

Electronic Supplementary Information

Photoswitching the melting point of a semicrystalline polymer by the azobenzene terminal group for reversible solid-to-liquid transition

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Video S1. Revealing the hidden QR code under UV light irradiation.

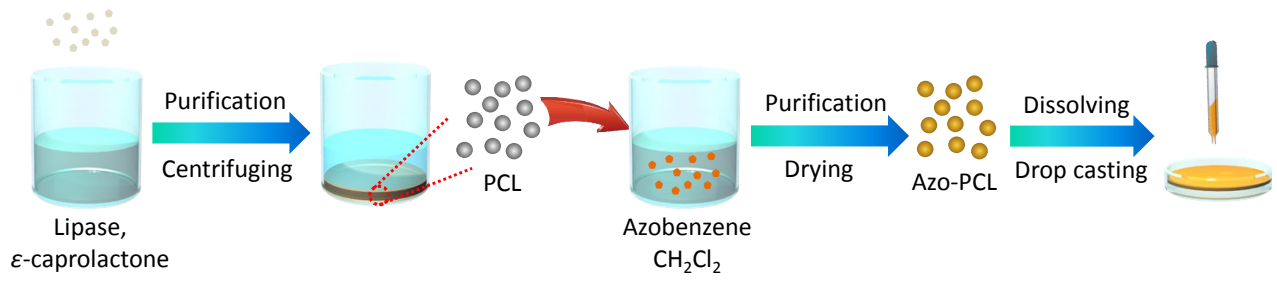


Fig. S1 Schematic illustration indicating the fabrication process.

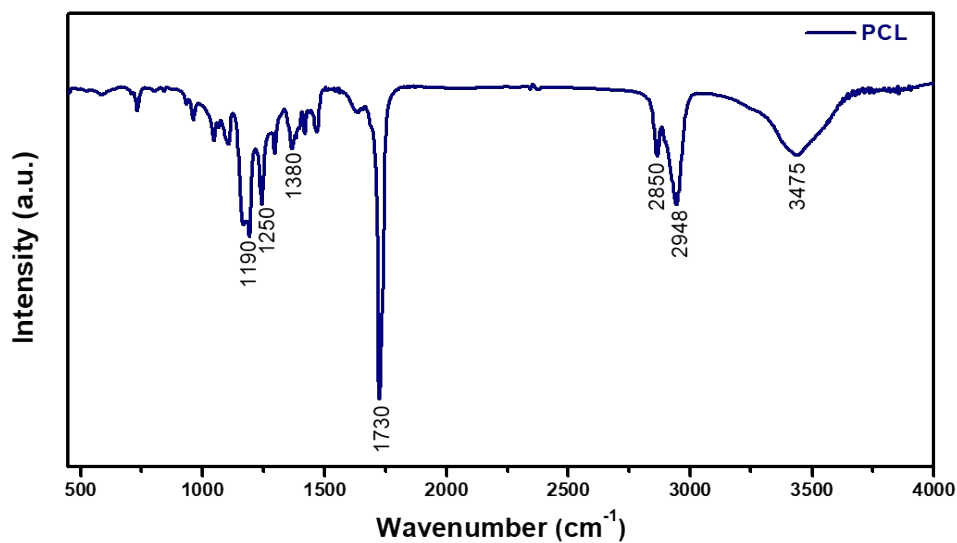


Fig. S2 The FTIR spectrum of the pristine PCL. The peaks at 3475 cm⁻¹ and 1730 cm⁻¹ are from the stretching vibration of -OH and C=O, respectively. The peaks at 2850 cm⁻¹ and 2948 cm⁻¹ can be ascribed to the stretching vibration of C-H. The peak at 1380 cm⁻¹ is from the bending vibration of C-H. The peaks at 1250 cm⁻¹ and 1190 cm⁻¹ are from the stretching vibration of C-O.

