

Electronic Supplementary Information (ESI)

Photoresponsive nanostructures of azobenzene-containing block copolymers at solid surfaces

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1. Synthesis of PAA-*b*-PAzo

The PAA-*b*-PAzo was synthesized by RAFT polymerization. This method involved the synthesis of PAA chain-transfer agent (CTA), which was then used to polymerize the azobenzene monomer to generate PAA-*b*-PAzo. The detail of the synthesis was reported in our previous work.^{1,2}

2. Synthesis and characterization of PAzo monomer and PAzo

The PAzo monomer was synthesized with the method reported previously.³ The PAzo was synthesized by RAFT polymerization and the detail of the synthesis was in the following way. 1 mmol (0.366 g) 6-(4-(*p*-tolyl diazenyl)phenoxy)hexyl acrylate and 0.09 mmol (19.6 mg) 2-(2-cyanopropyl)dithiobenzoate (CPDB) and 0.02 mmol (3.3 mg) 2,2'-azobisisobutyronitrile (AIBN) were dissolved in 1 mL anhydrous tetrahydrofuran (THF). After 3 freeze-thaw cycles, the flask was sealed in a vacuum. Polymerization was conducted at 65 °C for 24 hours. The obtained polymer was precipitated in methanol, and the purification was repeated three times in a THF/methanol system. The ¹H NMR (400 MHz) spectra of PAzo monomer and PAzo were shown in Figure S1 with peak assignments in CDCl₃.

