

## Supporting Information

### Self-recovery of Chiral Microphase Separation in Achiral Diblock Copolymer System

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## S1 Materials and Characterization

### Materials.

*L*-(+)-tartaric acid (*L*-TA) (*ee* > 99.0%) and *D*-(-)-tartaric acid (*D*-TA) (*ee* > 99.0%) were purchased from Aladdin corporation and used without further purification. Poly(ethylene oxide) monomethyl ether with number-averaged molecular weight of about 4,000 was purchased from Aldrich corporation. Azo-containing monomer 4-methoxy-4'-(2-hexyloxy methacrylate) azobenzene (Az) and 4-(2-hydroxy ethoxy)-4'-(2-hexyloxy methacrylate) azobenzene (AzOH) were synthesized as reported previously.<sup>1</sup>

### Characterization.

**Nuclear magnetic resonance spectroscopy (NMR).** <sup>1</sup>H NMR spectra were recorded on a Bruker nuclear magnetic resonance instrument (300 MHz, Bruker, Kalsruhe, Germany) using CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> as solvent and tetramethylsilane (TMS) as the internal standard.

**Gel-permeation chromatograph (GPC).** GPC measurements were conducted on the TOSOH HLC-8320 gel permeation chromatograph (GPC), equipped with refractive-index and UV detectors using two TSKgel SuperMultiporeHZ-N (4.6 × 150 mm, 3.0 μm beads size) columns arranged in series. Polymers can be separated in the molecular weight range of 500-190k Da. DMF was used as the eluent with a flow rate of 0.35 mL/min at 40 °C. The number average molecular weight (*M*<sub>n</sub>) and molecular weight distribution (*M*<sub>w</sub>/*M*<sub>n</sub>) of sample was calculated with polystyrene (PS) standards.

**Circular dichroism (CD).** The CD spectra were recorded on a JASCO J-1500 spectropolarimeter equipped with a Peltier-controlled housing unit using a SQ-grade cuvette, a single accumulation, a bandwidth of 2 nm, a scanning rate of 200 nm min<sup>-1</sup>, a path length of 10 mm, and a response time of 1 s. The magnitude of the circular polarization at the ground state is defined as  $g_{CD} = 2 \times (\epsilon_L - \epsilon_R) / (\epsilon_L + \epsilon_R)$ , where  $\epsilon_L$  and  $\epsilon_R$  denote the extinction coefficients for left and right circularly polarized light, respectively. Experimentally,  $g_{CD}$  value is defined as  $\Delta\epsilon/\epsilon = [\text{ellipticity}/32980]/\text{absorbance}$  at the CD extremum.

**Differential scanning calorimetry (DSC).** The thermal property of the polymer was measured with a TA-Q100 DSC instrument. The temperature range is 20 °C to 200 °C with the first heating-cooling speed of 20 °C/min and second heating speed of 10 °C.

**Polarized optical microscope (POM).** LC textures and birefringence of the samples were examined under a POM (Olympus Corporation, BX51-P) equipped with a hot stage (Linkam THMS600).

**Small-angle X-ray scattering (SAXS).** SAXS experiments were performed with a high-flux X-ray instrument (SAXSess mc<sup>2</sup>, Anton Paar) equipped with a line collimation system and a 2200 W sealed-tube X-ray generator (CuK $\alpha$ ,  $\lambda = 0.154$  nm). The polymer samples were wrapped in aluminum foils and sandwiched in a steel sample holder.

**Atomic force microscope (AFM).** The morphology of polymer films was captured on a Multimode 8 AFM (Bruker Co., tapping mod) in air scan mode.

## S2 Experimental Procedures

### 1. Synthesis of macro-initiator PEO-Br.

A solution of poly(ethylene oxide) monomethyl ether (4.0 g, 1.0 mmol), triethylamine (6.0 mL, 43.2 mmol) in dried dichloromethane (50 mL) was stirred at 0 °C for 0.5 h. Then the bromoisobutyryl bromide (0.9 g, 4.0 mmol, dissolved in 10 mL dichloromethane) was added dropwise to the mixture. After 30 min of stirring at 0 °C, the reaction liquid was kept at 30 °C for 12 h. Then the solution was concentrated to 2~5 mL and added dropwise to 100 mL n-hexane to precipitate the solid. Collected the solid and dissolved it in ethanol. The pure **PEO-Br** was obtained by recrystallization and characterized via <sup>1</sup>H NMR and GPC measurement.

