**Electronic Supplementary Information**

**Facile preparation of recyclable photodeformable azobenzene polymer fibers with chemically crosslinked networks**

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**Materials**

Dichloromethane (CH$_2$Cl$_2$, Tianjin Jiangtian Chemicals, analytical grade (AR)) and chloroform (CHCl$_3$, Tianjin Chemical Reagents Wholesale Co., AR) were refluxed over calcium hydride and then distilled. Anisole (Tianjin Fuchen Chemical Reagent Factory, AR) was purified by being washed with an aqueous solution of sodium hydroxide (2 M, its volume is 2-fold of anisole) thrice and distilled water thrice successively, dried with anhydrous calcium chloride overnight, and then distilled under vacuum. Azobisisobutyronitrile (AIBN, Sinopharm Chemical Reagent Co., Ltd, AR) was recrystallized from ethanol before use. Methyl methacrylate (MMA, Heowns Biochem Technologies, LLC, Tianjin, AR) was purified by distillation under vacuum. Thionyl chloride (Tianjin Jiangtian Chemicals, 99.5%) was purified by distillation just prior to use. Acrylic chloride was prepared by the reaction between acrylic acid (Tianjin Damao Chemical Reagent Factory, 99.5%) and benzoyl chloride (Tianjin Jiangtian Chemicals, 98%). 4-((4-Hydroxy)phenylazo)benzoic acid, 4-((4-(ω-hydroxydecyloxy))phenylazo)benzoic acid (HAzoA-10), and 4-((4-(ω-acryloyloxydecyloxy))phenylazo)benzoic acid (AAzoA-10) were synthesized according to our previously reported procedure (Scheme S1) (H. Zhang, W. Huang, C. Li and B. He, Acta Polym. Sin., 1999, 1, 48). 4-(Dimethylamino)pyridine (DMAP, Merck, AR), N,N'-dicyclohexylcarbodiimide (DCC, Tianjin Jiangtian Chemicals, AR), 2-bromoethanol (Heowns Biochem Technologies, LLC, Tianjin, AR), potassium ethyl xanthogenate (Heowns Biochem Technologies, LLC, Tianjin, AR), n-butylamine (Tianjin Kemiou Chemical Reagent Co., 99%), aqueous solution of hydrogen peroxide (H$_2$O$_2$)(30 wt.%, Heowns Biochem Technologies, LLC, Tianjin, AR), tributylphosphine (TBP, Heowns Biochem Technologies, LLC, Tianjin, AR), and all the other chemicals were commercially available and used without further purification.
Scheme S1  Synthetic route and chemical structures of M10-PT, HP10-PT, CP10-PT-x (x = 19%, 32%, 50%, 66%), HP10-T, CP10-T-x (x = 19%, 32%, 50%, 66%), and PMMA.

Synthesis of S-(2-hydroxylethyl)-O-ethyl dithiocarbonate (Scheme S1)

S-(2-Hydroxylethyl)-O-ethyl dithiocarbonate was synthesized following a literature procedure (R. Nicolaÿ, Macromolecules, 2012, 45, 821): Potassium ethyl xanthogenate (10.77 g, 67.186 mmol) was first dissolved in acetone (42 mL). To this solution was added dropwise a solution of 2-bromoethanol (6.96 g, 55.693 mmol) in acetone (18 mL). After being magnetically stirred at ambient temperature for 12 h, the reaction mixture was filtered and the filtrate was evaporated to remove the solvent. The obtained solid was dissolved in CHCl₃ (100 mL) and the resulting solution was washed with deionized water and an aqueous solution of sodium chloride (10 wt%), dried with anhydrous magnesium sulphate overnight, and then evaporated to dryness to afford a yellow liquid (yield: 93%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 4.69-4.60 (q, 2H, -(C=S)OCH₂-), 3.90-3.84 (t, 2H, HOCH₂-), 3.38-3.31 (t, 2H, -(C=S)SCH₂-), 1.46-1.38 (t, 3H, -CH₃).
Synthesis of 2-((ethoxycarbonothioyl)thio)ethyl 4-((4-(ω-acryloyloxydecyloxy))phenylazo) benzoate (M10-PT) (Schemes S1 and 1a)