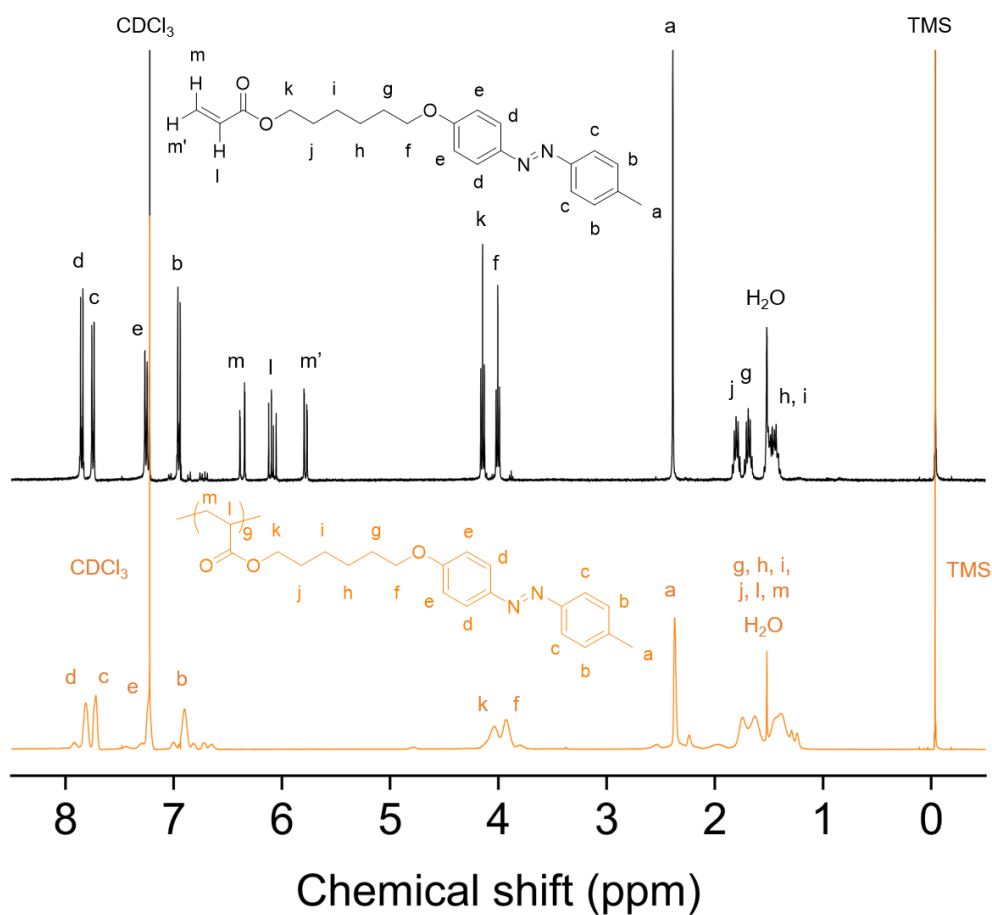


Figure S1. ^1H NMR spectra of 6-(4-(p-tolyldiazenyl)phenoxy)hexyl acrylate and PAzo used in the control experiments.

3. Photoisomerization of PAA-*b*-PAzo

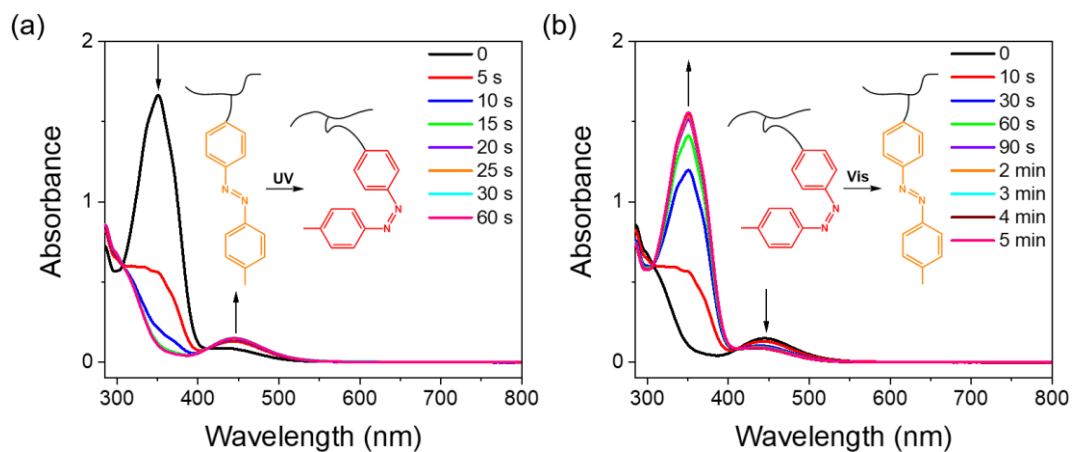


Figure S2. UV-vis absorption spectra of (a) PAA-*b*-PAzo in tetrahydrofuran (THF) under UV light

irradiation at 365 nm for different time periods and (b) the *cis*-saturated PAA-*b*-PAzo under visible light irradiation at 530 nm for different time periods.