### 2. Synthesis of PEO-*b*-(Az-AzOH).

The amphiphilic block copolymer PEO-*b*-(Az-AzOH) with side-chain containing Azo groups were synthesized by atom transfer radical polymerization (ATRP). The monomer Az (105.0 mg, 0.378 mmol), AzOH (107.0 mg, 0.252 mmol), initiator PEO-Br (25.2 mg, 6.3  $\mu$ mol), ligand HMTETA (14.5 mg, 63  $\mu$ mol), CuBr (3.6 mg, 25  $\mu$ mol) and dried anisole (1.5 mL) were added successfully into a 5 mL ampoule

bottle. The polymerization ratio is 70/1/10/4 ([monomer]<sub>0</sub>/[PEO-Br]<sub>0</sub>/[HMTETA]<sub>0</sub>/[CuBr]<sub>0</sub>). The reaction tube was flame-sealed under an argon atmosphere after deoxygenated with three freeze-thaw cycles. Then the polymerization was carried out at 80 °C for 7 h. After quenching the polymerization, the reaction mixture was diluted with THF (2 mL) and precipitated into an excess of methanol (80 mL) twice. The polymer solid was collected by filtration and then dried in a vacuum oven overnight at 30 °C. The hydroxyl content and molecular weight were calculated from the <sup>1</sup>H NMR spectra and GPC curves (Figures S1 and S2).

### **3. Preparation of the chiral polymer films.**

The chiral polymer films for CD and AFM measurements with thickness in the range of 100-200 nm were prepared by drop coating the polymer solution (with or without *D/L*-TA, in THF for composite film, the molar ratio of PEO and TA was fixed at 1.2/1.0, the relative weight ratio of TA and LC-BCP was 3.0/5.0; polymer concentrations of all samples were maintained at 2.5 mg/mL) onto a clean quartz plate or silicon substrate. After slowly evaporating the solvent in THF atmosphere, the film was dried in vacuum before thermal annealing.

### **4. Removal of chiral dopants.**

The polymer film containing chiral dopant was immersed in LiBr/ethanol for 24 h, during which the soaking solution was changed for three times. After that, the chiral films were washed by pure ethanol. The residual contents of chiral dopant in the polymer films were measured by <sup>1</sup>H NMR and IR spectra (Figure S3).

