

## ***Supporting Information***

### Photoresponsive side-chain liquid crystalline polymers with an easily cross-linkable azobenzene mesogen

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## **Experimental**

### **Synthesis of the intermediates**

**4-[(4-Hydroxy)phenylazo]benzoic acid.** 4-[(4-Hydroxy)phenylazo]benzoic acid was prepared according to the literature method (yield: 90%).<sup>1</sup> <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 13.14 (s, -COOH), 10.44 (s, Ar-OH), 8.17-8.07 (d, 2H, Ar-H), 7.94-7.82 (m, 4H, Ar-H), 7.02-6.93 (d, 2H, Ar-H).

**4-[(4-( $\omega$ -Hydroxyethoxy))phenylazo]benzoic acid (HAzoA-2).** HAzoA-2 was synthesized following the literature procedure (yield: 56 %).<sup>2</sup> <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 13.18 (s, -COOH), 8.20-8.08 (t, 2H, Ar-H), 8.00-7.88 (m, 4H, Ar-H), 7.23-7.12 (d, 2H, Ar-H), 4.92 (s, 1H, -OH), 4.18-4.09 (t, 2H, Ar-OCH<sub>2</sub>-), 3.82-3.71 (t, 2H, -CH<sub>2</sub>OH).

**4-[(4-( $\omega$ -Hydroxyhexyloxy))phenylazo]benzoic acid (HAzoA-6).** Prepared as for HAzoA-2 (yield: 57 %). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 13.18 (s, -COOH), 8.18-8.09 (d, 2H, Ar-H), 7.98-7.88 (m, 4H, Ar-H), 7.20-7.10 (d, 2H, Ar-H), 4.34 (s, 1H, -OH), 4.14-4.05 (t,

2H, Ar-OCH<sub>2</sub>-), 3.40 (the peak is partially overlapped with the peak of water in DMSO-d<sub>6</sub>, 2H, -CH<sub>2</sub>OH), 1.82-1.70 (m, 2H, Ar-OCH<sub>2</sub>CH<sub>2</sub>-), 1.50-1.29 (m, 6H, -(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>OH).

**4-[(4-(ω-Hydroxydecyloxy))phenylazo]benzoic acid (HAzoA-10).** Prepared as for HAzoA-2 (yield: 55%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ (ppm) = 13.14 (s, -COOH), 8.16-8.07 (d, 2H, Ar-H), 7.97-7.86 (m, 4H, Ar-H), 7.20-7.11 (d, 2H, Ar-H), 4.34 (s, 1H, -OH), 4.15-4.05 (t, 2H, -Ar-OCH<sub>2</sub>-), -(overlapped with the peak of water in DMSO-d<sub>6</sub>, 2H, -CH<sub>2</sub>OH), 1.81-1.69 (m, 2H, -Ar-OCH<sub>2</sub>CH<sub>2</sub>-), 1.49-1.20 (m, 14H, -(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>OH).

**4-[(4-Methacryloyloxy)phenylazo]benzoic acid (MAzoA-0).** MAzoA-0 was synthesized by reacting methacrylic acid anhydride and 4-[(4-hydroxy)phenylazo]benzoic acid according to the literature method (yield: 70%).<sup>3</sup> <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ (ppm) = 13.24 (s, 1H, -COOH), 8.21-8.12 (d, 2H, Ar-H), 8.07-7.93 (dd, 4H, Ar-H), 7.51-7.42 (d, 2H, Ar-H), 6.34 (s, 1H, CH=C), 5.96 (s, 1H, CH=C), 2.04 (s, 3H, -CH<sub>3</sub>).

