

Supporting Information

**New Benzylidene Oxazolone Derived Polymeric Photoswitches for Light-Induced Tunable Thermoresponsive Behaviors**

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## **Experimental Section**

### **Materials**

Dimethyl acrylamide (DMA) was purified by passing it through a column filled with basic alumina to remove inhibitors. 3-vinylbenzaldehyde (VBA) (99.0 %), 2-dodecylsulfanylthiocarbonylsulfanyl-2-methylpropionic acid (CTA) and acetic anhydride were purchased from Aldrich and used without further purification. Sodium acetate and hippuric acid were purchased from TCI and used as received.

### **Instrumentation**

<sup>1</sup>H NMR spectra of the monomers and polymers were collected in CDCl<sub>3</sub> and D<sub>2</sub>O on a Bruker Avance 300 MHz NMR spectrometer. The apparent molecular weight and molecular weight distributions were measured by GPC (Agilent Technologies 1200 series) using a polystyrene standard with DMF as the eluent, at 30 °C with a flow rate of 1.00 mL/min. A 75-W medium-pressure Hg lamp with wavelength filters (365 nm and 650 nm) was used as the light source for irradiation of the polymeric photoswitches and 0.6 mL of polymer samples was used for photoisomerisation measurements. The UV–Vis spectra were recorded using an Optizen 3220 UV–Vis spectrophotometer equipped with a digital temperature controller. A 650 nm wavelength was used to determine LCST. The temperature was varied from 51 to 70 °C with a heating and cooling rate of 1 °C/min. DLS measurements were carried out using a Zetasizer (Nano ZS90, Malvern, UK) with Zetasizer software 7.03.

### **Synthesis of polymer (P1)**

Initial feed ratio (DMA:VBA = 95:5). VBA (0.14g, 1.06 mmol), DMA (2.0 g, 20.17 mmol), CTA (0.036g, 0.106 mmol), and AIBN (0.165 mg, 0.00106 mmol) were added to a Schlenk flask with 8 mL of dry DMF. The reaction mixture was purged for 30 minutes to remove the oxygen and then heated for 12 h at 80 °C. The reaction mixture was concentrated, and then precipitated in diethyl ether. The obtained polymer was then further purified by re-

precipitation. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, δ in ppm): 9.95 (1H, s, CHO), 7.59-7.17 (4H, m, Ar-H), 3.07-0.85 (118H, s, S-CH<sub>2</sub> and aliphatic H). GPC: M<sub>n</sub> = 24100, PDI = 1.07.

## **P2**

Initial feed ratio (DMA:VBA = 92.5:7.5). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, δ in ppm): 9.96 (1H, s, CHO), 7.69-7.16 (4H, m, Ar-H), 3.08-0.82 (44H, s, N-(CH<sub>3</sub>)<sub>2</sub>, S-CH<sub>2</sub> and aliphatic H). GPC: M<sub>n</sub> = 16300, PDI = 1.10.

## **P3**

Initial feed ratio (DMA:VBA = 90:10). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, δ in ppm): 10.0 (1H, s, CHO), 7.71-7.15 (4H, m, Ar-H), 3.09-0.86 (31H, s, N-(CH<sub>3</sub>)<sub>2</sub>, S-CH<sub>2</sub> and aliphatic H). GPC: M<sub>n</sub> = 11800, PDI = 1.10.

## **Post modification of P1-BO ~ P3-BO**

Post modification of the aldehyde groups in the polymers P1, P2 and P3 into benzylidene oxazolone was carried out by following the procedure reported in the literature.<sup>1</sup> Briefly, hippuric acid (5 equivalents) and sodium acetate (5 equivalents, 20 mmol) in 15 ml of acetic anhydride was added to the corresponding aldehyde-containing polymer (1 equivalent, 20 mmol). The resulting mixture was stirred for 4 hours at 120 °C. The mixture was then stirred overnight at 25 °C. The acetic anhydride was then removed by vacuum distillation, and the polymers were then precipitated in cold diethyl ether. The pale yellow solid product was further purified by performing multiple precipitations.