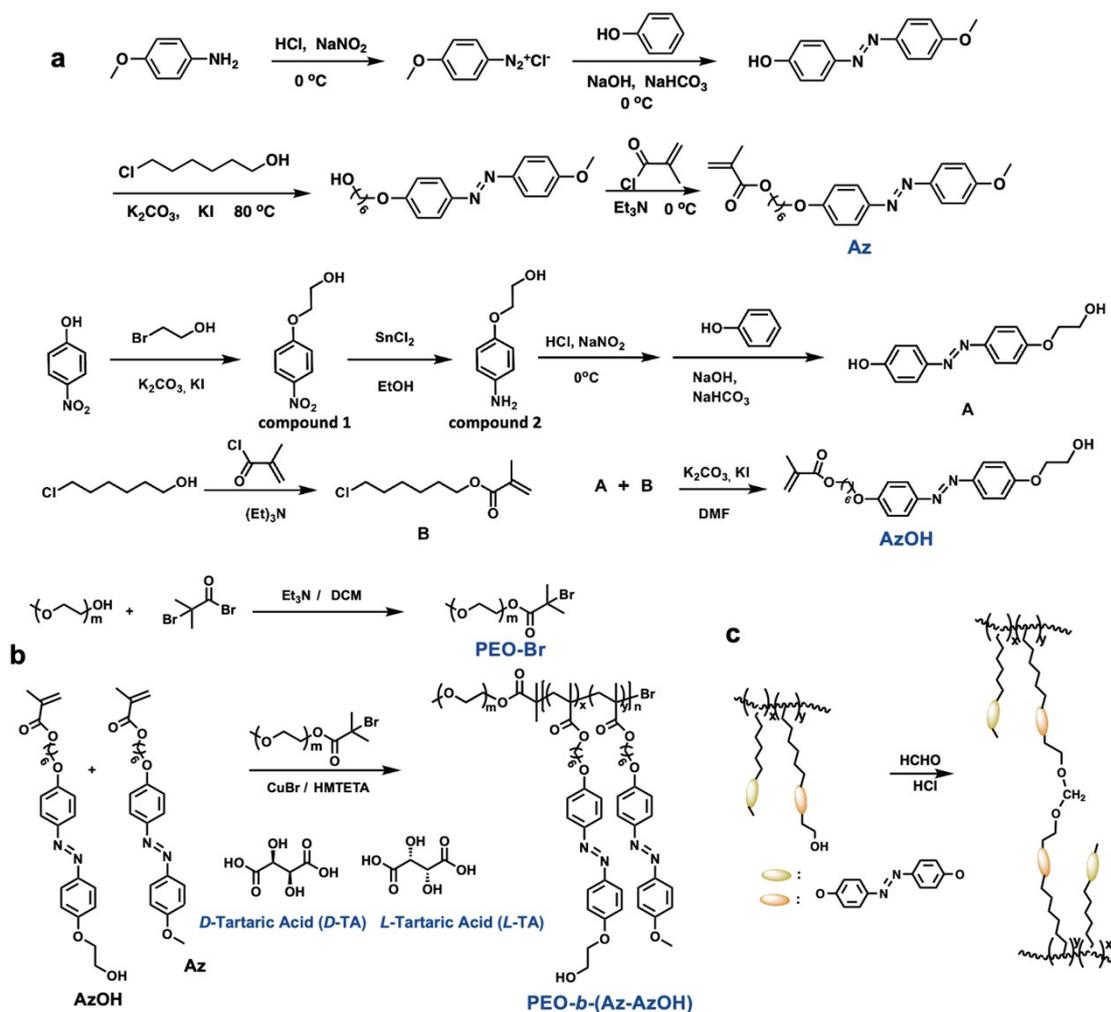
### **5. The storage of the supramolecular chirality.**

The hydroxyl-containing polymer films after chiral induction and removal of chiral dopants were placed in the top of a larger beaker in which two small beakers with 30% formaldehyde aqueous and 6 N hydrochloric acid solution were placed in separately. Then the cross-linking of the polymer chains was carried out when exposed to HCl and HCHO vapor at 25 °C for 20 h. The cross-linked polymer films were washed with pure water and dried in the vacuum at 35 °C for 12 h.

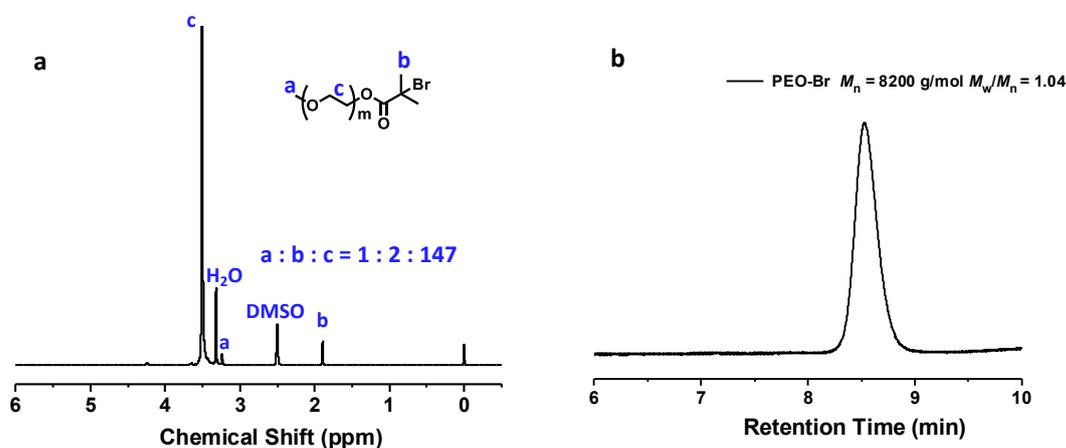
## **6. Photoisomerization process of polymer films.**

Photoisomerization of Azo-containing chiral polymer film was conducted with a 500 W high-pressure mercury lamp (Tokyo, Japan), Optiplex SX-UID and 502HUV) equipped with a narrow bandpass filter for the wavelength of 365 nm. The irradiation intensity was 2.5 mW cm<sup>-2</sup>.