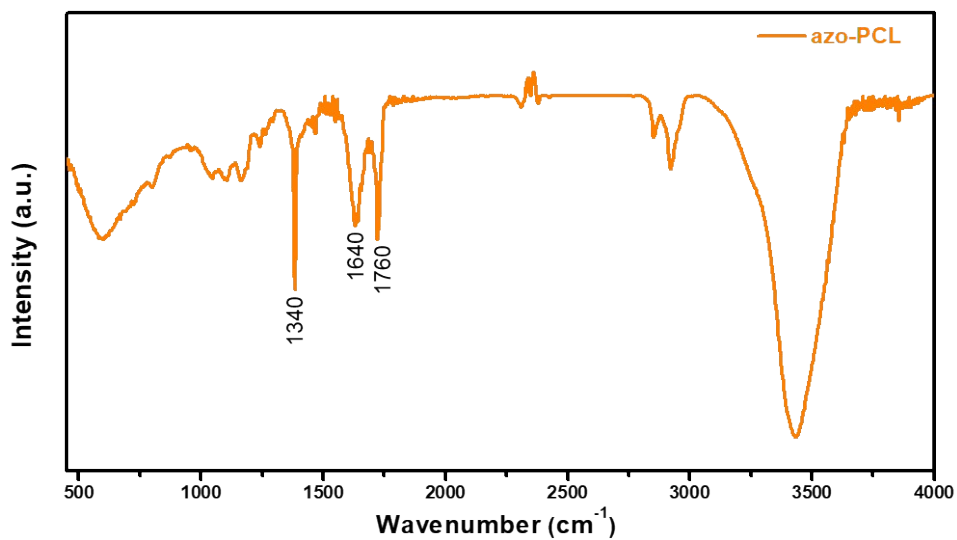


Fig. S3 The FTIR spectrum of azo-PCL. In addition to the same peaks as those of pristine PCL, the C=O stretching vibration at 1760 cm^{-1} , the characteristic absorption peak of N=N at 1640 cm^{-1} and stretching vibration of aromatic amine -C-N- on benzene ring at 1340 cm^{-1} , could be observed.

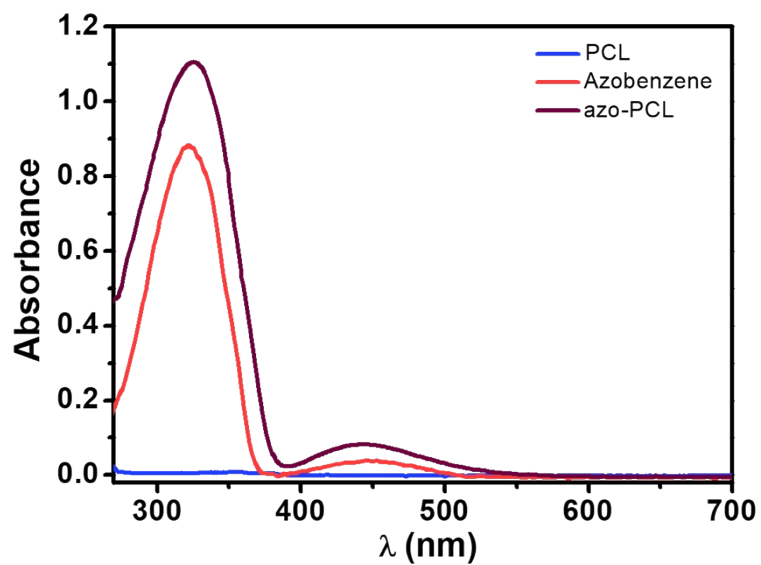


Fig. S4 UV-Vis spectra of the PCL (blue), azobenzene (red) and azo-PCL (brown) in the spectrum region from 250 to 700 nm, respectively. Pristine PCL exhibits no absorption peak between 250 and 700 nm. Azobenzene shows the absorption peaks at 330 and 450 nm which originate from the π - π^* and n - π^* transition, respectively. Azo-PCL shows both absorption peaks from azobenzene.

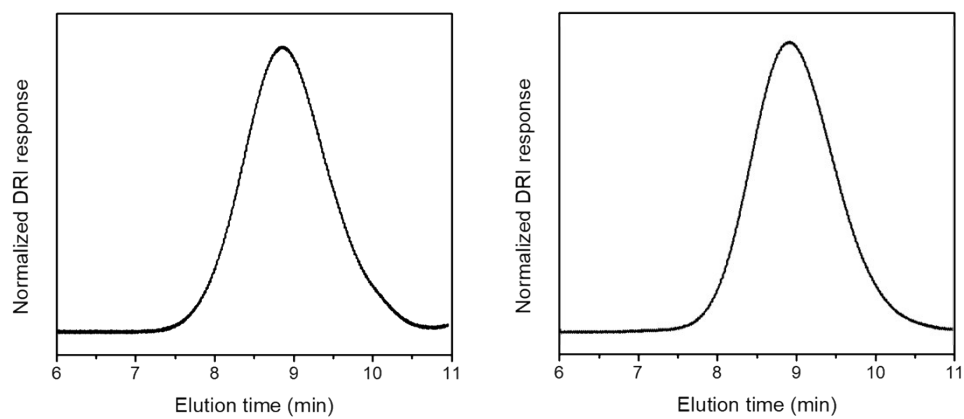


Fig. S5 The GPC of the azo-PCL (a) before and (b) after 2 min UV irradiation.