AAzoA-10 (5.30 g, 11.712 mmol), S-(2-hydroxylethyl)-O-ethyl dithiocarbonate (2.34 g, 14.074 mmol), and DMAP (0.144 g, 1.176 mmol) were dissolved in dried CH₂Cl₂ (80 mL) and the solution was cooled down to 0 °C. To this mixture was added dropwise a solution of DCC (2.42 g, 11.76 mmol) in dried CH₂Cl₂ (30 mL) under stirring. After being magnetically stirred at ambient temperature for 24 h, the reaction mixture was filtered and the filtrate was evaporated to dryness to afford an orange red viscous liquid. The resulting crude product was purified with silica gel column chromatography by using a mixture of petroleum ether, CH₂Cl₂, and ethyl acetate (10:1:0.1 v/v) as the eluent to provide an orange product (yield: 50%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.19-8.14 (d, 2H, Ar-H), 7.97-7.87 (d, 4H, Ar-H), 7.04-6.98 (d, 2H, Ar-H), 6.43-6.35 (d, 1H, CH=C-COO-), 6.16-6.07 (q, 1H, C=CH-COO-), 5.83-5.78 (d, 1H, CH=C-COO-), 4.71-4.64 (q, 2H, -(C=S)OCH₂-), 4.62-4.56 (t, 2H, -ArCOOCH₂-), 4.18-4.13 (t, 2H, -CH₂OAr-), 4.08-4.03 (t, 2H, C=C-COOCH₂-), 3.59-3.53 (t, 2H, -(C=S)SCH₂-), 1.87-1.28 (m, 19H, -(CH₂)₈- and -CH₃).

Synthesis of side-chain polymers bearing pendant azo mesogens with a protected thiol substitutent (Schemes S1 and 1b)

Synthesis of side-chain homopolymer bearing pendant azo mesogens with a protected thiol substitutent (i.e., HP10-PT)

For convenience, the homopolymer of M10-PT is named as HP10-PT, where HP10 refers to the homopolymer with a flexible spacer of 10 methylene unit and PT refers to the protected thiol group. HP10-PT was prepared via the conventional free radical polymerization of M10-PT as follows: M10-PT (300.10 mg, 0.500 mmol), AIBN (2.18 mg, 0.013 mmol), and freshly distilled anisole (3.6 mL) were added into a one-neck round-bottom flask (10 mL) and a clear solution was obtained after magnetic stirring. After being purged with argon for 20 min in an ice bath, the reaction system was sealed and immersed into a thermostated oil bath at 70 °C and magnetically stirred for 24 h. After being cooled down to the room temperature, the reaction solution was added dropwise into diethyl ether (50 mL) under stirring. The precipitate was collected by centrifugation, washed thoroughly with diethyl ether until no monomer was detectable with thin layer chromatography. Finally, the product was dried at 30 °C under vacuum for 24 h to provide the orange solid product (yield: 32%, entry 1 in Table S1).
Table S1 Characterization and thermal transition data of side-chain polymers bearing azo mesogens with a protected thiol substituent.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample $^a$</th>
<th>Initial azo monomer content in the monomer feed (mol%)</th>
<th>Azo content in the polymer (mol%) $^b$</th>
<th>Yield (%)</th>
<th>$M_{n,GPC}$ $^c$</th>
<th>$D$ $^c$</th>
<th>Thermal transition T (°C) $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HP10-PT</td>
<td>100</td>
<td>100</td>
<td>32</td>
<td>8550</td>
<td>1.11</td>
<td>G 35 S 112 I $^e$ I 110 S 29 G $^f$</td>
</tr>
<tr>
<td>2</td>
<td>CP10-PT-66%</td>
<td>80</td>
<td>66</td>
<td>45</td>
<td>10700</td>
<td>1.19</td>
<td>G 20 S 90 I $^e$ I 91 S 16 G $^f$</td>
</tr>
<tr>
<td>3</td>
<td>CP10-PT-50%</td>
<td>60</td>
<td>50</td>
<td>51</td>
<td>12700</td>
<td>1.42</td>
<td>G 19 S 78 I $^e$ I 80 S 15 G $^f$</td>
</tr>
<tr>
<td>4</td>
<td>CP10-PT-32%</td>
<td>40</td>
<td>32</td>
<td>72</td>
<td>14900</td>
<td>1.45</td>
<td>G 25 S 52 I $^e$ I 59 S 21 G $^f$</td>
</tr>
<tr>
<td>5</td>
<td>CP10-PT-19%</td>
<td>20</td>
<td>19</td>
<td>81</td>
<td>16300</td>
<td>1.45</td>
<td>G 44 $^c$ G 38 $^f$</td>
</tr>
<tr>
<td>6</td>
<td>PMMA</td>
<td>0</td>
<td>0</td>
<td>84</td>
<td>18000</td>
<td>1.40</td>
<td>G 119 $^c$ G 114 $^f$</td>
</tr>
</tbody>
</table>