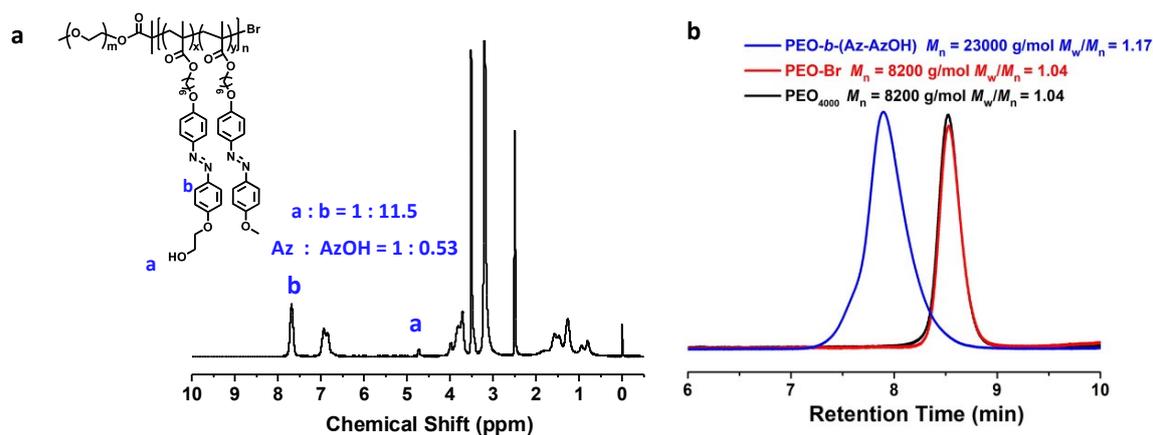
### S3 Results and Discussion



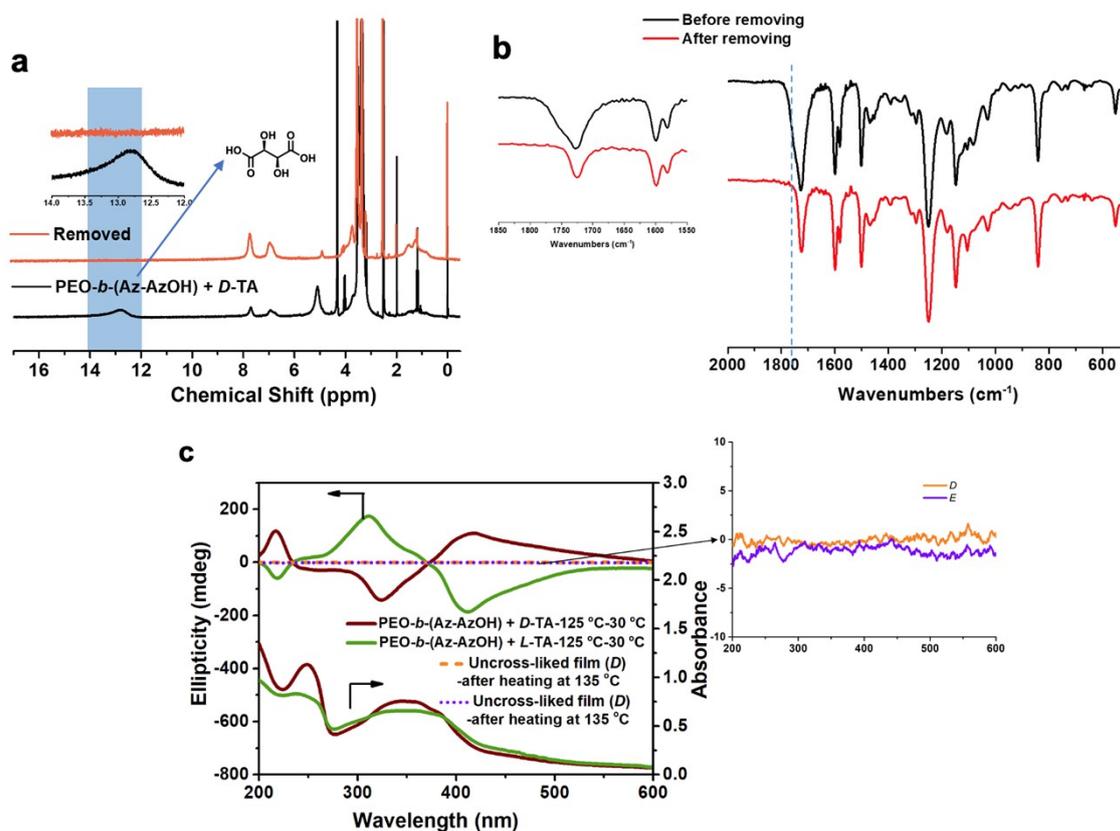
**Scheme S1.** (a) Synthetic route to monomer **Az**, **AzOH** and initiator **PEO-Br**. (b) Synthetic route to polymer **PEO-*b*-(Az-AzOH)** and chemical structure of **D/L-TA**. (c) illustration for cross-linking step.