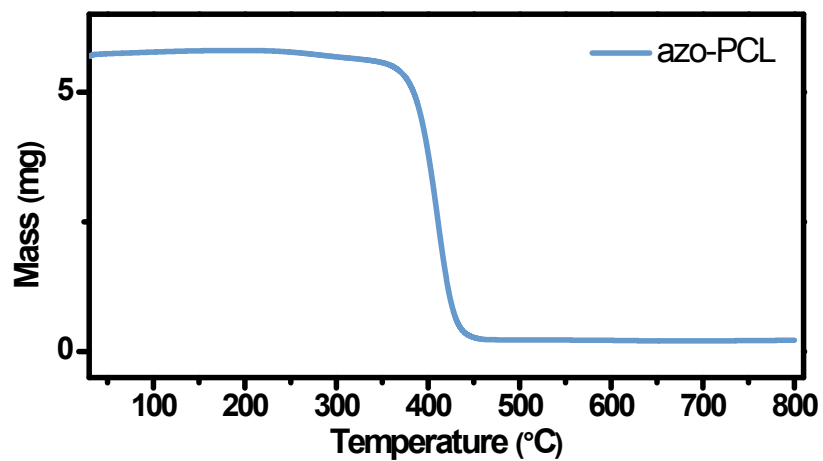


Fig. S6 The TGA curve of azo-PCL. The material is heated at a rate of 10 °C min⁻¹ under the N₂ environment.

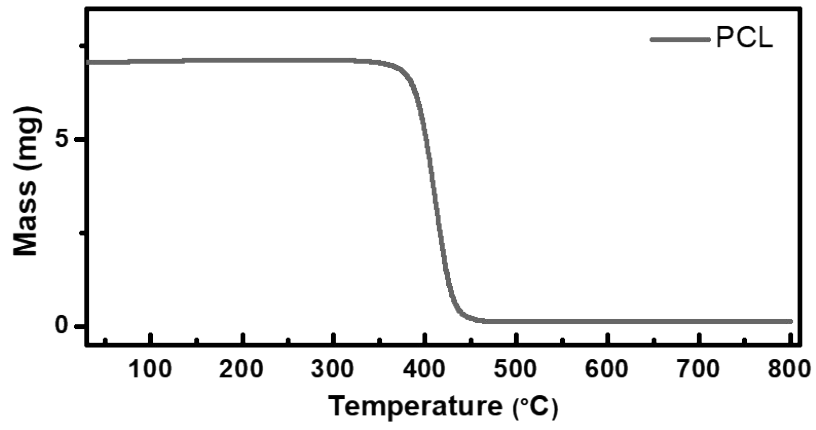


Fig. S7 The TGA curve of PCL. The material is heated at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under the N_2 environment.