### **P1-BO**

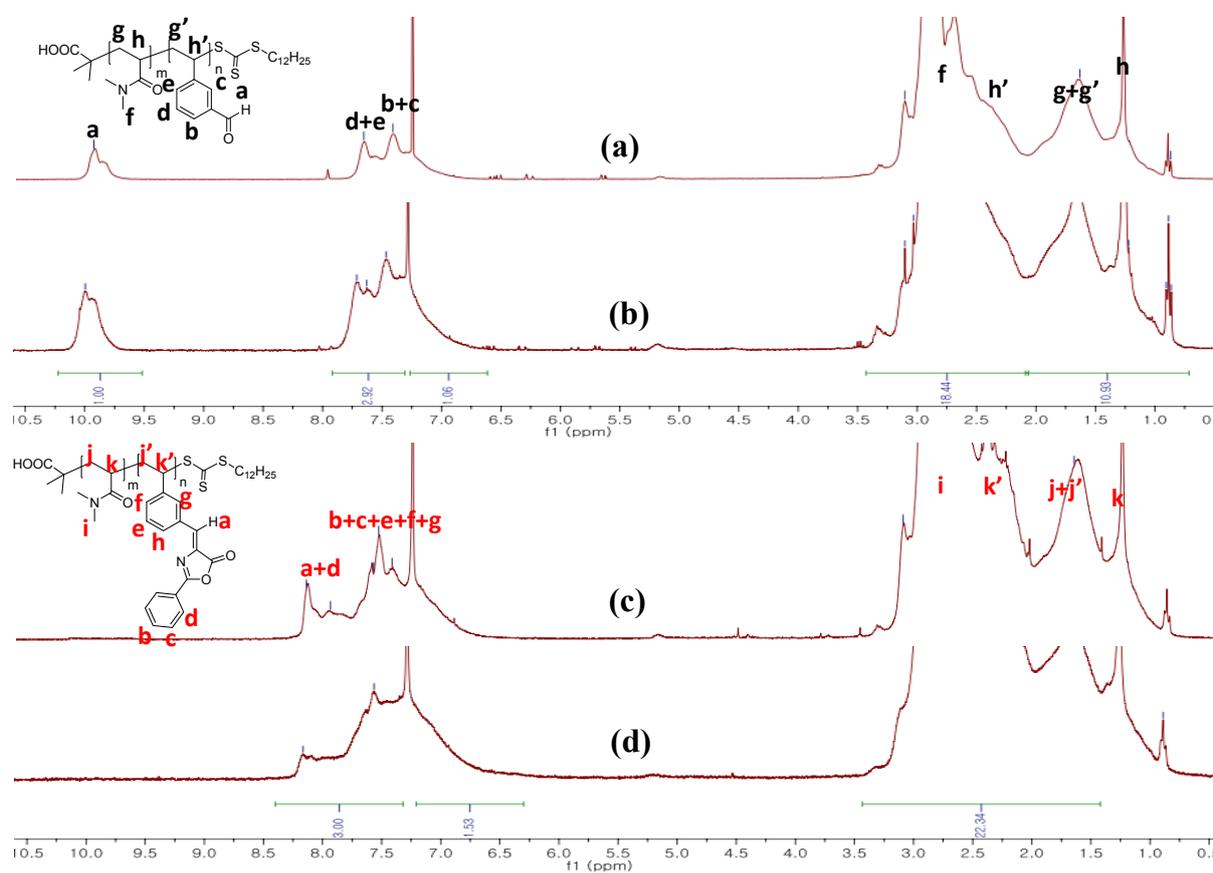
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, δ in ppm): 8.19 (1H, s, vinyl-H), 7.98-7.20 (9H, m, Ar-H), 3.13-0.81 (118H, s, S-CH<sub>2</sub> and aliphatic H).

