at a flow rate of 1.0 mL/min, and the calibration curve was obtained by using polystyrene standards.

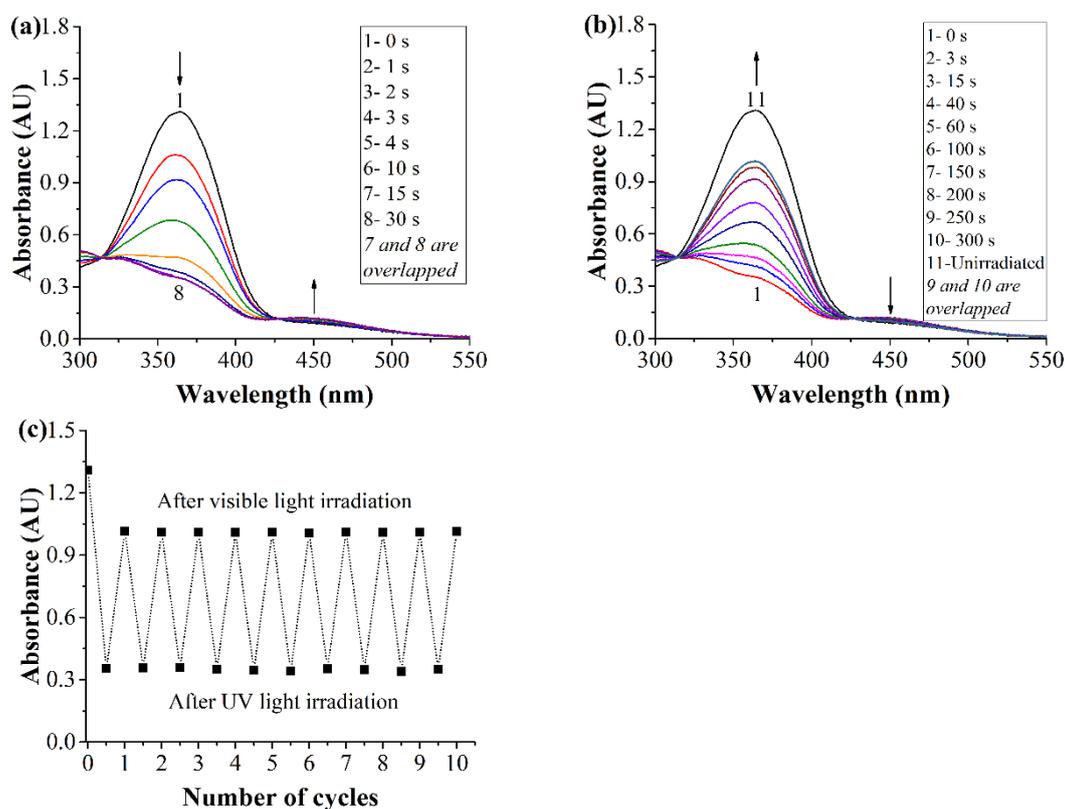
A UV-vis scanning spectrophotometer (TU1900, Beijing Purkinje General Instrument Co., Ltd) was used to measure the UV-vis spectra of the samples and characterize the photoisomerization processes of both a PEU-10 film and a PEU-10 solution.

A PEU-10 thin film was cast from a PEU-10 solution in chloroform (3.3 mg/mL, 100  $\mu$ L) on a clean quartz glass plate (12  $\times$  45 mm). After the solvent was evaporated slowly at ambient temperature for 12 h, a transparent light yellow film was formed on the quartz glass plate. The thickness ( $l$ ) of the film is estimated to be 611 nm by using the equation  $l = VC/\rho S$ , where  $V$  is the volume of PEU-10 solution cast on the quartz glass plate,  $C$  the concentration of PEU-10 solution,  $\rho$  the density of the solid PEU-10 film ( $\rho$  is assumed to be 1 g/mL here), and  $S$  the surface area of the quartz glass plate.

The photochemical isomerization of the above PEU-10 thin film and a diluted PEU-10 solution in DMF ( $C = 50 \mu\text{M}$  repeat azo unit of PEU-10) was studied by first irradiating them with 365 nm UV light (90 mW cm<sup>-2</sup>) until their photostationary states were reached. The photostationary PEU-10 film and solution were then irradiated with visible light ( $\lambda > 510$  nm, 35 mW cm<sup>-2</sup>). The UV-vis spectra of the samples were recorded during the above studies (Figs. 3, S1, and S2). The used UV light and visible light were obtained from a high-pressure mercury lamp (USHIO SP-7) by using the corresponding glass filters.