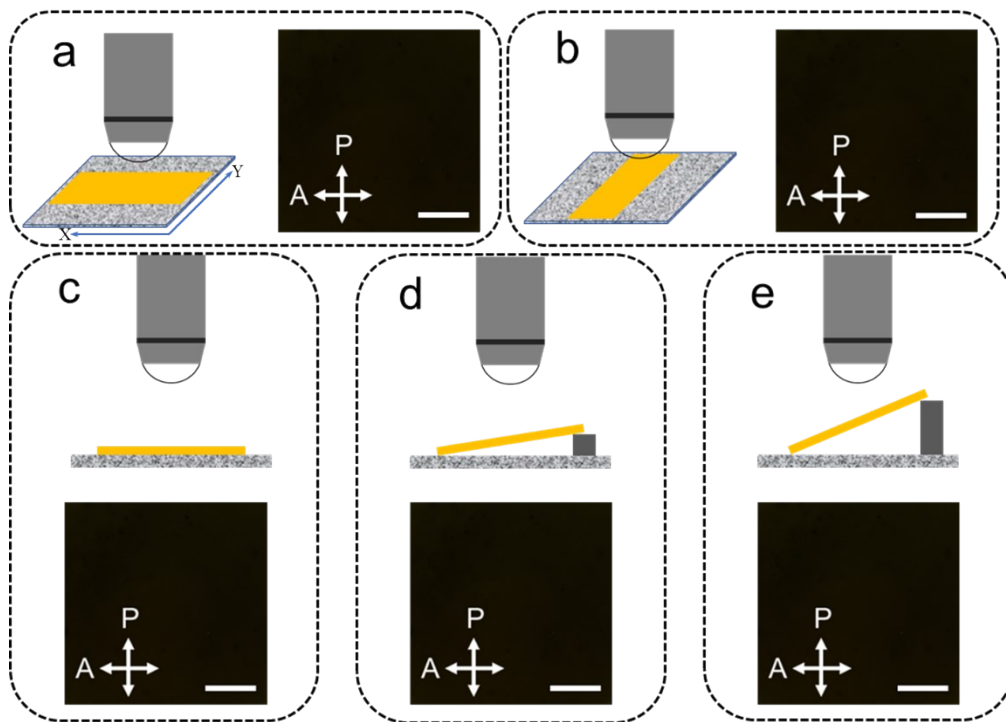


Fig. S8 The polarized microscopic images of the irradiated azo-PCL film along (a) X and (b) Y axis, and at different angles (0 , 15 , 30° for c, d and e, respectively). The polarization extinction occurs in all cases, which indicates the semi-crystalline to amorphous transition after UV illumination. P: polarizer; A: analyzer.

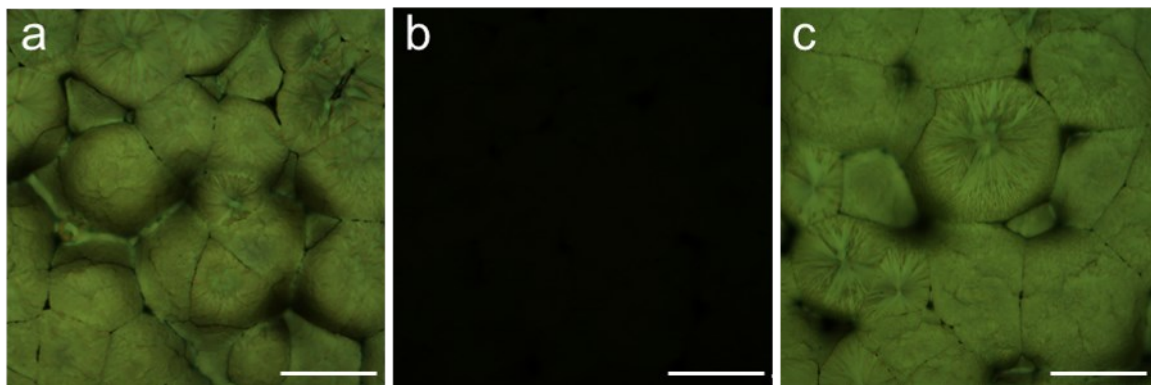


Fig. S9 The polarized optical microscopic images of (a) the pristine 64 μm thick azo-PCL film, (b) after UV irradiation and (c) recovery under indoor light. Scale bars are 50 μm .

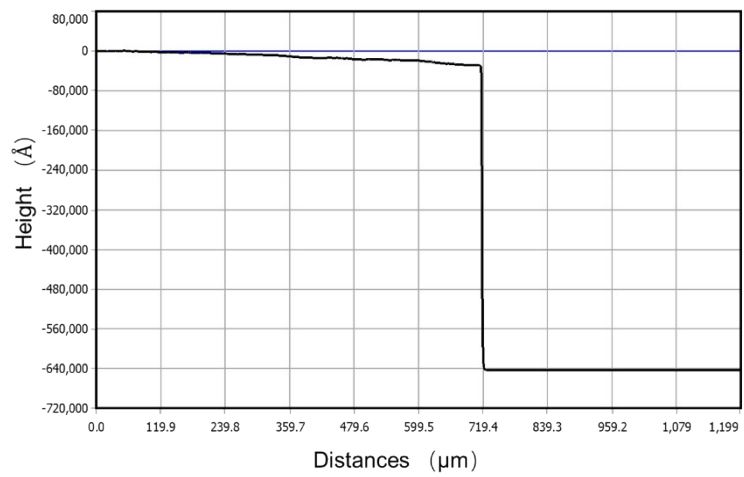


Fig. S10 The step profiler characterization of the thin azo-PCL film with a thickness of 64 μm.

