

## Supporting Information

### Dual Thermo- and Light-responsive Dendron-Jacketed

### Homopolymer Containing Photoswitchable Azobenzene Groups via macromonomer route

ChangAn Yang\*, Ling Chen, Ying Lu, He Huang

*Department of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang  
414006, Hunan Province, PR China.*

\* To whom correspondence should be addressed.

Chang\_anyang@163.com (ChangAn Yang)

#### 1. Materials

Tosylated diethylene glycol monomethyl ether (Me-DEG-Ts) and tosylated triethylene glycol monoethyl ether (Me-TEG-Ts) was synthesized according to literature method.<sup>S1</sup> Ethyl *p*-aminobenzoate was purchased from Aldrich Chemical Co. Methyl 3, 4, 5-trihydroxybenzoate was purchased from Aldrich Chemical Co. Azobisisbutyronitrile (AIBN) was purified by recrystallization from ethanol. THF (AR; Beijing Chemical Co.) and Triethylamine (Acros, 99%) were heated under reflux over calcium hydride for at least 8 h and distilled before use. Deionized water (DI-water) was obtained from a reagent water system (Aquapro) with a specific resistivity of 18.25 M $\Omega$  cm<sup>-1</sup>. All other reagents were used as received from commercial sources.

#### 2. Measurements

The NMR measurements were performed on a Bruker ARX400 MHz spectrometer using CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature.

Mass spectrometry (MALDI-ToF) analysis was performed with a Bruker Aupoflex III equipped with a neodymium-doped yttrium aluminium garnet laser (Nd:YAG).

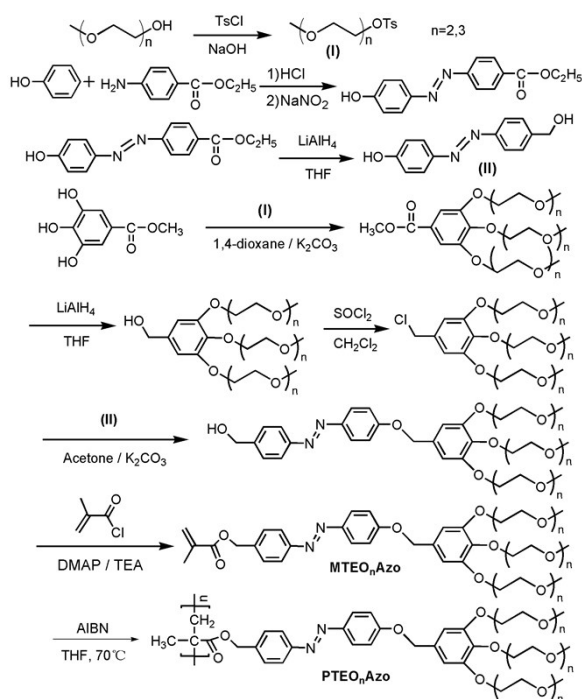
The apparent number-average MW ( $M_n$ ) and MW distribution ( $M_w/M_n$ ) were measured on a GPC (PL-GPC120) instrument with a column set consisting of two PL gel 5  $\mu$ m MIXED-D columns (7.5 $\times$ 300 mm, effective molecular weight range of 0.2-400.0 kg mol<sup>-1</sup>) using DMF that contained 0.01 M LiBr as the eluent at 80 °C at a flow rate of 1.0 mL min<sup>-1</sup>.

DSC examination was carried out on a TA DSC Q100 calorimeter with a programmed heating procedure in nitrogen. The sample size was about 5 mg and encapsulated in hermetically sealed aluminum pans, whose weights were kept constant. The temperature and heat flow were calibrated using standard materials (indium and zinc) at the cooling rate ( $10\text{ }^{\circ}\text{C min}^{-1}$ ) and the heating rate ( $10\text{ }^{\circ}\text{C min}^{-1}$ ). The temperature and heat flow scale at different cooling and heating rates were calibrated, using standard materials such as indium and benzoic acid.

UV-visible spectrophotometry (UV-vis) was conducted using a Carry 100 spectrophotometer equipped with a Peltier temperature-control programmer ( $\pm 0.1\text{ }^{\circ}\text{C}$ ). The transmittance of the aqueous sample solutions were measured by UV-Vis at 600 nm and the LCST was defined as the temperature at 50% transmittance of solutions. The photo-isomerization of azobenzene was obtained by using a 365 nm UV LED(FUWO, FUV-6BK,  $160\text{ mW cm}^{-2}$ ) or a 470 nm Vis LED(FUWO, F7B-B20,  $160\text{ mW cm}^{-2}$ ).

The surface morphology of the  $\text{MTEO}_3\text{Azo}$ ,  $\text{MTEO}_2\text{Azo}$  and  $\text{PTEO}_3\text{Azo}$  was investigated using a JEOL JSM-6610 scanning electron microscope (SEM) operating at 30 KV.