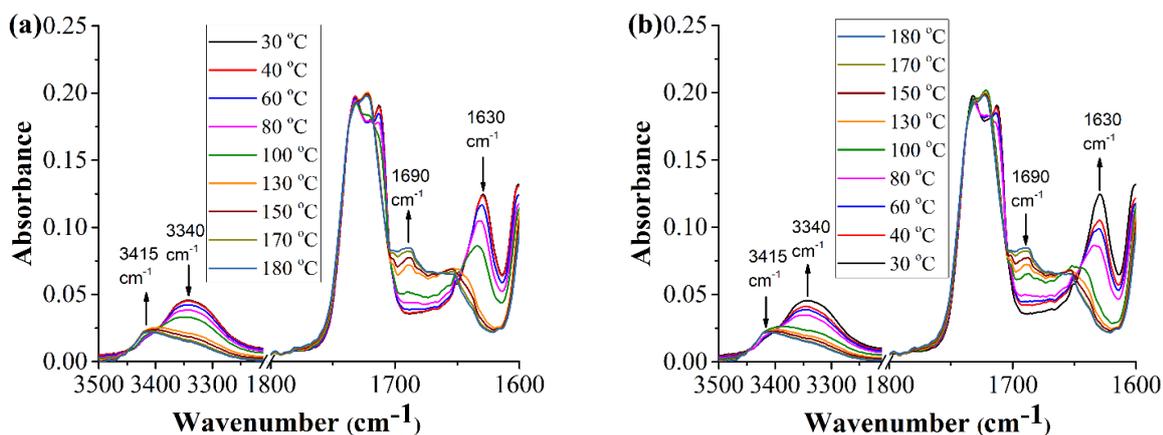


**Fig. S1** UV and visible light-induced photoisomerization cycles of PEU-10 thin film at 25 °C; in each cycle, the polymer film was first irradiated with 365 nm UV light for 15 s and then with visible light ( $\lambda > 510$  nm) for 120 s, respectively.



**Fig. S2** (a,b) UV-vis spectral changes in dependence of time for the diluted PEU-10 solution in DMF ( $C = 50 \mu\text{M}$  repeat azo unit) at 25 °C upon irradiation with 365 nm UV light (a) and upon irradiating the polymer solution at the photostationary state with visible light ( $\lambda > 510$  nm) (b). (c) UV and visible light-induced photoisomerization cycles of the PEU-10 solution at 25 °C; in each cycle, the polymer solution was first irradiated with 365 nm UV light for 15 s and then with visible light ( $\lambda > 510$  nm) for 250 s, respectively.

A Perkin Elmer Frontier FT-IR spectrometer equipped with a VT CELL GS21525 variable temperature sample cell accessory was used to carry out the variable temperature FT-IR measurements. The studied polymer sample was sandwiched between two KBr slides, and its temperature was changed at a rate of  $2\text{ }^{\circ}\text{C min}^{-1}$ . Fig. S3a,b shows the FT-IR spectra of PEU-10 at different temperatures during the heating and cooling processes, respectively.