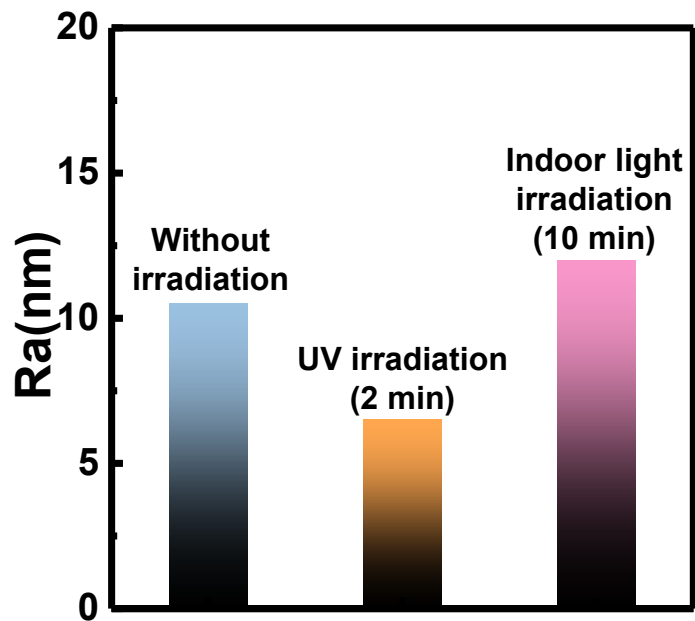


Fig. S11 Surface roughness (Ra) of the azo-PCL film before UV irradiation, after UV irradiation for 2 min and after indoor light irradiation for 10 min.

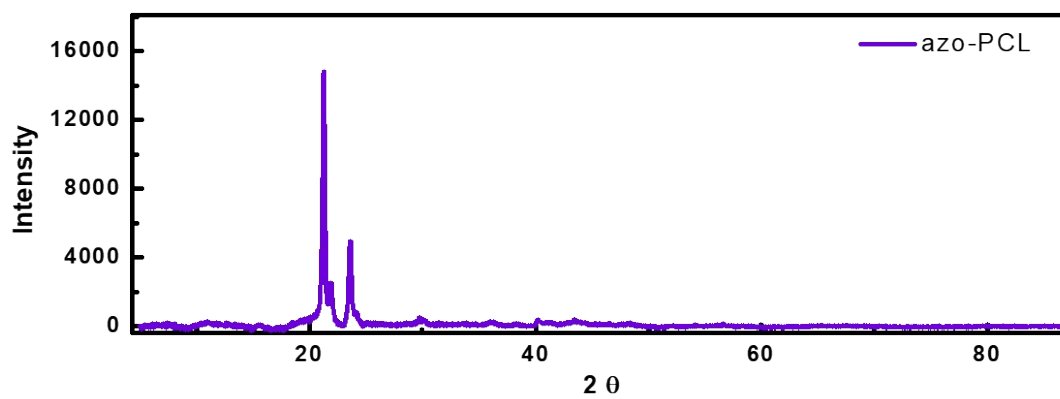


Fig. S12 The XRD analysis of azo-PCL.

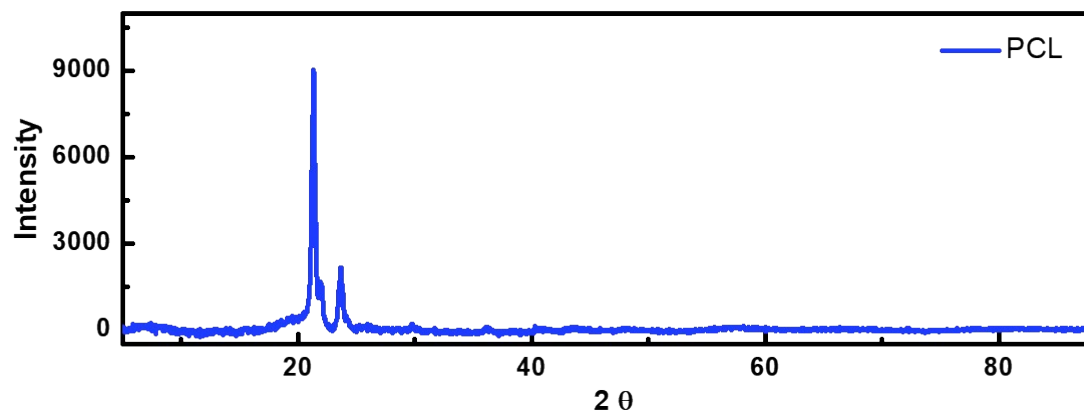


Fig. S13 The XRD analysis of the pristine PCL.