### **P2-BO**

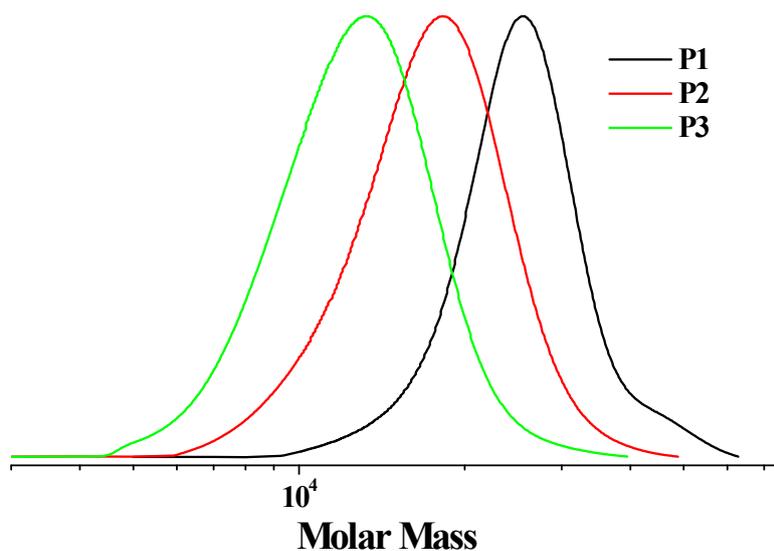
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  in ppm): 8.20 (1H, s, vinyl-**H**), 7.99-7.19 (9H, m, Ar-**H**), 3.12-0.82 (44H, s, N-( $\text{CH}_3$ )<sub>2</sub>, S- $\text{CH}_2$  and aliphatic **H**).

### P3-BO

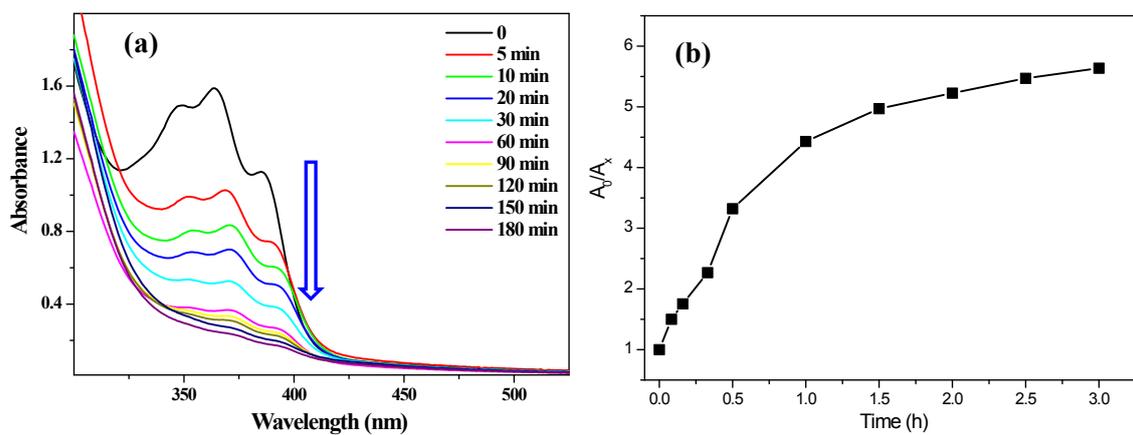
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  in ppm): 8.16 (1H, s, vinyl-**H**), 7.96-7.17 (9H, m, Ar-**H**), 3.13-0.80 (31H, s, N-( $\text{CH}_3$ )<sub>2</sub>, S- $\text{CH}_2$  and aliphatic **H**).