4. AFM phase images of the PAA-*b*-PAzo thin films

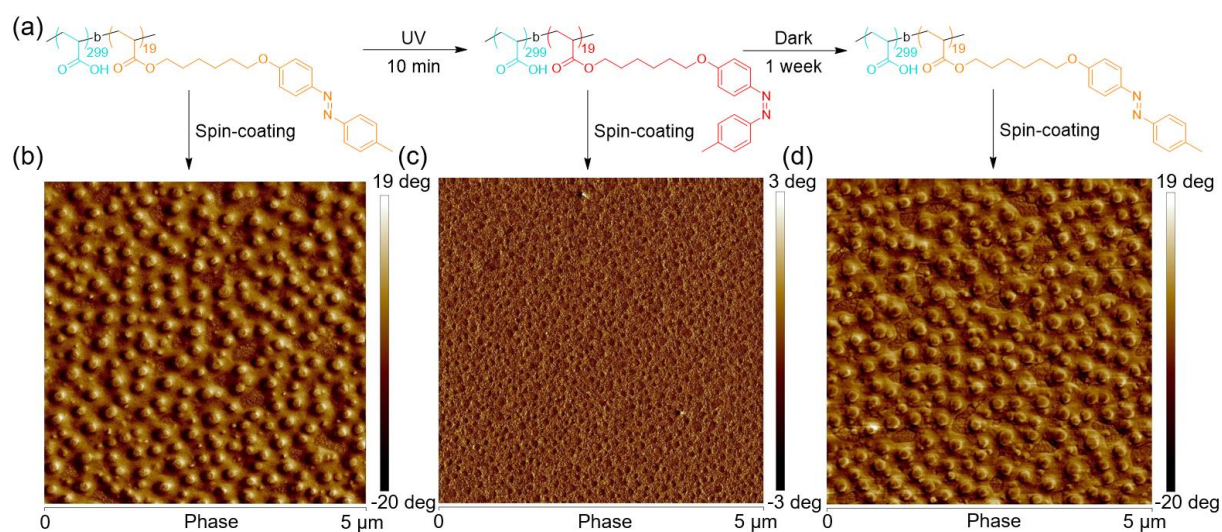


Figure S3. (a) The PAA-*b*-PAzo in cyclopentanone underwent *trans-cis* isomerization under UV irradiation for 10 min and back reversion in the dark for 1 week. The *trans* or *cis* films were prepared by spin-coating the solutions. (b–d) AFM phase images of the PAA-*b*-PAzo thin films prepared via the PAA-*b*-PAzo solutions (b) before UV irradiation, (c) after UV irradiation for 10 min, and (d) kept in the dark for 1 week.

5. Enlarged AFM images of the PAA-*b*-PAzo thin films

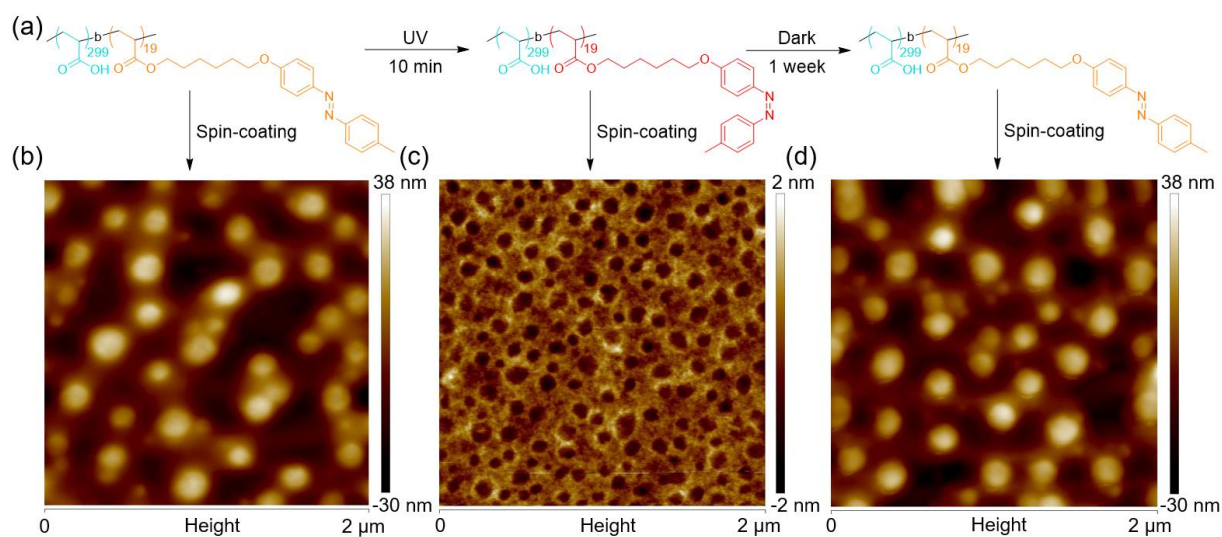


Figure S4. (a) The PAA-*b*-PAzo in cyclopentanone underwent *trans-cis* isomerization under UV irradiation for 10 min and back reversion in the dark for 1 week. The *trans* or *cis* films were prepared by spin-coating the solutions. (b–d) Enlarged AFM images of the PAA-*b*-PAzo thin films prepared via the PAA-*b*-PAzo solutions (b) before UV irradiation, (c) after UV irradiation for 10 min, and (d) kept in the dark for 1 week.