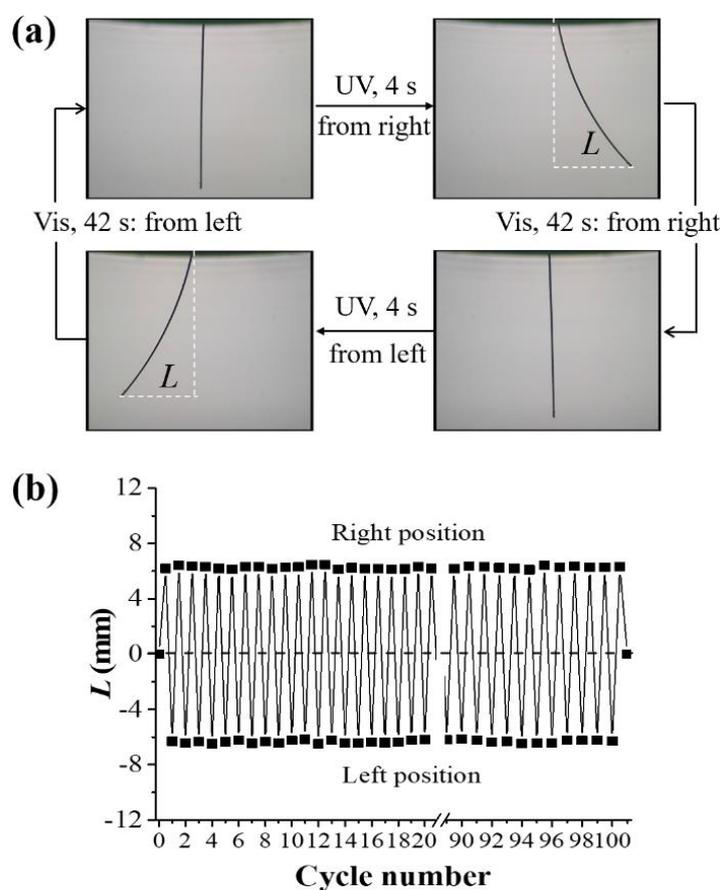


**Fig. S3** FT-IR spectra of PEU-10 at different temperatures during the heating (a) and cooling (b) processes.

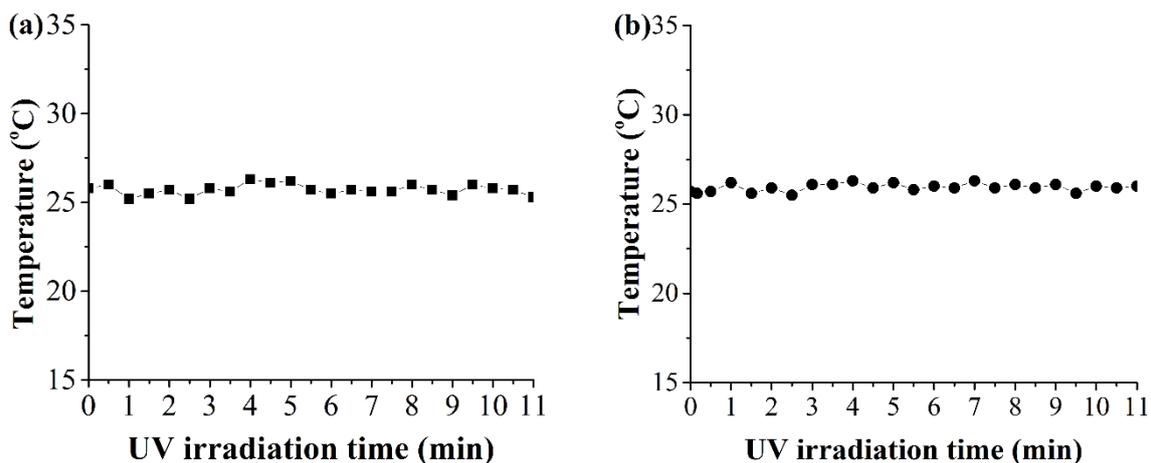
It can be seen from Fig. S3 that two bands around 3415 (very weak shoulder) and 3340  $\text{cm}^{-1}$  (strong peak) are present at 30 °C, which correspond to the “free” and hydrogen-bonded N-H (from urea groups) stretching modes, respectively. Moreover, there also exist two bands around 1690 and 1630  $\text{cm}^{-1}$ , which can be assigned to the “free” and hydrogen-bonded C=O (from urea groups) stretching modes, respectively. The amounts of the “free” N-H and C=O units in the urea groups increased with increasing the temperature (as shown by the increase in the intensities of both the “free” N-H band around 3415  $\text{cm}^{-1}$  and “free” C=O band around 1690  $\text{cm}^{-1}$  and the simultaneous decrease in the intensities of the hydrogen-bonded N-H band around 3340  $\text{cm}^{-1}$  and the hydrogen-bonded C=O band around 1630  $\text{cm}^{-1}$ ), whereas they recovered to the original levels following the temperature decrease. These results revealed that the hydrogen bonds between urea groups could be destroyed by heat. However, the broken hydrogen bonds quickly reformed after cooling to room temperature (as shown by the full recovery of the hydrogen-bonded N-H and C=O bands), which demonstrated that the hydrogen bonding interactions among urea groups are reversible following the temperature change and these hydrogen bonds are of dynamic nature.