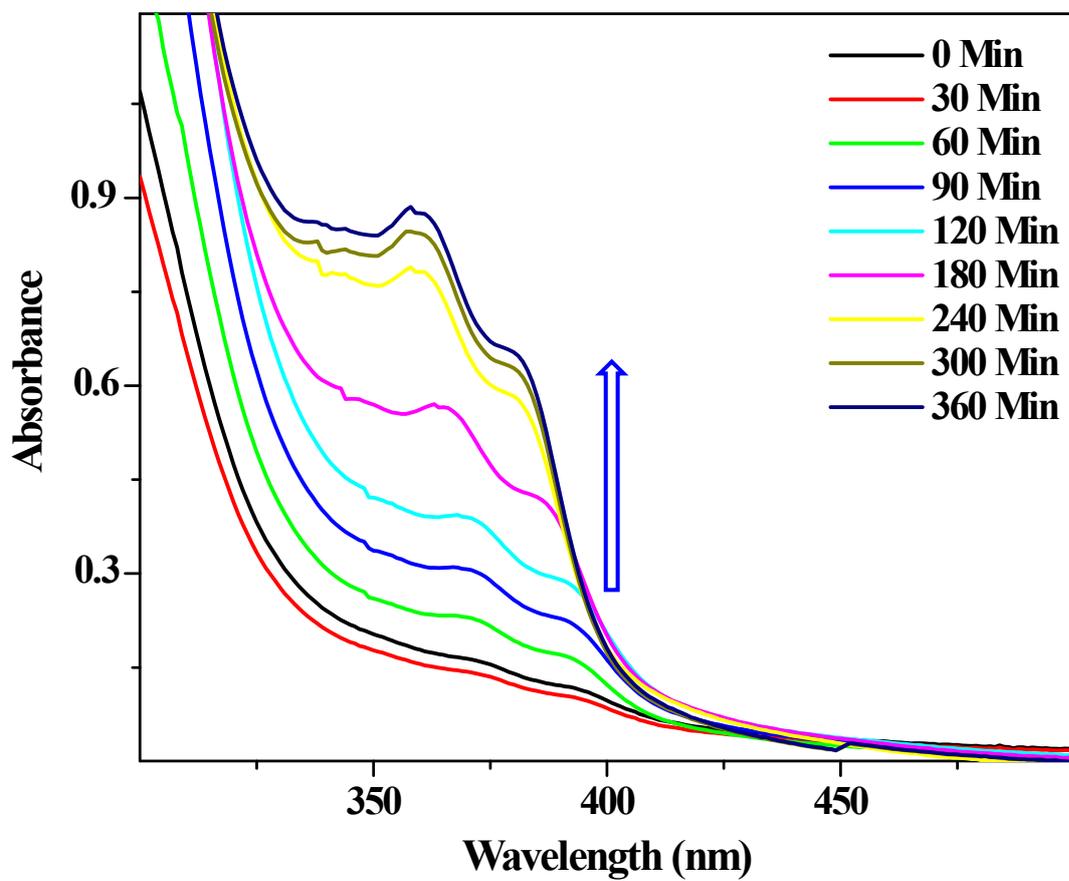
**Figure S1.**  $^1\text{H-NMR}$  spectra of (A) P2, (B) P3, (C) P2-BO, and (D) P3-BO.



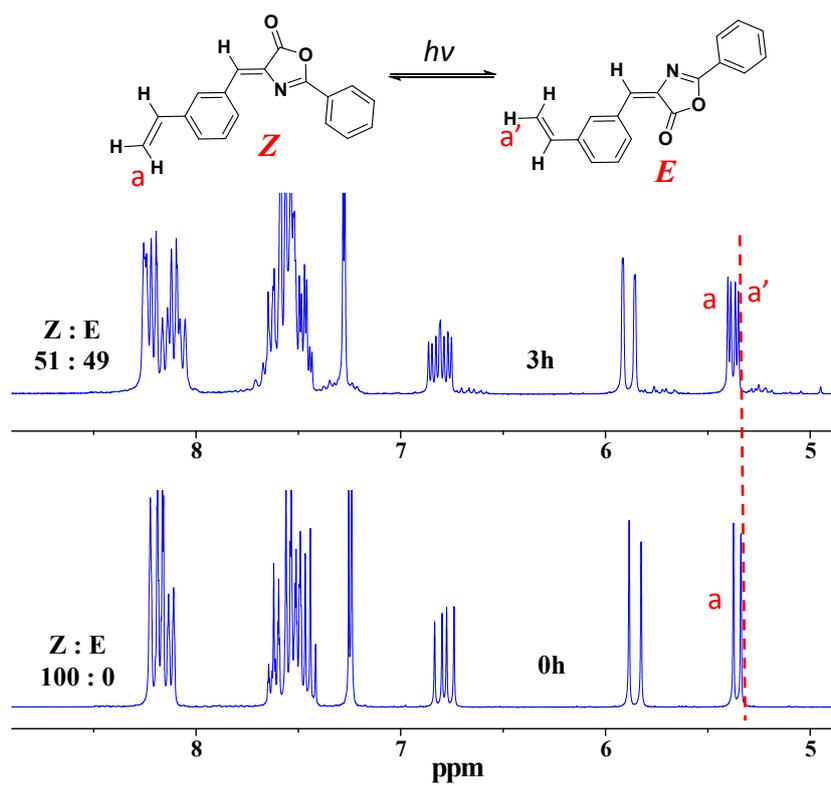
**Figure S2.** GPC chromatogram of polymeric photoswitches.