**4-[(4-(ω-Methacryloyloxyethoxy))phenylazo]benzoic acid (MAzoA-2).** MAzoA-2 was synthesized by the hydrolysis of 4-[(4-(ω-methacryloyloxyethoxy))phenylazo]benzoyl methacryloyl anhydride (MAzoM-2, Scheme 1 in the manuscript) following our previously reported procedure (yield: 95%).<sup>4</sup> <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ (ppm) = 13.18 (s, 1H, -COOH), 8.18-8.04 (d, 2H, Ar-H), 8.00-7.83 (dd, 4H, Ar-H), 7.25-7.11 (d, 2H, Ar-H), 6.05 (s, 1H, CH=C), 5.70 (s, 1H, CH=C), 4.51-4.34 (tt, 4H, -OCH<sub>2</sub>CH<sub>2</sub>O-), 1.89 (s, 3H, -CH<sub>3</sub>).

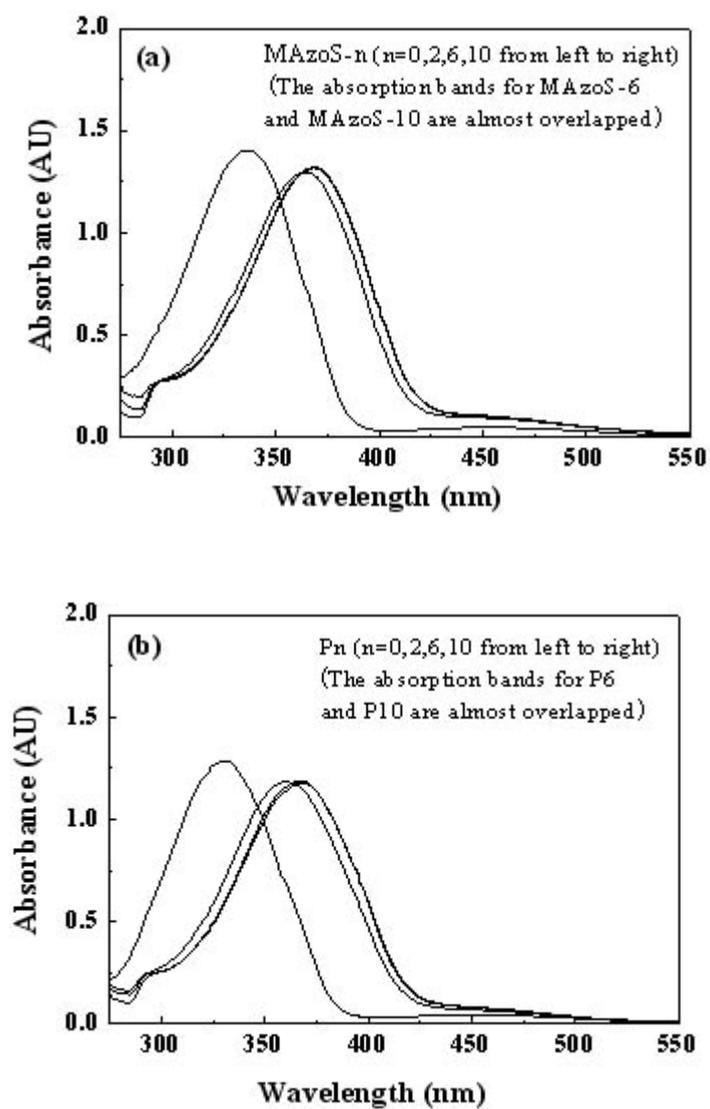
**4-[(4-(ω-Methacryloyloxyhexyloxy))phenylazo]benzoic acid (MAzoA-6).** Prepared as for MAzoA-2 (yield: 96%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ (ppm) = 13.16 (s, 1H, -COOH), 8.17-8.08 (d, 2H, Ar-H), 7.98-7.86 (dd, 4H, Ar-H), 7.20-7.09 (d, 2H, Ar-H), 6.02 (s, 1H, CH=C), 5.66 (s, 1H, CH=C), 4.15-4.04 (m, 4H, -OCH<sub>2</sub>- and -CH<sub>2</sub>O-), 1.88 (s, 3H, -CH<sub>3</sub>),

1.84-1.34 [m, 8H, -(CH<sub>2</sub>)<sub>4</sub>-].