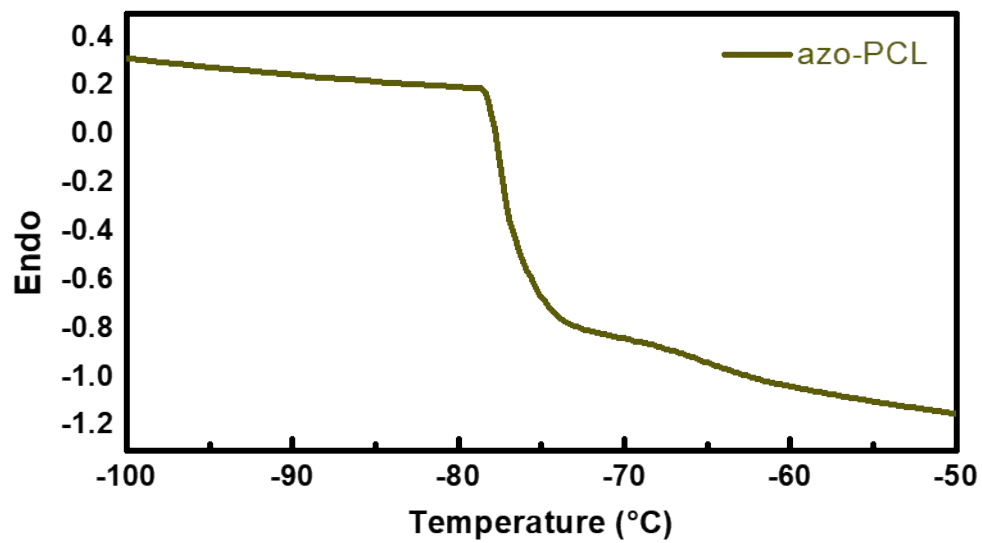


Fig. S14 The DSC curve of azo-PCL, which is measured at a constant heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

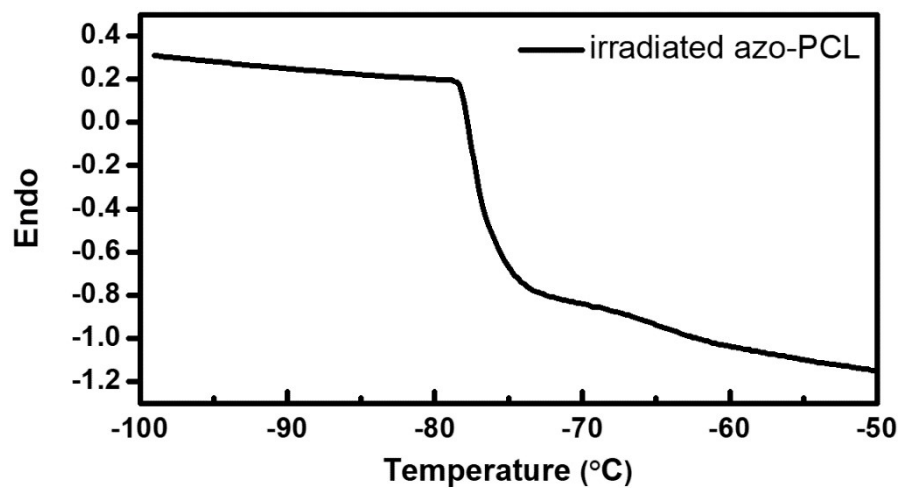


Fig. S15 The DSC curve ($10\text{ }^{\circ}\text{C min}^{-1}$ heating rate) of azo-PCL which is irradiated under UV light for 2 min.

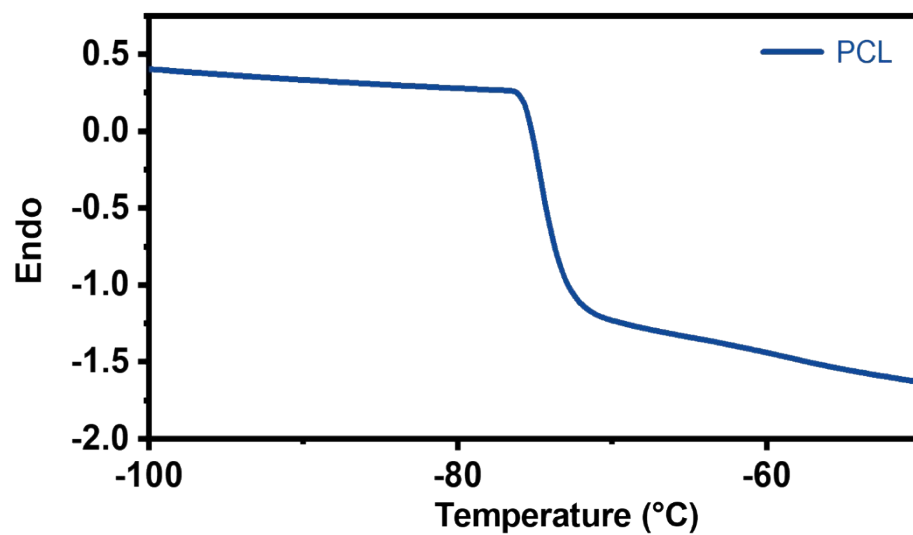


Fig. S16 The DSC curve of PCL, which is obtained at a constant heating rate of 10 °C min⁻¹.