$^a$ HP10-PT refers to the homopolymer of M10-PT, CP10-PT-x ($x = 66\%, 50\%, 32\%, 19\%$) refer to the copolymers of MP10-PT and MMA with different azo contents, and PMMA refers to the homopolymer of MMA. $^b$ The molar percentage of the azo unit in the polymers determined by $^1$H NMR. $^c$ Number-average molecular weights ($M_{n,GPC}$) and molar-mass dispersities ($D$) of the polymers measured by GPC using PS standards. $^d$ G = glassy; S = Smectic; I = isotropic. $^e$ DSC second heating scan under nitrogen (10 °C min$^{-1}$). $^f$ DSC first cooling scan under nitrogen (-10 °C min$^{-1}$).

Synthesis of side-chain copolymers bearing pendant azo mesogens with a protected thiol substituent (i.e., CP10-PT-x)

The copolymers of M10-PT and MMA are named as CP10-PT-x, where CP10-PT refers to the copolymer of M10-PT and MMA and x the molar percentage of the azo unit incorporated into the copolymers determined by $^1$H NMR (Fig. S1) by using the following equation:

$$x = (S_m/k)/[S_{m+k}/4 + (S_{1+p} - S_m/k)/3]$$

where $S_{m+k}$ and $S_{1+p}$ refer to the integral of the peaks between 4.49 and 4.73 ppm and that of the peaks between 3.43 and 3.75 ppm, respectively.

CP10-PT-x were prepared via the conventional free radical copolymerization of M10-PT and MMA. A typical procedure for the synthesis of CP10-PT-50% is presented as follows: M10-PT (300.04 mg, 0.500 mmol), MMA (35 μL, 0.330 mmol), AIBN (4.15 mg, 0.025 mmol), and freshly distilled anisole (3 mL) were added into a one-neck round-bottom flask (10 mL) and a clear solution was obtained after magnetic stirring. The reaction mixture was bubbled with...
argon for 20 min in an ice bath and the polymerization was then allowed to take place under argon atmosphere at 70 °C for 24 h under stirring. After being cooled down to the room temperature, the reaction mixture was added dropwise into diethyl ether (50 mL) under stirring. The precipitate was collected by centrifugation, washed with diethyl ether until no monomer was detectable with thin layer chromatography. Finally, the product was dried at 30 °C under vacuum for 24 h to provide the orange yellow solid product (yield: 51%, entry 3 in Table S1).

The other azo copolymers (i.e., CP10-PT-x, x = 66%, 32%, 19%, orange yellow color) were prepared following the similar procedure as for CP10-PT-50% (entries 2, 4, and 5 in Table S1).