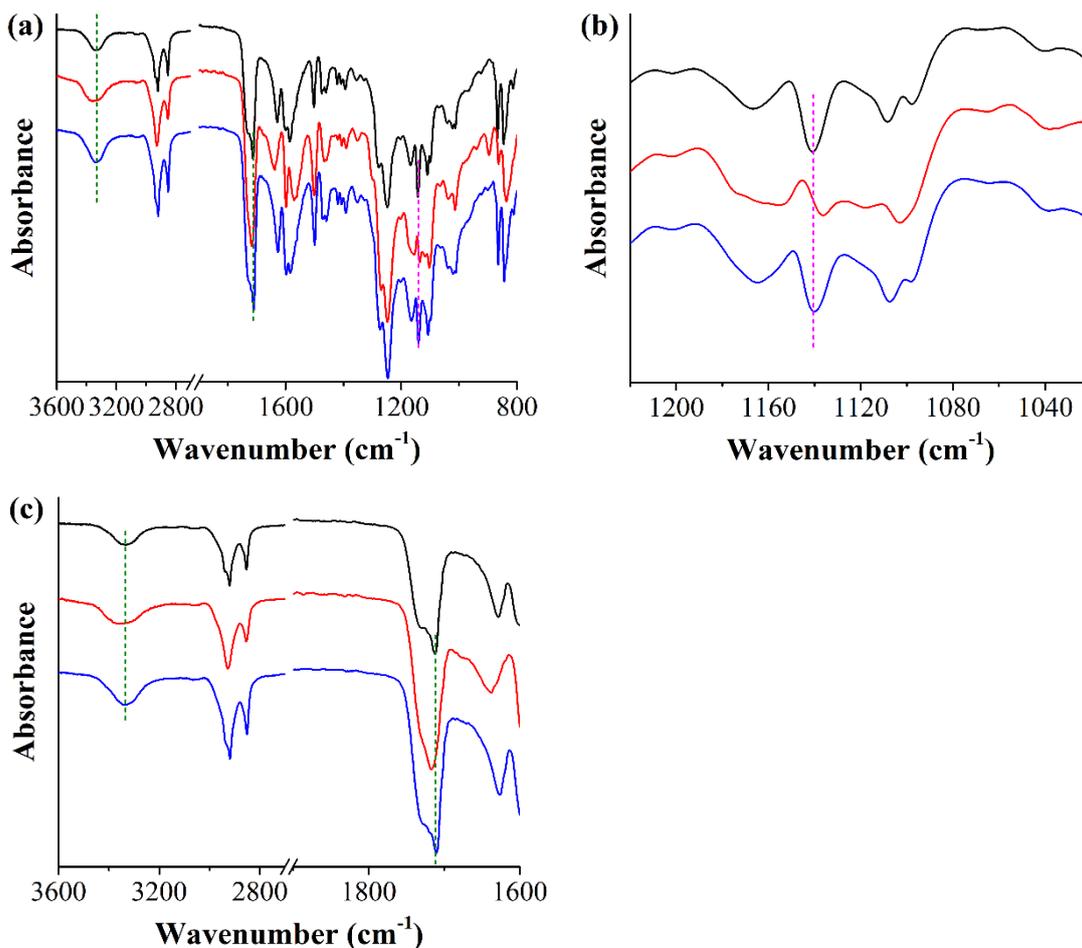
**Fig. S4** Photographs of a free-standing PEU-10 film (prepared via the special melt pressing method) that is transparent (a) and flexible (b) at room temperature.



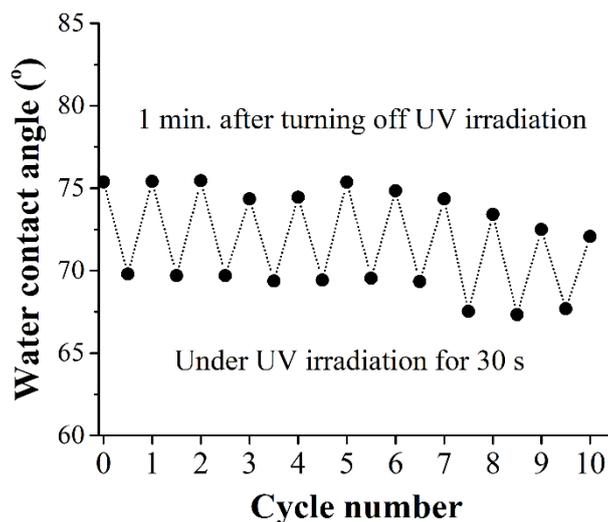
**Fig. S5** (a) Photographs of a PEU-10 fiber that exhibits photoinduced bending and unbending upon irradiation with 365 nm UV light and visible light ( $\lambda > 510$  nm) at 60 °C. (b) The reversible deformation of the PEU-10 fiber characterized by tracing the bent distance from its straight state at 60 °C. The size of the PEU-10 fiber is 11 mm  $\times$  21  $\mu$ m.