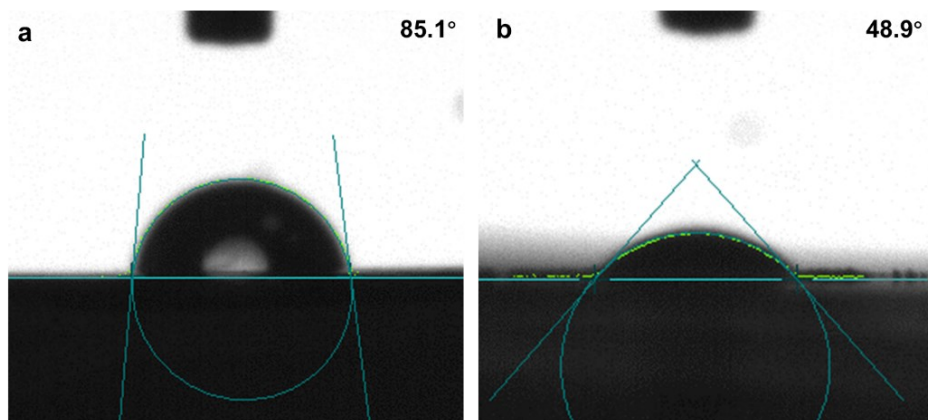


Fig. S17 The contact angle of azo-PCL (a) before and (b) after UV irradiation.

As illustrated in Fig. 3e, the strong UV absorption peak at 330 nm originating from the π - π^* of the trans azobenzene end functional group (Fig. 3e black curve) first decreases upon UV light irradiation (Fig. 3e blue curve) with the increase of the peak at 450 nm (n - π^* of the cis isomer) and then recovers after the removal of the UV light (Fig. 3e green curve), indicating the azo-PCL film undergoes trans-cis isomerization during the UV light illumination process.¹ The trans-cis photoisomerization of the azo-PCL film is also reflected in the contact angle variations, as shown in Fig. S11. The contact angle decreases from the original 85.1° to 48.9° after UV irradiation, which is likely due to the different surface tension between the trans and cis isomers.^{2,3}

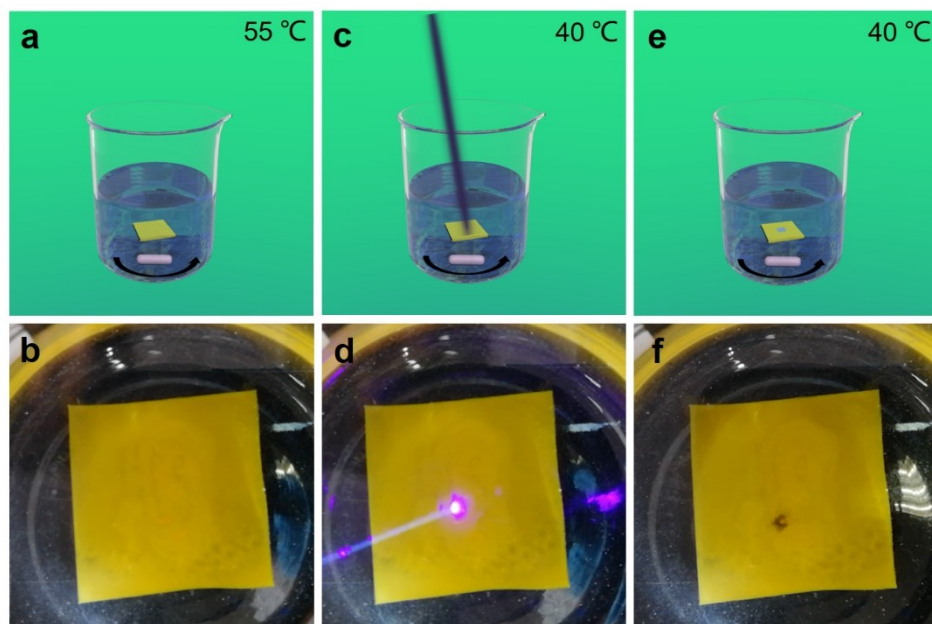


Fig. S18 (a,b) Schematic and CCD image showing the transparency of the azo-PCL film does not change in the absence of UV light when placed in a 55 °C water bath. (c-f) Schematic and CCD image indicating the irradiated area of the azo-PCL film (applying a UV laser (365 nm, UVEC-4II from SZ Lamplic Science Company)) becomes transparent in 90 s when placed in 40 °C water bath.