**Synthesis of PMMA (i.e., the homopolymer of MMA)**

PMMA was prepared via the conventional free radical polymerization of MMA as follows: MMA (106 μL, 0.999 mmol), AIBN (5.12 mg, 0.031 mmol), and freshly distilled anisole (3.5 mL) were added into a one-neck round-bottom flask (10 mL) and a clear solution was obtained after magnetic stirring. The reaction mixture was bubbled with argon for 20 min in an ice bath and the polymerization was then allowed to take place under argon atmosphere at 70 °C for 24 h under stirring. After being cooled down to the room temperature, the reaction mixture was added dropwise into diethyl ether (50 mL) under stirring. The precipitate was collected by centrifugation, washed with diethyl ether, and dried at 30 °C under vacuum for 48 h to provide PMMA (yield: 84%, entry 6 in Table S1).

**Synthesis of side-chain polymers with thiol-substituted azo mesogens (Schemes S1 and 1b)**

The side-chain polymers with thiol-substituted azo mesogens (i.e., HP10-T, CP10-T-x) were readily obtained by treating those bearing protected thiol-substituted azo mesogens (i.e., HP10-PT, CP10-PT-x) with n-butylamine under mild conditions. A small amount of TBP was added into the reaction system to prevent the oxidation of thiol groups. A typical procedure for the synthesis of CP10-T-50% is shown as follows: To a solution of CP10-PT-50% (79.90 mg, the amount of the protected thiol group is 0.114 mmol) in CHCl₃ (3 mL) was added TBP (0.14 μL) and n-butylamine (33 μL). After being purged with argon for 5 min, the reaction system was sealed and immersed into a water bath at 30 °C. After the reaction took place for 5 h under magnetic stirring, the reaction mixture was precipitated into diethyl ether. The resulting solid was collected by centrifugation, washed with diethyl ether, and then dried at 30 °C under vacuum for 24 h, leading to an orange yellow solid product (yield: 96%).

HP10-T (orange color) and CP10-T-x (x = 66%, 32%, and 19%, orange yellow color) were also prepared by treating their corresponding polymers bearing protected thiol-substituted azo mesogens with n-butylamine similarly, with their yields being 96%, 97%, 97%, and 95%, respectively.
The chemical structures of the above-obtained side-chain polymers with thiol-substituted azo mesogens were confirmed with $^1$H NMR (Fig. S2).

**Fabrication of the uncrosslinked fibers for side-chain polymers with thiol-substituted azo mesogens**

The azo polymer fibers were fabricated by using the simple melt spinning method. A typical procedure for the generation of CP10-T-50% fibers is presented as follows: About 2 mg of CP10-T-50% was placed onto a glass slide heated to 140 °C by using a hot stage (IKA, C-MAG HP 7). After the sample became completely melted, the fibers were drawn by dipping the tip of a metallic tweezer into the melted sample and pulling it quickly.

The CP10-T-32% and CP10-T-19% fibers were fabricated similarly as for CP10-T-50% fibers, except that their spinning temperatures were changed to 145 and 150 °C, respectively.

**Preparation of the post-crosslinked azo polymer fibers**

A typical post-crosslinking procedure is presented as follows: Some uncrosslinked CP10-T-50% fibers were immersed into a mixture of an aqueous solution of H$_2$O$_2$ (30 wt.%) and methanol (a non-solvent for the polymer) (1:1 v/v) at 25 °C for 2 h. After being washed with methanol and dried at ambient temperature under vacuum for 48 h, the post-crosslinked fibers were obtained and subsequently used for the photodeformation studies.

All the other post-crosslinked azo polymer (CP10-T-32% and CP10-T-19%) fibers were prepared following the same procedure.

**Recyclability of the post-crosslinked azo polymer fibers**

Some post-crosslinked CP10-T-50% fibers were immersed into a solution of TBP in CHCl$_3$ (0.032 mmol/L, 1 mL) at ambient temperature. A clear orange yellow solution was obtained after the above mixture was gently incubated for 2 h, which was then poured into diethyl ether (10 mL) to precipitate the azo polymer. After being dried at 30 °C under vacuum for 24 h, the resulting orange yellow product was characterized with FT-IR (Fig. 2d) and $^1$H NMR (Fig. S9b).