6. FT-IR spectra of the cyclopentanone and PAA-*b*-PAzo thin films

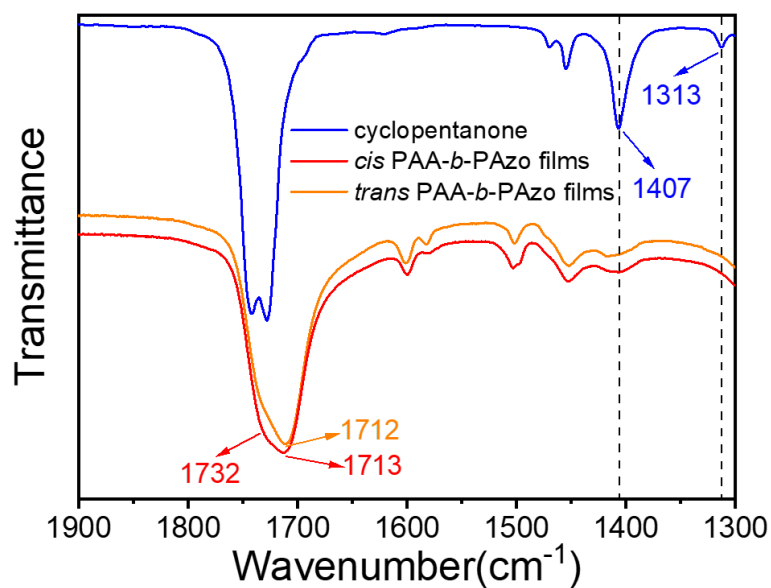


Figure S5. FT-IR spectra of the cyclopentanone (blue curve), *cis* (red curve), and *trans* (orange curve) PAA-*b*-PAzo films.

7. Contact angle measurements for the *trans* and *cis* PAA-*b*-PAzo thin films

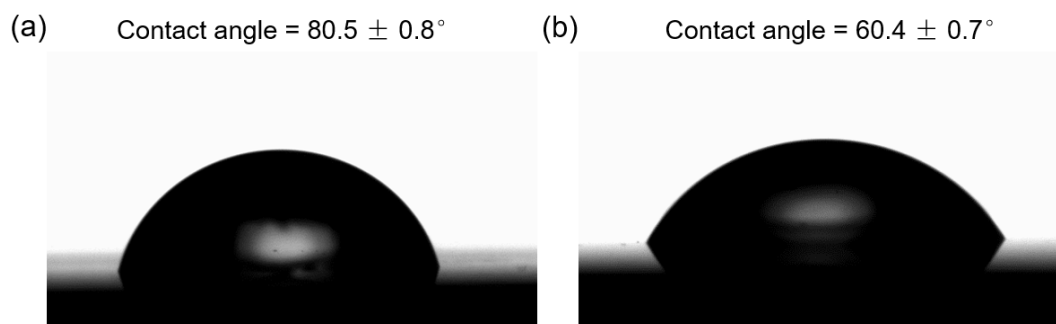


Figure S6. Contact angle data of water droplets (5 μ L) on (a) *trans* and (b) *cis* PAA-*b*-PAzo thin films.