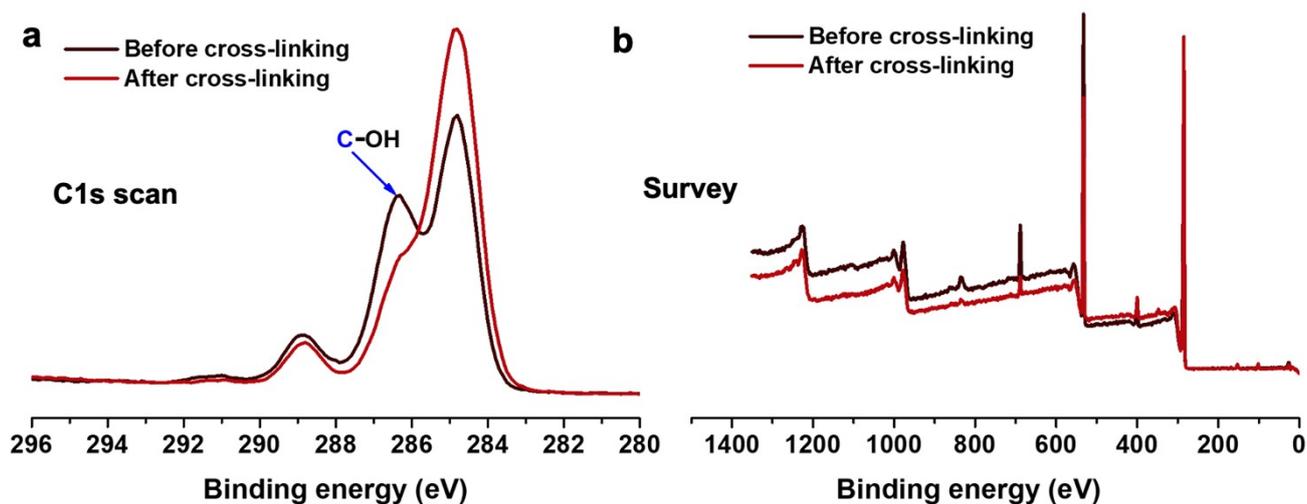
**Fig. S1.**  $^1\text{H}$  NMR spectra (a) and GPC curves (b) of PEO-Br.



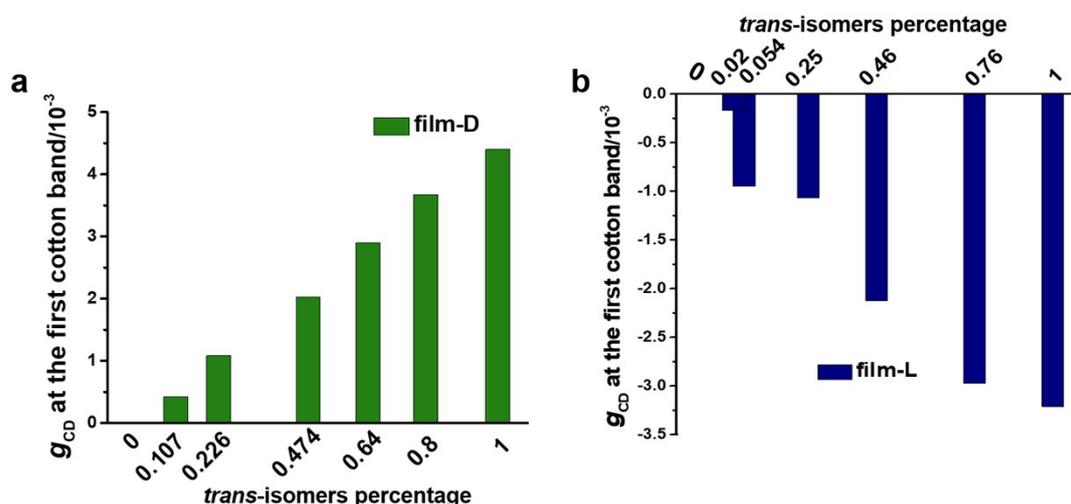
**Fig. S2.**  $^1\text{H NMR}$  spectra (a) and GPC curves (b) of  $\text{PEO-}b\text{-(Az-AzOH)}$ .