The recycled azo polymer was also used to reconstruct the post-crosslinked fibers, following the procedure described in the above sections. They proved to show reversible photoinduced bending and unbending behaviours rather similar with the initially prepared post-crosslinked fibers (Fig. S10).

**Characterization**

Proton nuclear magnetic resonance ($^1$H NMR) spectra of the samples were recorded on a Bruker Avance III 400 MHz NMR spectrometer (Figs. 1, S1, S2, and S9).
FT-IR spectra of the samples were recorded on a Bio-Rad FTS6000 spectrometer with the diffuse reflectance method (Fig. 2).

The number-average molecular weights (\(M_{n,\text{GPC}}\)) and molar-mass dispersities (\(D\)) of side-chain polymers with protected thiol-substituted azo mesogens were determined using an Agilent 1200 gel permeation chromatograph (GPC) equipped with an Agilent 1200 series manual injector, an Agilent 1200 high-performance liquid chromatography (HPLC) pump, an Agilent 1200 refractive index detector, and three Agilent Plgel columns with 200-3 M, 4000-400 K, and 500-20 K molecular ranges (the temperature of the column oven was 35 °C). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL min\(^{-1}\), and the calibration curve was obtained by using polystyrene (PS) standards. The results are shown in Table S1.

Differential scanning calorimetry (DSC, Netzsch 200 F3) was used to study thermal transitions of polymers at a heating/cooling rate of 10 °C min\(^{-1}\) 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 polymers 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 (Fig. S3 and Table S1).

The liquid crystalline textures of the azo polymers (Fig. S4) and the alignment states of the polymer fibers (Figs. 3a, S6 and S7) were observed by using an Olympus BX51 polarizing optical microsphere (POM, with crossed polarizer and analyzer) equipped with a Linksys 32 THMSE600 hot stage and a digital camera (micropublisher 5.0 RTV).

A UV-vis scanning spectrophotometer (TU 1900, Beijing Purkinje General Instrument Co., Ltd) was utilized to obtain the UV-vis spectra of the samples at 25 °C. The photochemical isomerization of the polymer solution was investigated by irradiating it first with a 365 nm UV lamp (12 W) until the photostationary state was reached and then with a 450 nm visible light lamp (18 W, wavelength range 400-550 nm, \(\lambda_{\text{max}} = 450\) nm; a filter was put between the samples and the lamp during the study in order to block the light with wavelength \(\lambda < 430\) nm). The results are shown in Fig. S5.

The photoinduced bending and unbending behaviors of the azo polymer fibers were investigated as follows: Part of a polymer fiber was first pasted onto an aluminum block, which was heated to a certain temperature with a hot stage under the control of a thermocouple (IKA C-MAG HP 7). Irradiation of the polymer fiber with 365 nm UV light and visible light (\(\lambda > 510\) nm) was performed using a high-pressure mercury lamp (USHIO SP-7) through glass filters. The photographs of the
bending and unbending behaviors of the polymer fiber were taken by using a CCD camera (KBier-1202). The experimental results are presented in Figs. 3b,c, S8, and S10.

**Fig. S1** ¹H NMR spectra of HP10-PT (a), CP10-PT-66% (b), CP10-PT-32% (c), CP10-PT-19% (d), and PMMA (e) in CDCl₃.
Fig. S2  $^1$H NMR spectra of HP10-T (a), CP10-T-66% (b), CP10-T-32% (c), and CP10-T-19% (d) in CDCl$_3$. 
**Fig. S3**  DSC curves of PMMA (a1,b1) and side-chain azo polymers (CP10-PT-19% (a2,b2), CP10-PT-32% (a3,b3), CP10-PT-50% (a4,b4), CP10-PT-66% (a5,b5), and HP10-PT (a6,b6)) from the first cooling scan (a) and from the second heating scan (b) (±10 °C min⁻¹).