8. AFM images of the PAA-*b*-PAzo thin films on OTS modified hydrophobic Si wafers

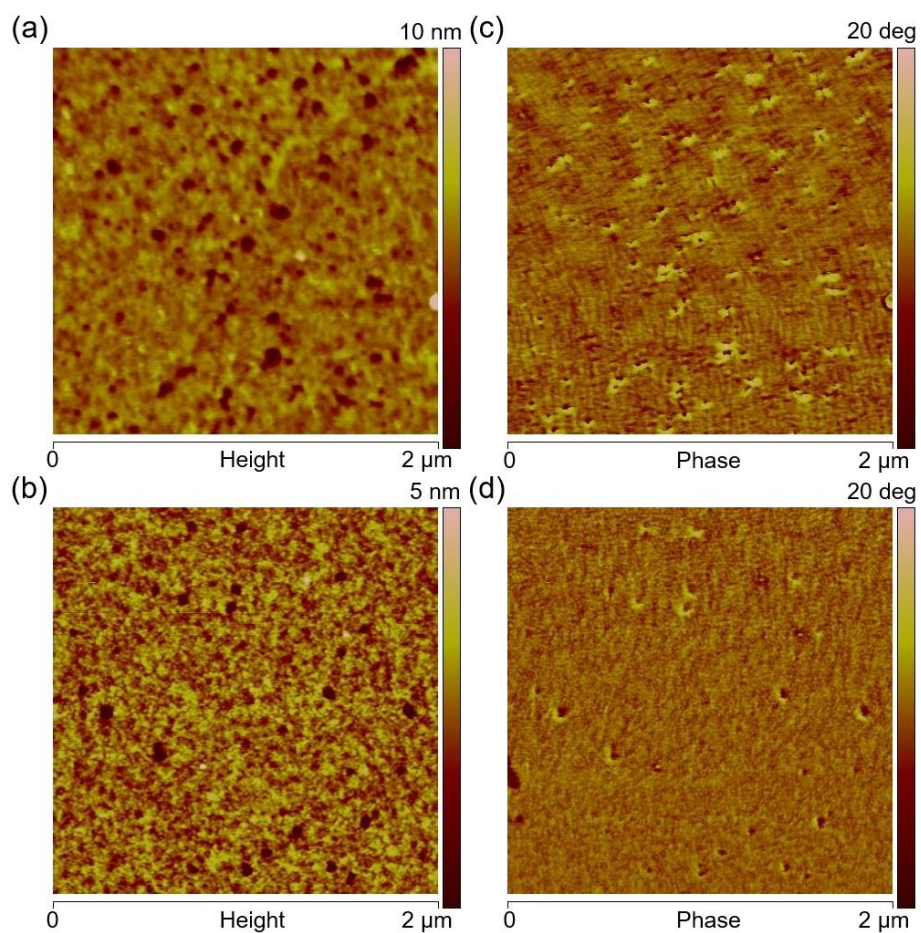


Figure S7. AFM (a and b) height and (c and d) phase images of the PAA-*b*-PAzo thin films prepared via the PAA-*b*-PAzo solutions (a and c) before UV irradiation, and (b and d) after UV irradiation for 10 min on OTS modified hydrophobic Si wafers.