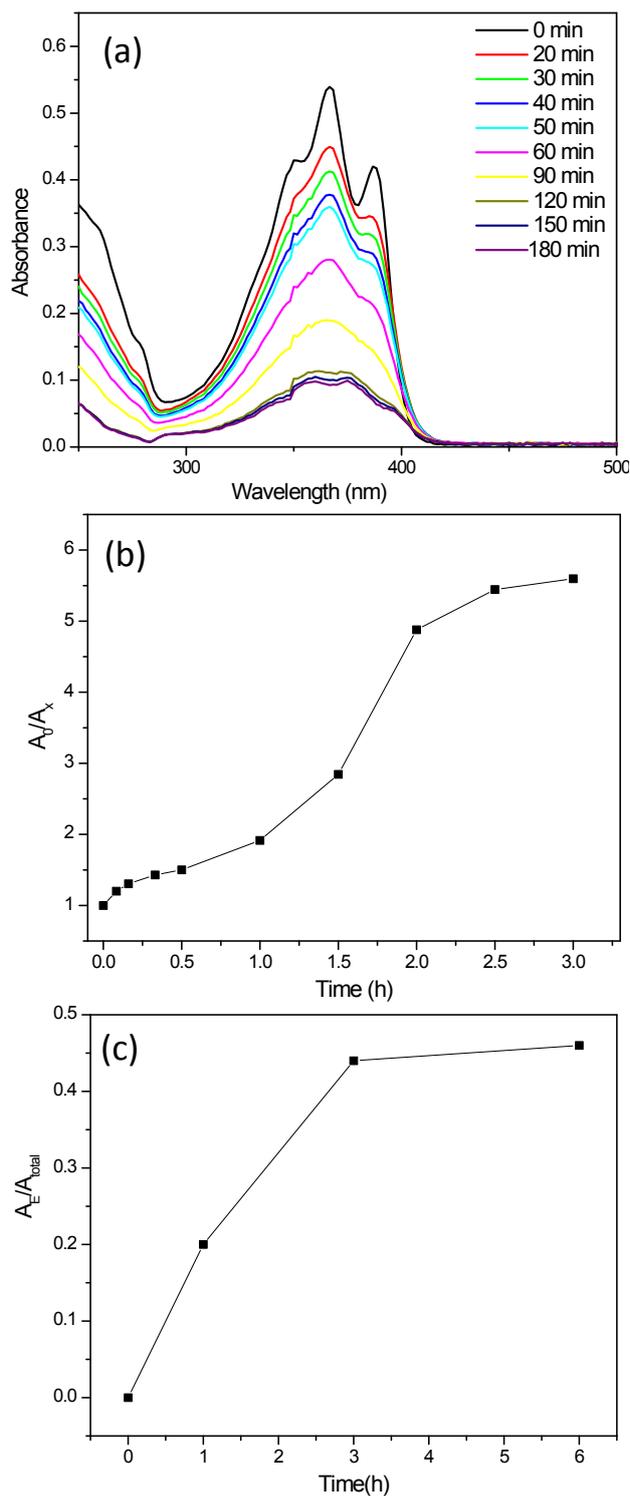
**Figure S3.** (a) UV-Vis absorption responses of P3-BO under UV irradiation (365 nm) at different time intervals. (b) The plot of  $A_0/A_x$  versus irradiation time ( $A_0$  = initial absorbance,  $A_x$  = absorbance after x h UV irradiation).