**Fig. S6** Time dependence of PEU-10 fiber (a) and film (b) temperatures (as determined by using a Fluke TiS10 Infrared Camera 9Hz (Fluke International Corporation)) under the irradiation of UV light ( $90 \text{ mW cm}^{-2}$ ).



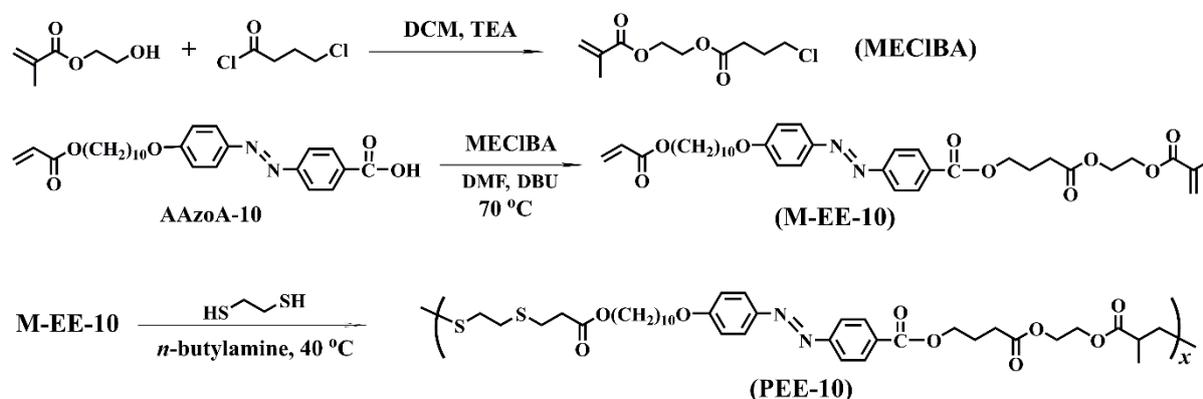
**Fig. S7** FT-IR spectra of the PEU-10 film at the same side under different conditions: the black, red, and blue curves correspond to the PEU-10 film before UV light irradiation, immediately after UV light irradiation for 30 s ( $90 \text{ mW cm}^{-2}$ ), and 1 min after UV light was turned off.



**Fig. S8** Contact angle changes of a PEU-10 film measured under UV light irradiation ( $90 \text{ mW cm}^{-2}$ ) for 30 s and 1 min after turning off UV light alternatively.

### Synthesis and characterization of PEE-10

PEE-10 was prepared via first the synthesis of the azo monomer M-EE-10 and its subsequent Michael addition polymerization with 1,2-ethanedithiol (in a molar ratio of 1:1) in DCM at  $40^\circ\text{C}$  for 24 h under the catalysis of *n*-butylamine. The synthetic route is presented in Scheme S2.



**Scheme S2** Chemical structures and synthetic procedures of the azo monomer M-EE-10 and its corresponding polymer (PEE-10) prepared via Michael addition polymerization.

### Synthesis of 2-(methacryloyloxy)ethyl 4-chlorobutanoate (MECIBA)

To a one-neck round-bottom flask (25 mL) were added HEMA (200 mg, 1.54 mmol), DCM (3 mL), and TEA (230  $\mu\text{L}$ , 1.66 mmol) successively. After the above mixture was cooled to  $0^\circ\text{C}$  in an ice-water bath, a solution of 4-chlorobutryl chloride (210  $\mu\text{L}$ , 1.85 mmol) in dried DCM

(3 mL) was added dropwise into the reaction mixture under magnetic stirring. The reaction mixture was then allowed to take place at 25 °C for 12 h. The reaction mixture was washed successively with saturated aqueous NaHCO<sub>3</sub> solution thrice and saturated aqueous NaCl solution thrice. The organic phase was then dried with anhydrous magnesium sulfate overnight. After filtration, the solvent in the collected organic phase was removed by using an evaporator to dryness, leading to light yellow product with a yield of 92%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 6.17 [s, 1H,  $\underline{\text{CH}}=\text{C}(\text{CH}_3)\text{-COO-}$ ], 5.64 [s, 1H,  $\underline{\text{CH}}=\text{C}(\text{CH}_3)\text{-COO-}$ ], 4.40 (m, 4H, -COO-CH<sub>2</sub>-CH<sub>2</sub>-O-CO-), 3.64 (t, 2H, -CH<sub>2</sub>-Cl), 2.59 (t, 2H, -O-CO-CH<sub>2</sub>-), 2.14 (tt, 2H, -C-CH<sub>2</sub>-C-), 2.00 (s, 3H, -CH<sub>3</sub>).