### 3. Synthetic Procedure



**Scheme S1.** Synthetic route of the thermo/light dual-responsive monomers ( $\text{MTEO}_n\text{Azo}$ ) and corresponding homopolymers ( $\text{PTEO}_n\text{Azo}$ ) ( $n = 2, 3$ ).

The monomers (MTEO<sub>3</sub>Azo and MTEO<sub>2</sub>Azo) were prepared through a multi-step synthetic route and their corresponding homopolymers (PTEO<sub>3</sub>Azo and PTEO<sub>2</sub>Azo) were synthesized via macromonomer route as depicted in the (Scheme S1).

**Synthesis of monomers.** The synthetic route of the dual thermo- and light-responsive monomers, 4-(4'-(3, 4, 5-tris (2-(2-methoxyethoxy) ethoxy) benzyloxy) phenylazo) benzyl methacrylate (MTEO<sub>2</sub>Azo) and 4-(4'-(3, 4, 5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzyloxy)) phenylazo) benzyl methacrylate (MTEO<sub>3</sub>Azo), were illustrated in Scheme S1. The experimental details are described as follows using 4-(4'-(3, 4, 5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzyloxy)) phenylazo) benzyl methacrylate (MTEO<sub>3</sub>Azo) as an example.

**Synthesis of 4-((4'-hydroxy) phenylazo) benzoate.** 4-((4'-Hydroxy) phenylazo) benzoate was synthesized according to literature method.<sup>S2</sup> <sup>1</sup>H NMR (δ, ppm, DMSO): 8.20-8.17 (m, 2H, Ar-H); 7.93-7.90 (m, 4H, Ar-H); 6.99-6.97 (m, 2H, Ar-H); 5.61 (s, 1H, -OH); 4.44-4.42 (m, 2H, -CH<sub>2</sub>-); 1.45-1.42 (t, 3H, -CH<sub>3</sub>).

**Synthesis of 4-((4'-hydroxy) phenylazo) benzyl alcohol.** 4-((4'-Hydroxy) phenylazo) benzyl alcohol was synthesized by reduction of 4-((4'-hydroxy) phenylazo) benzoate with LiAlH<sub>4</sub>. Orange solid, yield: 92%. <sup>1</sup>H NMR (δ, ppm, DMSO): <sup>1</sup>H NMR (δ, ppm, DMSO): 7.73-7.70 (m, 4H, Ar-H); 7.45-7.43 (m, 2H, Ar-H); 6.78-6.80 (m, 2H, Ar-H); 4.55 (s, 2H, -CH<sub>2</sub>O-).

**Synthesis of Methyl 3, 4, 5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzoate.** Tosylated triethylene glycol monoethyl ether (Me-TEG-Ts) (77.27 g, 0.243 mol) in dry 1,4-dioxane (50 mL) was added to a solution of Methyl 3, 4, 5-trihydroxybenzoate (10.00 g, 0.054 mol) and K<sub>2</sub>CO<sub>3</sub> (45.00 g, 0.326 mol) in dry 1,4-dioxane (200 mL) stirring at room temperature for 30 min. Then the mixture was stirred and warmed to 100 °C over 12 h. The resulting precipitate was filtered, and 1,4-dioxane was evaporated. Purification by column chromatography with ethyl acetate/ acetone (3:1) afforded the product as a light yellow oil (42.20 g), yield: 83.1%. <sup>1</sup>H NMR (δ, ppm, CDCl<sub>3</sub>): 7.30-7.28 (m, 2H, Ar-H); 4.22-4.18 (t, 6H, -OCH<sub>2</sub>-); 3.88 (s, 3H, -COOCH<sub>3</sub>); 3.86-3.80 (t, 6H, -OCH<sub>2</sub>-); 3.74-3.72 (t, 6H, -OCH<sub>2</sub>-); 3.67-3.63 (t, 12H, -OCH<sub>2</sub>-); 3.55-3.53 (t, 6H, -OCH<sub>2</sub>-); 3.37 (s, 9H, -OCH<sub>3</sub>).