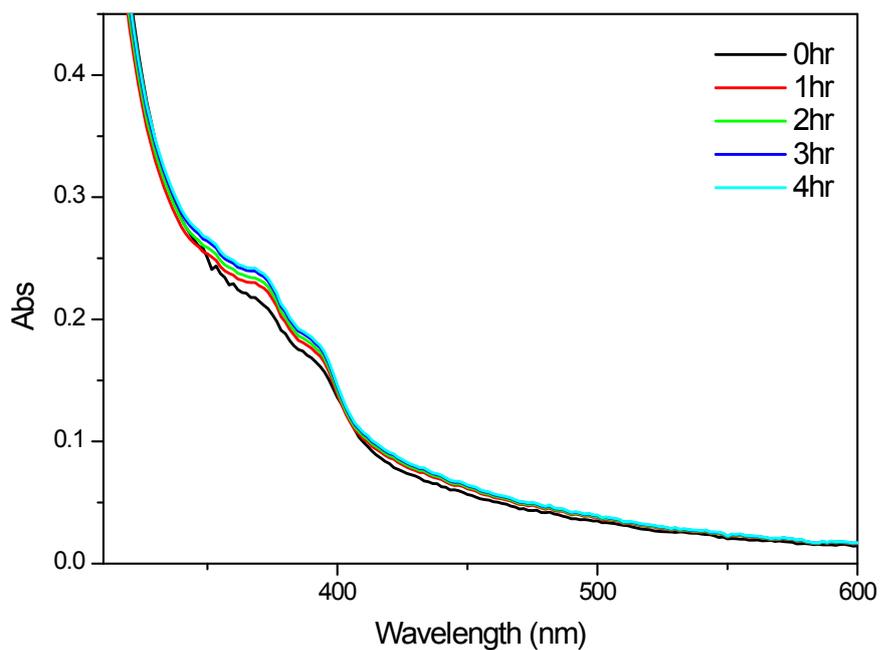
**Figure S4.** (a) UV-Vis absorption responses of P2-BO under visible light irradiation (650 nm) at different time intervals (E-Z isomerization).



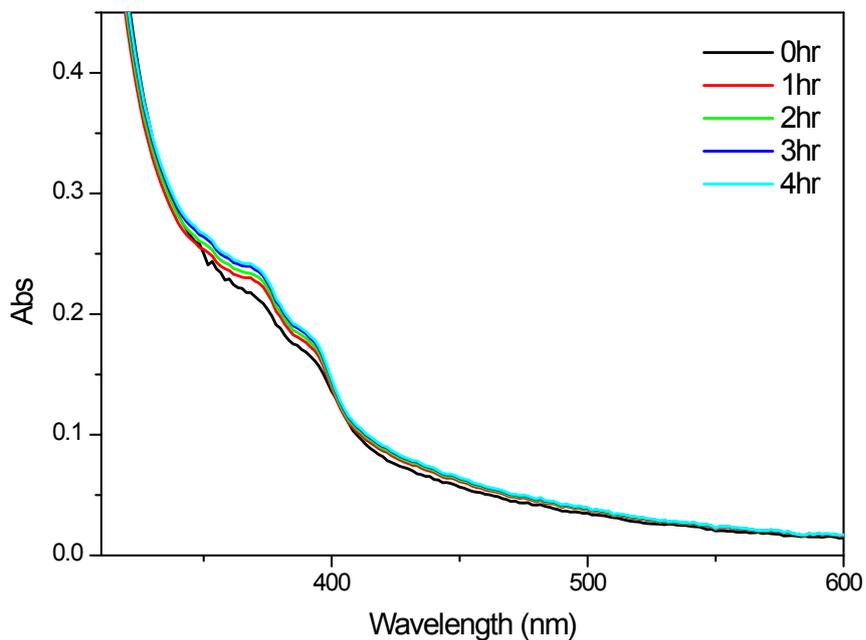
**Figure S5.** NMR spectra of vinylbenzylidene oxazolone (VBO) monomer upon photo-irradiation with UV light for various time intervals.