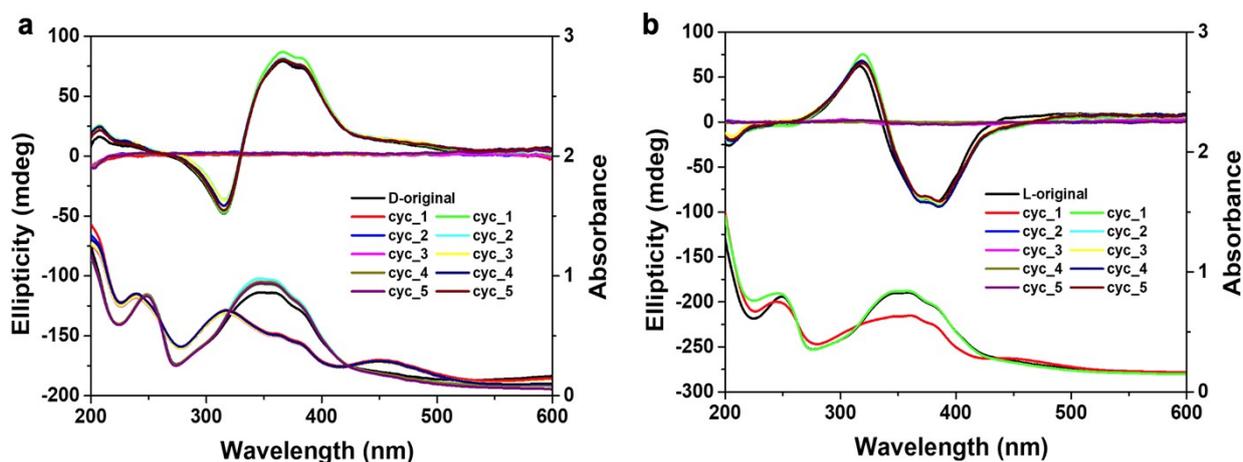
**Fig. S3.** (a)  $^1\text{H NMR}$  and (b) IR spectra of the chiral polymer film measured before and after removal of chiral dopant. (c) Clearing of CD signals of the uncross-linked polymer films (after removing the chiral TA molecules) by heating at 135 °C for 10 min.