To further verify that the effect of trans-to-cis isomerization on T_m , we have carried out two control experiments. First, the azo-PCL film is immersed in 40 °C water in the absence of UV light. When the temperature of the water bath increases to 55 °C, the transparency of the film does not change after 30 min. Second, the UV irradiated area on the azo-PCL film immersed in water bath at a constant temperature of 40 °C becomes transparent after 90 s. These indicate that the decreased T_m caused by photoisomerization is necessary for the transparency change.

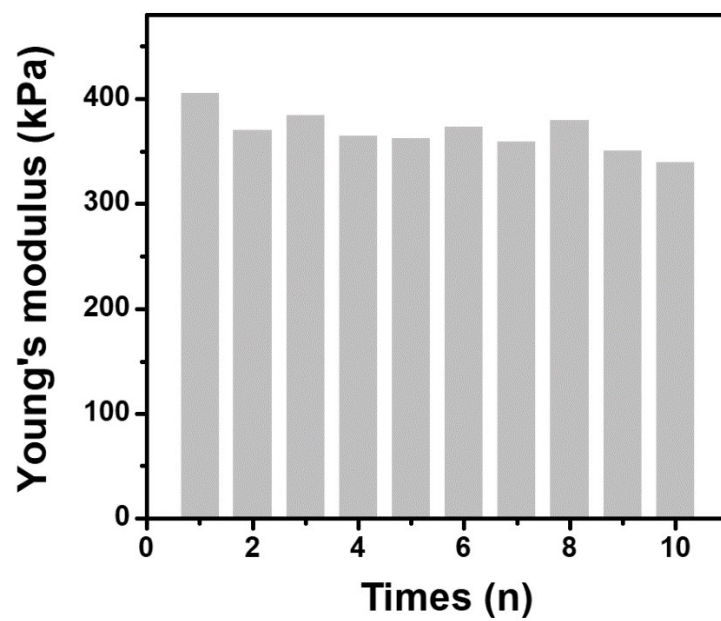


Fig. S19 The Young's modulus of the azo-PCL film after cutting and self-healing for multiple cycles.

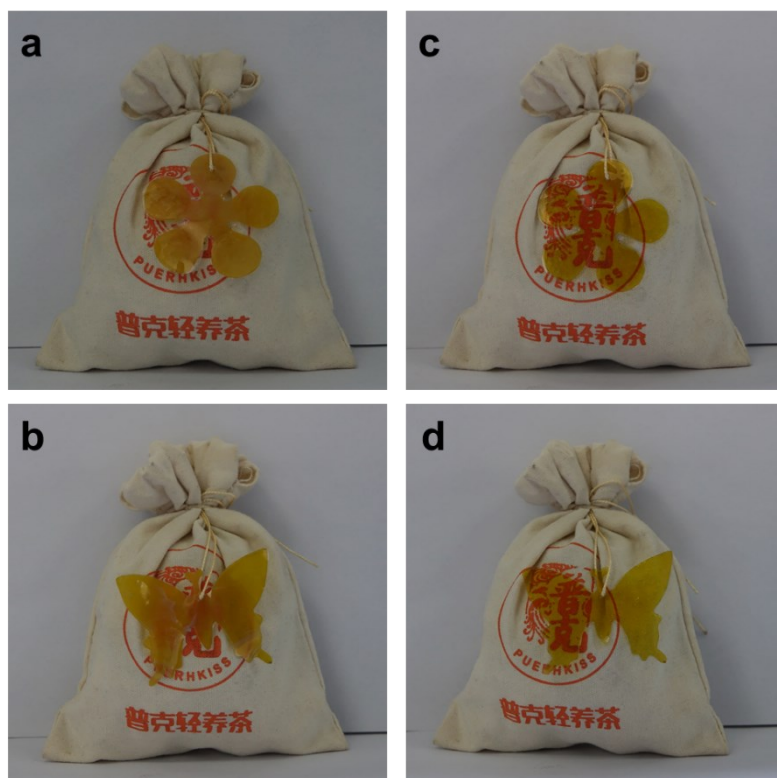


Fig. S20 Different shaped security tags made of the azo-PCL film (a,b) before and (c,d) after UV irradiation.

References

1. H. Zhou, C. Xue, P. Weis, Y. Suzuki, S. Huang, K. Koynov, G. Auernhammer, R. Berger, H. Butt and S. Wu, *Nat. Chem.*, 2017, **9**, 145-151.
2. S. Oh, M. Nakagawa and K. Ichimura, *J. Mater. Chem.*, 2002, **12**, 2262-2269.
3. A. Diguët, R. Guillermic, N. Magome, A. Saint-Jalmes, Y. Chen, K. Yoshikawa and D. Baigl, *Angew. Chem. Int. Ed.*, 2009, **48**, 9281-9284.