9. AFM images of the PAzo thin films

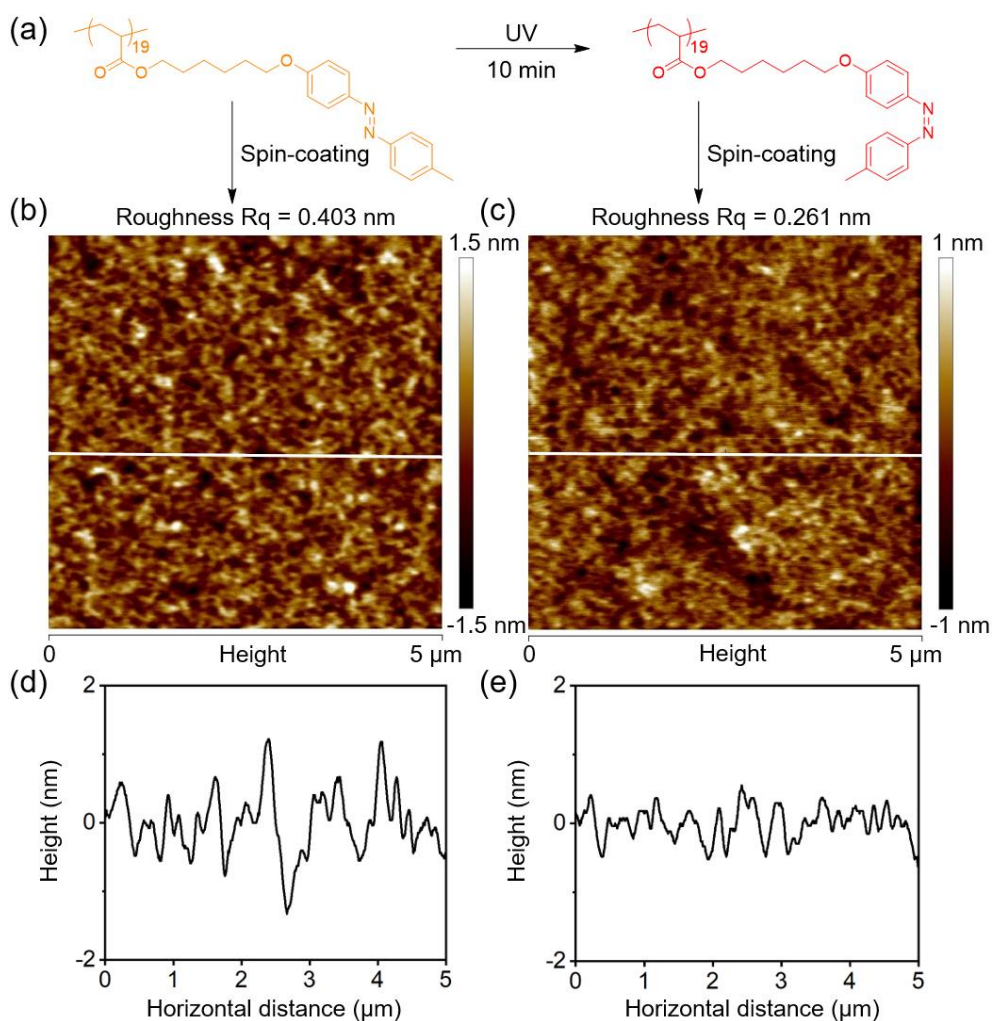


Figure S8. (a) The PAzo in cyclopentanone underwent *trans-cis* isomerization under UV irradiation for 10 min. The *trans* or *cis* films were prepared by spin-coating the solutions. (b and c) AFM images and (d and e) height profiles of the PAzo thin films prepared via the PAzo solutions (b and d) before UV irradiation, and (c and e) after UV irradiation for 10 min.

10. Macroscopic images of the PAzo powder and film

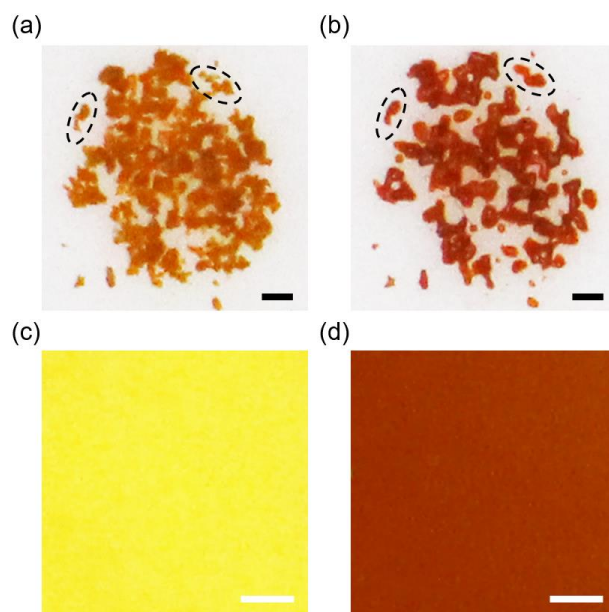


Figure S9. Macroscopic images of PAzo powders (a) before and (b) after UV irradiation for 10 min, scale bars: 0.5 mm. Macroscopic images of the PAzo film (c) before and (d) after UV irradiation for 10 min, scale bars: 0.1 cm.