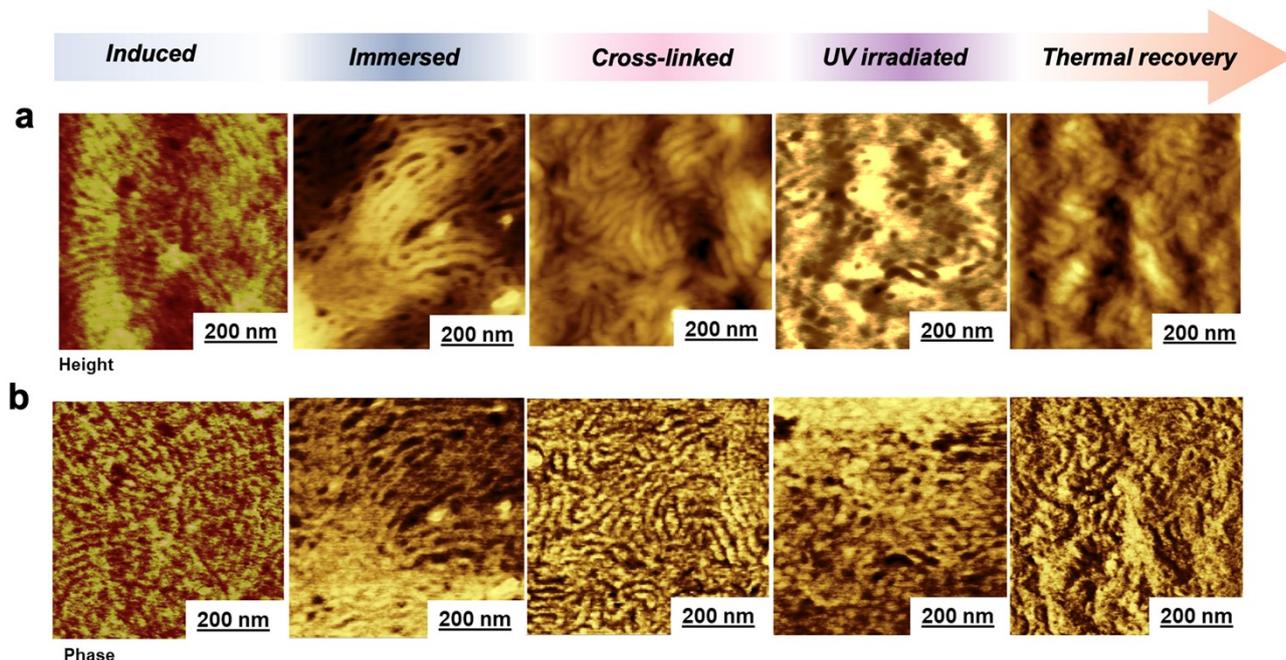
**Fig. S4.** Changes in C 1s (a) and full (b) XPS spectra of polymer film recorded before and after cross-linking.



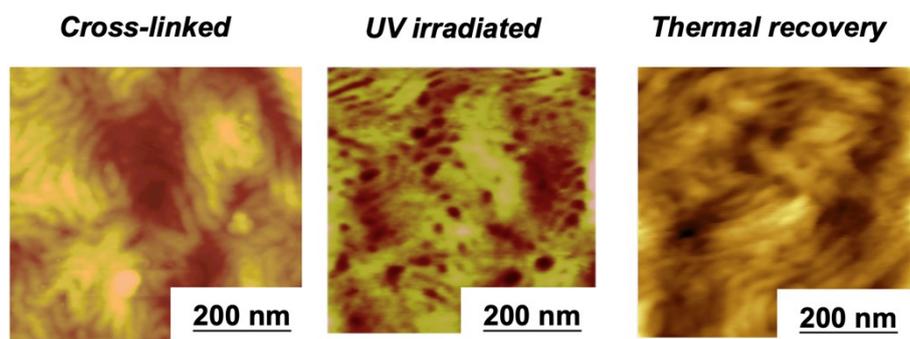
**Fig. S5.** Chiral expression of the polymer films corresponding to different degree of photoisomerization. We artificially defined the percentages of infinite time and time zero are 1 and 0, respectively. The percentage of *cis* and *trans* isomers is estimated by:  $p = (A_{\infty} - A_t) / (A_{\infty} - A_0)$ , where  $A_{\infty}$ ,  $A_t$ , and  $A_0$  are absorbance at about 365 nm corresponding to the  $\pi$ - $\pi^*$  transition of *trans* isomers at infinite time, time t and time zero with irradiation of 365 nm UV light (calculated from Fig. 4a).



**Fig. S6.** Changes in the CD and UV-vis spectra of the chiral polymer films (PAz-*r*-AzOH) in the switch of 365 nm light irradiation and heating-cooling process. The films are measured after removing the dopants and after cross-linking. (a) induced by *D*-TA; (b) induced by *L*-TA.



**Fig. S7.** Evolution of the topologic structure of PEO-*b*-(Az-AzOH) (induced by *L*-TA) measured during the chiral induction, immersing, cross-linking, UV-irradiation and thermal recovery process. (a) AFM height images; (b) AFM phase images.



**Fig. S8** Evolution of the topological structure of the chiral polymer film (induced by *D*-TA) measured during the UV light irradiation and thermal recovery treatment (height images).

## S4 References

1. T. F. Miao, X. X. Cheng, H. T. Ma, Z. X. He, Z. B. Zhang, N. A. C. Zhou, W. Zhang and X. L. Zhu, *Angew. Chem. Int. Ed.*, 2021, **60**, 18566-18571.