### ***Synthesis of M-EE-10***

To a solution of AAzoA-10 (150 mg, 0.3 mmol) and DBU (61 μL, 0.4 mmol) in DMF (5 mL) at 25 °C was added MECIBA (117 mg, 0.5 mmol). After the above reaction mixture was magnetically stirred at 70 °C for 12 h, it was poured into distilled water (50 mL). The obtained suspension was then acidified by using hydrochloride (15%) to a pH of 5-6. The precipitation was collected by filtration, washed with water to the neutral pH, and then purified with silica gel chromatography (petroleum ether/ethyl acetate = 1:1 v/v). A yellow product was obtained in a yield of 53%. UV-vis (CHCl<sub>3</sub>): λ<sub>max</sub>/nm (ε/L mol<sup>-1</sup> cm<sup>-1</sup>) = 361 (21430), around 450 (not available due to the overlap of the absorption bands). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.09 (d, 2H, Ar-H), 7.92-7.81 (m, 4H, Ar-H), 6.95 (d, 2H, Ar-H), 6.34 (dd, 1H, CH=C-COO-), 6.11 – 6.00 [m, 2H, C=CH-COO-,  $\underline{\text{CH}}=\text{C}(\text{CH}_3)\text{-COO-}$ ], 5.75 (dd, 1H, CH=C-COO-), 5.54-5.49 [m, 1H,  $\underline{\text{CH}}=\text{C}(\text{CH}_3)\text{-COO-}$ ], 4.34 (t, 2H, -CH<sub>2</sub>-O-CO-), 4.32-4.25 (m, 4H, -COO-CH<sub>2</sub>-C-), 4.10 (t, 2H, -CH<sub>2</sub>-O-Ph-), 4.00 (t, 2H, -COO-CH<sub>2</sub>-), 2.49 (t, 2H, -C-CH<sub>2</sub>-COO-), 2.13-2.03 (m, 2H, -C-CH<sub>2</sub>-C-), 1.88 (s, 3H, -CH<sub>3</sub>), 1.81-1.13 [m, 16H, -(CH<sub>2</sub>)<sub>8</sub>-].

### ***Synthesis of PEE-10***

PEE-10 was prepared via Michael addition polymerization of M-EE-10 and 1,2-ethanedithiol following the similar procedure as PEU-10 (yield: 65%).

### ***<sup>1</sup>H NMR and GPC characterization of PEE-10***

Fig. S9 shows the <sup>1</sup>H NMR spectra of M-EE-10 and PEE-10. It can be seen clearly that PEE-

10 also has methacrylate end-group instead of acrylate end-group, just as PEU-10. The  $M_{n,NMR}$  of PEU-10 was derived to be 8800 g/mol through comparing the integral of the peak  $q'$  ( $S_{q'}$ ) around 5.5 ppm for one proton in the methacrylate end-group and that of the peak  $g$  ( $S_g$ ) around 6.9 ppm for the aromatic protons in its  $^1H$  NMR spectrum (Fig. S9b;  $M_{n,NMR} = [(S_g/2)/S_{q'}] \times M_{n,unit}$ , where  $M_{n,unit}$  refers to the molecular weight of the repeat unit of PEE-10).

PEE-10 was also characterized with GPC, and its  $M_{n,GPC}$  and  $D$  were determined to be 10500 g/mol and 1.4, respectively