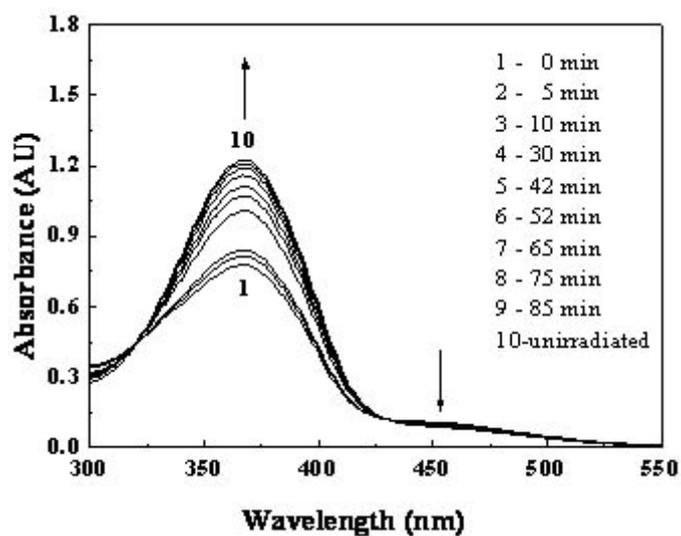
**4-[(4-( $\omega$ -Methacryloyloxydecyloxy))phenylazo]benzoic acid (MAzoA-10):** Prepared as for MAzoA-2 (yield: 98 %). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) =13.25 (s, 1H, -COOH), 8.18-8.09 (d, 2H, Ar-H), 7.99-7.87 (dd, 4H, Ar-H), 7.20-7.09 (d, 2H, Ar-H), 6.01 (s, 1H, CH=C), 5.66 (s, 1H, CH=C), 4.14-4.03 (m, 4H, -OCH<sub>2</sub>- and -CH<sub>2</sub>O-), 1.87 (s, 3H, -CH<sub>3</sub>), 1.81-1.21 [m, 16H, -(CH<sub>2</sub>)<sub>8</sub>-].

### Characterization

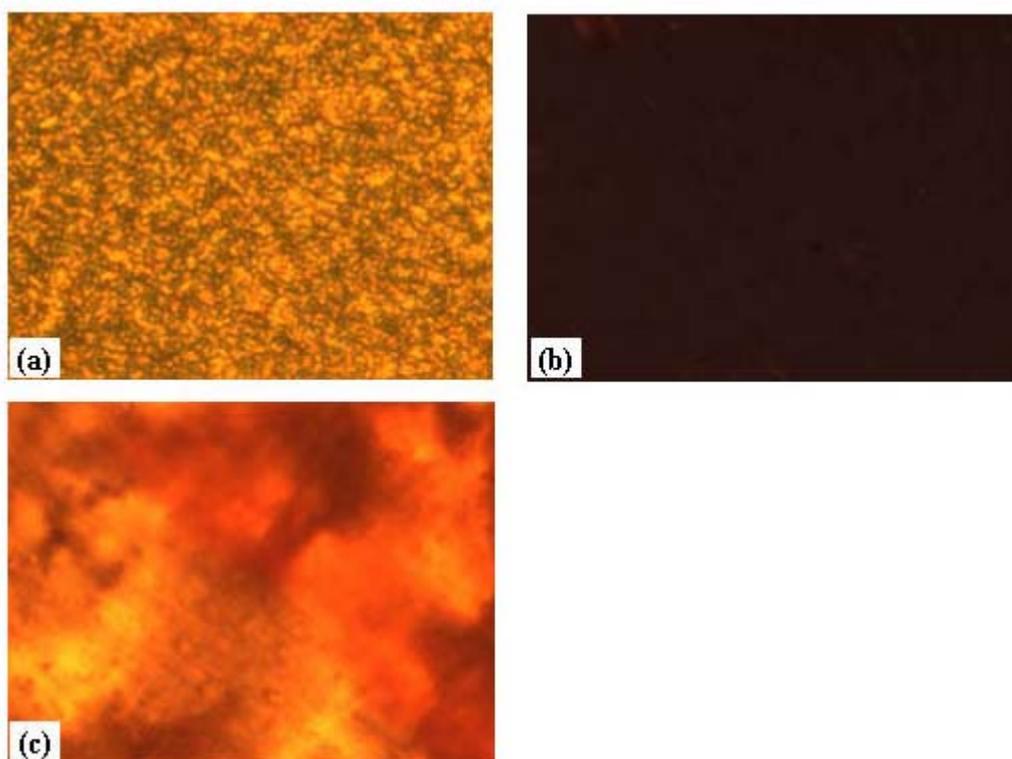
<sup>1</sup>H NMR spectra were recorded on a Varian Unity plus-400 spectrometer (400 MHz). An UV-vis scanning spectrophotometer (TU1900, Beijing Purkinje General Instrument Co., Ltd) was utilized to obtain the UV-vis spectra of the monomer and polymer samples at 25 °C. The thermal back-isomerization of the solution of P10 in THF was investigated by firstly irradiating it with a 365 nm UV lamp (12 w) for 4 min until the photostationary state was reached and then the UV-vis spectrum of the polymer solution in the dark was measured in different time at 25 °C. The liquid crystalline textures of the polymer films were observed by using an Olympus BX51 polarizing optical microscope (POM) equipped with a Linksys 32 THMSE600 hot stage and a digital camera (Micropublisher 5.0 RTV). The reversible photoisomerization of the crosslinked polymer film was studied by exposing the film to alternating UV (365 nm light) and visible light irradiation (430 <  $\lambda$  < 550 nm).