11. Polarized optical microscopy images of a *trans* PAA-*b*-PAzo thin film

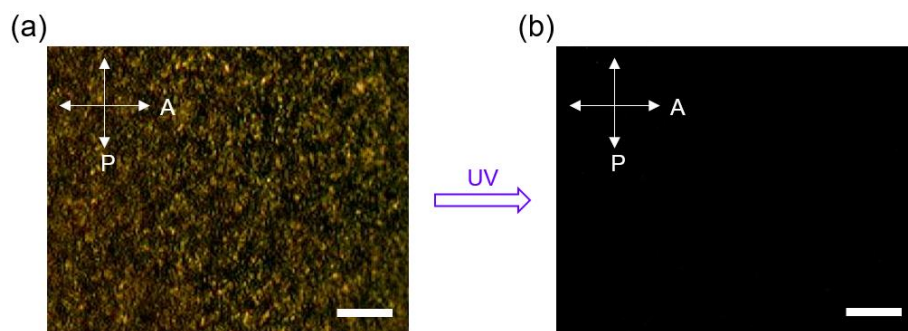


Figure S10. Polarized optical microscopy (POM) images of a *trans* PAA-*b*-PAzo thin film (a) before and (b) after UV irradiation for 10 min, scale bar: 50 μm . White arrows represent the transmission axes of the polarizer (P) and analyzer (A), respectively.

12. TGA curve of PAA-*b*-PAzo powders

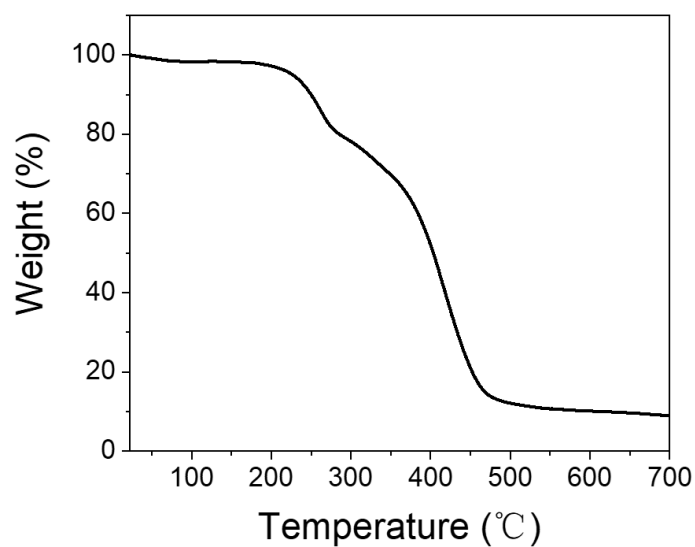


Figure S11. TGA curve of PAA-*b*-PAzo powders.