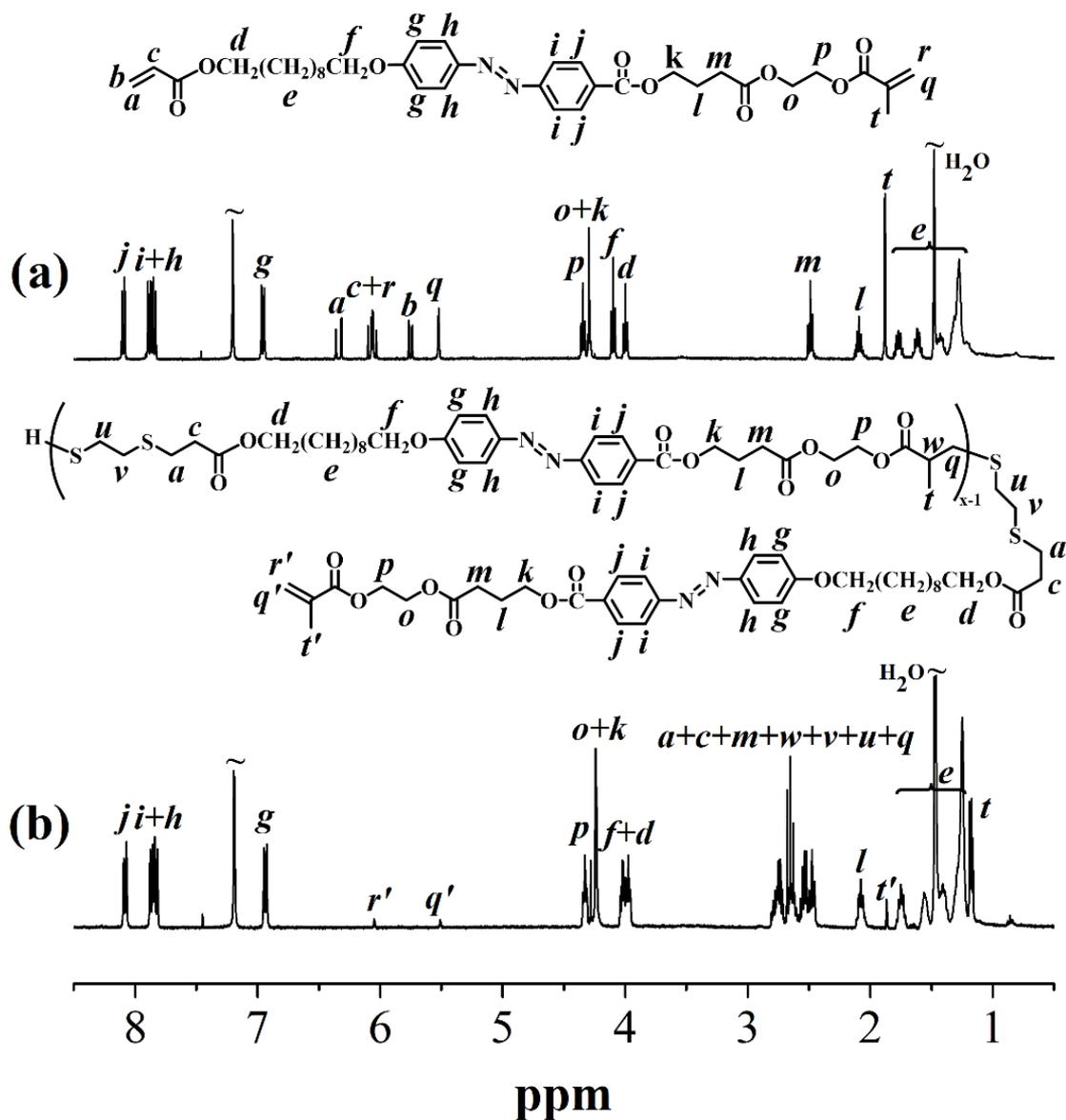
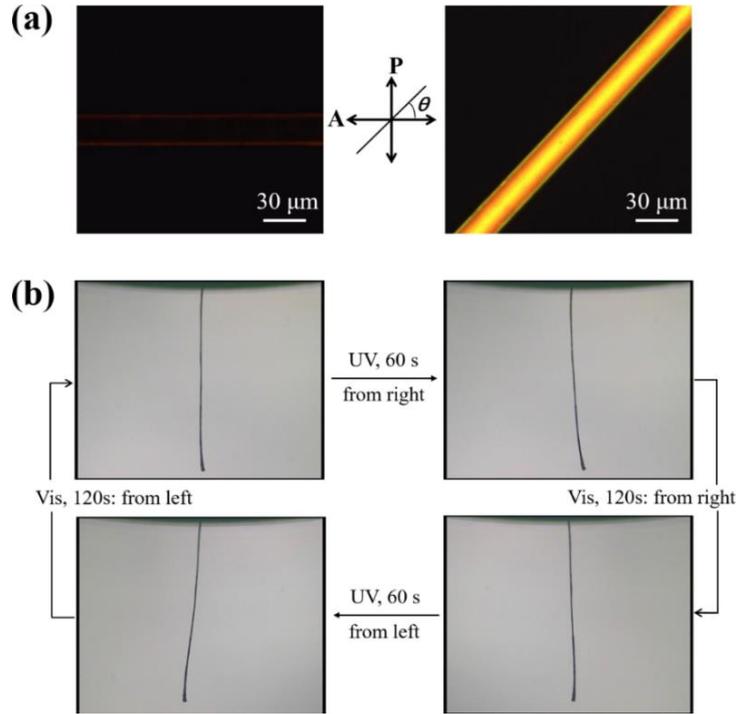
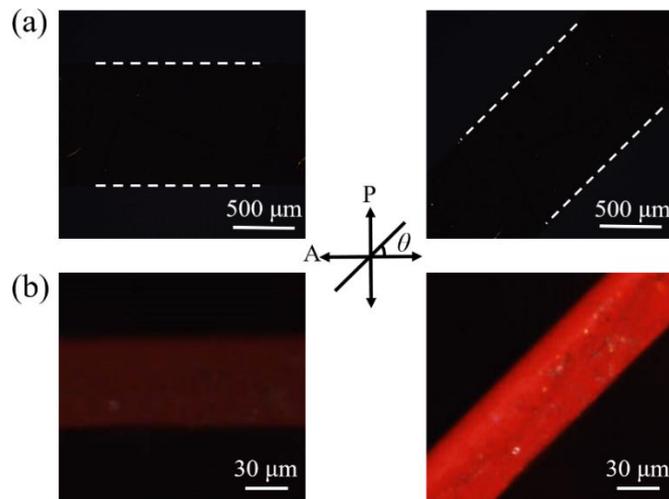