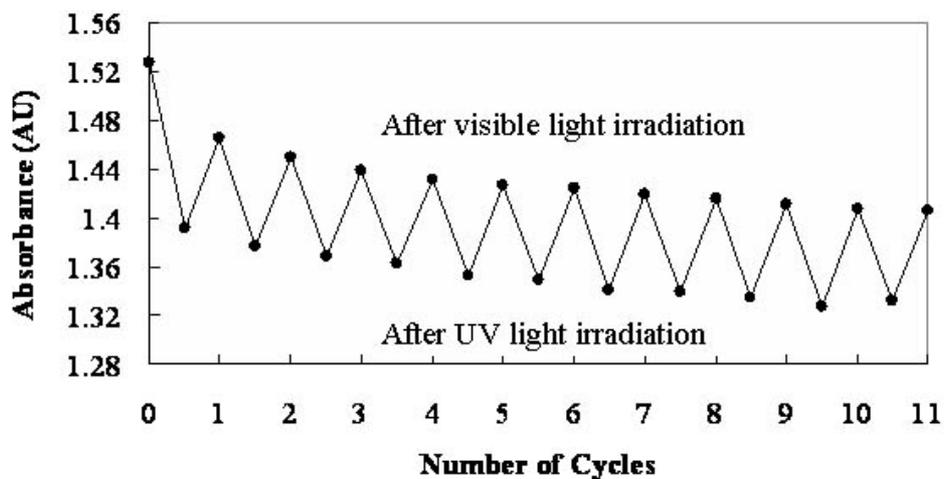
**Fig. S1** UV-vis spectra of the solutions of the azo monomers (a,  $C = 5 \times 10^{-5}$  M) and polymers (b,  $C = 5 \times 10^{-5}$  M of the repeat unit in the polymers) in THF at 25 °C.



**Fig. S2** UV-vis spectral changes in dependence of time for the solution of P10 in THF ( $C = 0.0282$  mg/mL) in the dark at  $25$  °C after being irradiated for 4 min with 365 nm light.



**Fig. S3** POM images upon cooling: uncrosslinked P10 film at  $155$  °C (annealed for 30 min) (a) and at  $170$  °C (b); crosslinked P10 film at  $200$  °C (annealed for 55 min) (c).



**Fig. S4** UV and visible light-induced photoisomerization cycles of the crosslinked polymer P10 film shown in Figure 8. In each cycle (from the 2<sup>nd</sup> cycle), the film was irradiated firstly with UV light for 3 min and then with visible light for 7 min, respectively.

## References

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