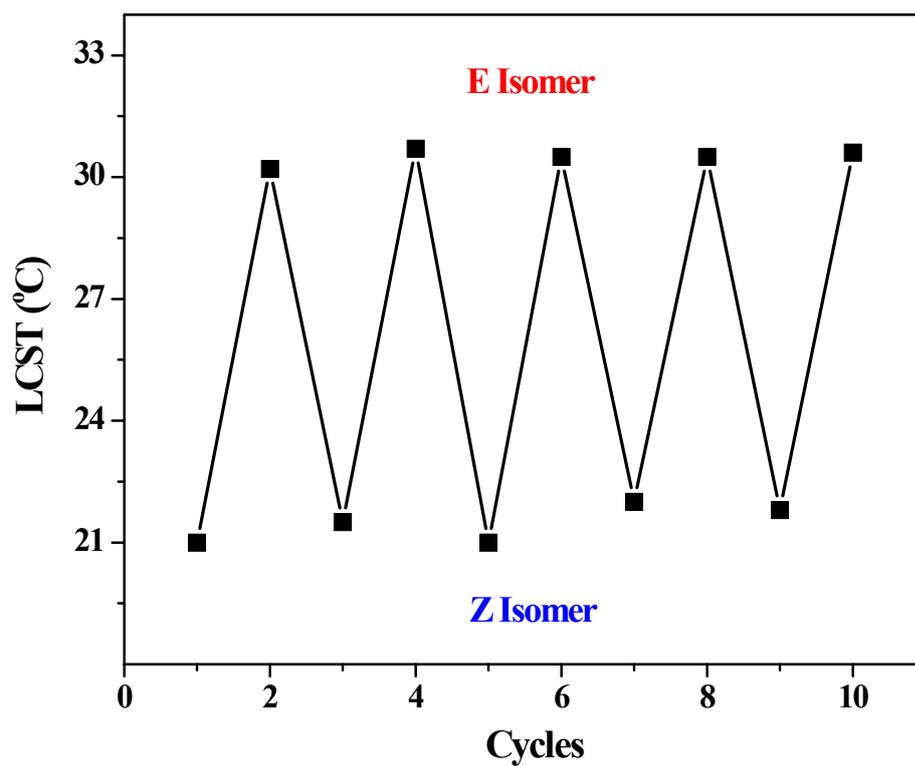
**Figure S6.** (a) UV-Vis absorption responses of vinylbenzylidene oxazolone (VBO) monomer under UV irradiation (365 nm) at different time intervals. (b) The plot of  $A_0/A_x$  versus irradiation time ( $A_0$  = initial absorbance,  $A_x$  = absorbance after x h UV irradiation). (c) The plot of  $A_E/A_{total}$  versus irradiation time ( $A_E$  is the area of NMR peak corresponding to the E isomer of proton 'a' at x h of photoirradiation, and  $A_{total}$  is area of the NMR peak corresponding to Z + E isomers of proton 'a' at x h of photoirradiation).



**Figure S7.** UV-Vis absorption responses of P2-BO upon heating at 65 °C with different time intervals.



**Figure S8.** UV-Vis absorption responses of P3-BO upon heating at 65 °C with different time intervals.



**Figure S9.** The reversibility plot of the LCST of P3-BO solution (3.0 wt. %) versus the number of cycles of alternating irradiation with UV and Visible light.

**Reference:**

1. Blanco-Lomas, M.; Campos, P. J.; Sampedro, D. *Org. Lett.* **2012**, 14, 4334-4337