Fig. S9  $^1H$  NMR spectra of M-EE-10 (a) and PEE-10 (b) in  $CDCl_3$ .



**Fig. S10** (a) POM images of the textures of a PEE-10 fiber taken at ambient temperature. Sample angle to the analyzer:  $\theta = 0^\circ$  (left);  $\theta = 45^\circ$  (right). (b) Photographs of a PEE-10 fiber that hardly exhibits photodeformation upon irradiating with 365 nm UV light ( $90 \text{ mW cm}^{-2}$ ) and visible light ( $\lambda > 510 \text{ nm}$ ,  $35 \text{ mW cm}^{-2}$ ) at  $25^\circ\text{C}$ . PEE-10 fiber was fabricated via the melt spinning method similarly as for PEU-10 fiber except changing the spinning temperature to  $70^\circ\text{C}$ . The size of PEE-10 fiber is  $10 \text{ mm} \times 21 \mu\text{m}$ .



**Fig. S11** POM images of the textures of the healed PEU-10 film (for a healing time of 48 h) [with its surface perpendicular to the incident light (a) and its lateral surface perpendicular to the incident light (b)] taken at room temperature. Sample angle to the analyzer:  $\theta = 0^\circ$  (left);  $\theta = 45^\circ$  (right).

**Table S1** Mechanical properties of the original PEU-10 films and the reconnected ones after healing at 60 °C for different time

| Entry | Sample <sup>a</sup> | Elastic modulus (MPa) | Yield strength (MPa) | Elongation at break (%) |
|-------|---------------------|-----------------------|----------------------|-------------------------|
| 1     | Original            | 194.1 ± 20.6          | 21.6 ± 1.6           | 40.2 ± 5.7              |
| 2     | 48 h                | 129.1 ± 14.3          | 18.7 ± 2.0           | 25.6 ± 3.8              |
| 3     | 36 h                | 125.2 ± 13.4          | 17.9 ± 1.9           | 22.8 ± 3.5              |
| 4     | 24 h                | 117.5 ± 12.8          | 16.3 ± 1.4           | 21.3 ± 2.5              |
| 5     | 12 h                | 92.8 ± 10.1           | 11.7 ± 0.9           | 14.1 ± 1.7              |
| 6     | 6 h                 | 64.1 ± 4.3            | 5.0 ± 0.6            | 7.9 ± 0.8               |

<sup>a</sup> The sample refers to the original PEU-10 film (entry 1) or the reconnected PEU-10 film after healing at 60 °C for a certain time (entries 2-6).

Supplementary Video

### Movie S1.

A movie clip that demonstrates a remotely controlled circuit by using a PEU-10 film (with attached filter paper slips soaked with aqueous NaCl solution on its both sides) as photoswitch.

### References

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- 2 H. Zhang, W. Huang, C. Li and B. He, *Acta Polym. Sin.*, 1999, **1**, 48-54.
- 3 B. E. Kane, M. K. Grant, E. E. El-Fakahany and D. M. Ferguson, *Bioorg. Med. Chem.*, 2008, **16**, 1376-1392.