**Fig. S4**  POM images upon cooling: (a) CP10-PT-32% at 57 °C (annealed for 2 h; note that only very weak optical birefringence was observed for CP10-PT-32% during the heating and cooling processes); (b) CP10-PT-50% at 76 °C (annealed for 1 h); (c) CP10-PT-66% at 87 °C (annealed for 1h); (d) HP10-PT at 107 °C (annealed for 1 h).
Fig. S5  (a,b) UV-vis spectral changes in dependence of time for the solution of CP10-PT-50% in chloroform ($C = 50 \mu M$ repeat unit of the studied polymer) at 25 °C upon irradiation with 365 nm UV light (a) and upon irradiating the polymer solution at the photostationary state with visible light ($\lambda > 430$ nm) (b). (c) UV and visible light-induced photoisomerization cycles of the CP10-PT-50% solution in chloroform ($C = 50 \mu M$ repeat unit of the studied polymer) at 25 °C. In each cycle, the polymer solution was first irradiated with UV light for 240 s and then with visible light for 480 s, respectively.
Fig. S6  POM images of the uncrosslinked CP10-T-50% fiber (a), CP10-T-32% fiber (b), and CP10-T-19% fiber (c) taken at room temperature. Sample angle to the analyzer: $\theta = 0^\circ$ (a1,b1,c1); $\theta = 45^\circ$ (a2,b2,c2); $\theta = 90^\circ$ (a3,b3,c3); $\theta = 135^\circ$ (a4,b4,c4).

Fig. S7  POM images of the post-crosslinked CP10-T-50% fiber (a), CP10-T-32% fiber (b), and CP10-T-19% fiber (c) taken at room temperature. Sample angle to the analyzer: $\theta = 0^\circ$ (a1,b1,c1); $\theta = 45^\circ$ (a2,b2,c2); $\theta = 90^\circ$ (a3,b3,c3); $\theta = 135^\circ$ (a4,b4,c4).
Fig. S8  (a) Schematic illustration of the experimental setup; (b,c) Photographs of the post-crosslinked polymer fibers that exhibit photoinduced bending and unbending behaviors upon irradiation with 365 nm UV light (150 mW cm$^{-2}$) and visible light ($\lambda > 510$ nm, 120 mW cm$^{-2}$): (b) Post-crosslinked CP10-T-32% fiber (size: 10 mm × 20 μm) at 45 °C, (c) Post-crosslinked CP10-T-19% fiber (size: 10 mm × 21 μm) at 65 °C.

Fig. S9  (a) The initial 20 cycles of the reversible deformation of the post-crosslinked CP10-T-32% fiber characterized by tracing the bent distance from its straight state at 45 °C (the irradiation times for the UV and visible light irradiation were kept at 68 and 138 s, respectively). The size of the fiber is 10 mm × 21 μm. (b) The fatigue resistance results of the post-crosslinked CP10-T-19% fiber characterized by tracing the bent distance from its straight state at 65 °C (the irradiation times for the UV and visible light during the first 10 cycles were kept at 125 and 305 s, respectively; for the 11 and 12th cycles, the irradiation time for the UV light was kept at 125 s, whereas that for the visible light was changed to 450 s because 305 s of visible light irradiation can not revert the bent fiber to its initial straight state; for the 13th cycle, the visible light can not revert the bent fiber to its initial straight state even after even longer irradiation). The size of the fiber is 10 mm × 21 μm.
Fig. S10 $^1$H NMR spectra of the original CP10-T-50% (a) and the recycled CP10-T-50% (b) in CDCl$_3$.

Fig. S11 Photographs of the photoinduced bending and unbending behaviors of the post-crosslinked polymer fiber (size: 10 mm $\times$ 19 $\mu$m) prepared by using the recycled CP10-T-50% upon irradiation with 365 nm UV light (150 mW cm$^{-2}$) and visible light ($\lambda > 510$ nm, 120 mW cm$^{-2}$) at 40 $^\circ$C.