13. DSC curves for PAA-*b*-PAzo

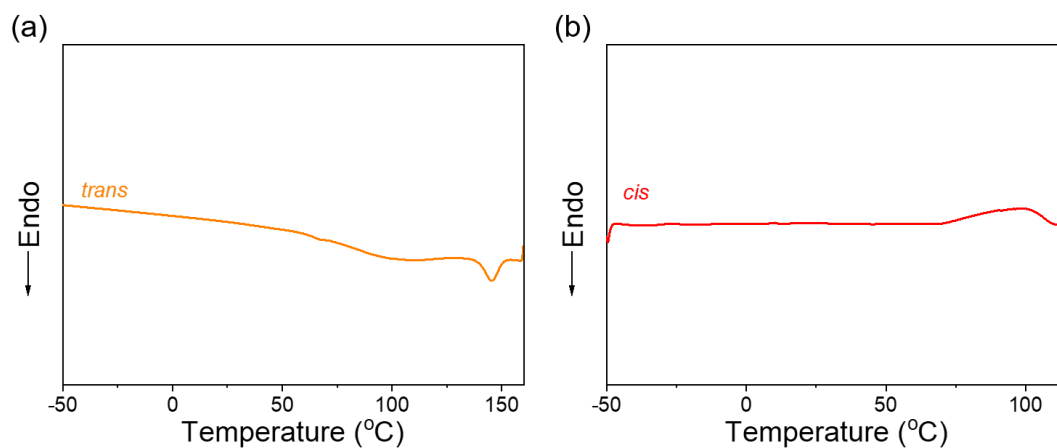


Figure S12. DSC first heating curves for (a) *trans* and (b) *cis* PAA-*b*-PAzo. *Trans* PAA-*b*-PAzo had a clearing point of 145 °C. *Cis* PAA-*b*-PAzo had a broad exothermic band at ~98 °C because of the thermal *cis*-to-*trans* isomerization.

14. Infrared thermal imaging of a *trans* PAA-*b*-PAzo thin film

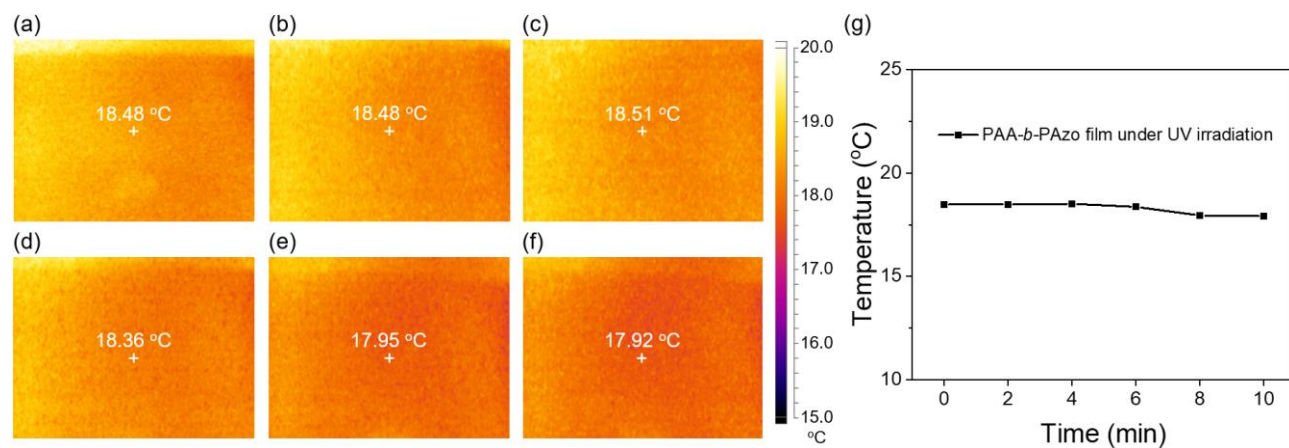


Figure S13. Infrared thermal images of a *trans* PAA-*b*-PAzo thin film (a) before UV irradiation, and after UV irradiation for (b) 2 min, (c) 4 min, (d) 6 min, (e) 8 min, and (f) 10 min. (g) The temperature of a *trans* PAA-*b*-PAzo thin film under UV irradiation.

15. References

1. W. Su, K. Han, Y. Luo, Z. Wang, Y. Li and Q. Zhang, *Macromol. Chem. Phys.*, 2007, **208**, 955-963.
2. W. Su, H. Zhao, Z. Wang, Y. Li and Q. Zhang, *Eur. Polym. J.*, 2007, **43**, 657-662.
3. H. Zhou, C. Xue, P. Weis, Y. Suzuki, S. Huang, K. Koynov, G. K. Auernhammer, R. Berger, H.-J. Butt and S. Wu, *Nat. Chem.*, 2017, **9**, 145-151.