**Synthesis of 3, 4, 5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzyl alcohol.** LiAlH<sub>4</sub> (3.66 g, 96 mmol) was suspended in 50 mL dry THF, and the

solution of methyl 3, 4, 5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzoate (40.00 g, 64 mmol) in 300 mL dry THF was added dropwise. After the addition was complete, the mixture was reacted for further 2 h at room temperature. The reaction was quenched by dropwise addition of water, and then diluted HCl was added to dissolve the precipitate. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed sequentially with saturated NaHCO<sub>3</sub> and brine, then drying over anhydrous MgSO<sub>4</sub>. After filtration, the solvent was evaporated in vacuo to obtain a colorless liquid (35.24 g), yield: 92.6%. <sup>1</sup>H NMR (δ, ppm, CDCl<sub>3</sub>): 6.62-6.63 (m, 2H, Ar-H); 4.50 (s, 2H, Ar-CH<sub>2</sub>OH); 4.17-4.15 (t, 6H, -OCH<sub>2</sub>-); 3.86-3.77 (t, 6H, -OCH<sub>2</sub>-); 3.73-3.71 (t, 6H, -OCH<sub>2</sub>-); 3.67-3.63 (t, 12H, -OCH<sub>2</sub>-); 3.55-3.53 (t, 6H, -OCH<sub>2</sub>-); 3.38 (s, 9H, -OCH<sub>3</sub>).

**Synthesis of 3, 4, 5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzyl chloride.** 3, 4, 5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzyl alcohol (30.00 g, 50 mmol) was dissolved in dry DCM (200 mL), and a mixture of SOCl<sub>2</sub> (7.80g, 65 mmol) and DCM (50 mL) was added dropwise at room temperature. After the addition was complete, the mixture was reacted for further 2h at room temperature. The reaction was quenched by dropwise addition of water. The organic layer was washed with water and dried over anhydrous MgSO<sub>4</sub>, and further evaporated under reduced pressure to obtain a colorless liquid (28.56 g), yield: 93.2%. <sup>1</sup>H NMR (δ, ppm, CDCl<sub>3</sub>): 6.62-6.63 (m, 2H, Ar-H); 4.50 (s, 2H, Ar-CH<sub>2</sub>Cl); 4.17-4.15 (t, 6H, -OCH<sub>2</sub>-); 3.86-3.77 (t, 6H, -OCH<sub>2</sub>-); 3.73-3.71 (t, 6H, -OCH<sub>2</sub>-); 3.67-3.63 (t, 12H, -OCH<sub>2</sub>-); 3.55-3.53 (t, 6H, -OCH<sub>2</sub>-); 3.38 (s, 9H, -OCH<sub>3</sub>).

**Synthesis of 4-(4'-(3, 4, 5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzyloxy) phenylazo) benzyl alcohol.** A mixture of 3, 4, 5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzyl chloride (19.00 g, 31 mmol), 4-((4'-hydroxy) phenylazo) benzyl alcohol (6.84 g, 30 mmol), KI (0.5 g), and K<sub>2</sub>CO<sub>3</sub> (8.28 g, 60 mmol) in dry acetone (200 mL) was stirred at 65 °C for 12 h. After removal of acetone in vacuo, the crude product was subsequently purified by flash column chromatography using acetone/ CH<sub>2</sub>Cl<sub>2</sub> (2:3) as eluent. The resulting purified product was an orange liquid (18.40 g), yield: 76.2%. <sup>1</sup>H NMR (δ, ppm, CDCl<sub>3</sub>): 7.95-7.85 (m, 4H, Ar-H); 7.51-7.49 (m, 2H, Ar-H); 7.09-7.07 (m, 2H, Ar-H); 6.69 (s, 2H, Ar-H); 5.03 (s, 2H, ArCH<sub>2</sub>O-); 4.78 (s, 2H, ArCH<sub>2</sub>OH-); 4.18-4.16 (t, 6H, -OCH<sub>2</sub>-); 3.87-3.79 (t, 6H, -OCH<sub>2</sub>-); 3.73-3.71 (t, 6H, -OCH<sub>2</sub>-); 3.66-3.64 (t, 12H, -OCH<sub>2</sub>-); 3.55-3.53 (t, 6H, -OCH<sub>2</sub>-); 3.37 (s, 9H, -OCH<sub>3</sub>).

**Synthesis of 4-(4'-(3, 4, 5-tris (2-(2-(2-methoxyethoxy) ethoxy) benzyloxy) phenylazo) benzyl methacrylate (MTEO<sub>3</sub>Azo).** To a solution of 4-(4'-(3, 4, 5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzyloxy) phenylazo) benzyl alcohol (16.1 g, 20 mmol) and NEt<sub>3</sub> (8.10 g, 80 mmol) and DMAP (0.07 g, 0.60 mmol) in THF (100 mL) was added methacryloyl chloride (2.72 g, 26 mmol) at 0-5 °C. After stirring overnight, a few drops of H<sub>2</sub>O were added to quench the reaction. The mixture was then partitioned between DCM and water. The organic layer was washed with dilute hydrochloric acid, aqueous solution of sodium bicarbonate, and brine, and dried over anhydrous MgSO<sub>4</sub> and further evaporated under reduced pressure to obtain an orange liquid. The crude product was purified by column chromatography with acetone/ CH<sub>2</sub>Cl<sub>2</sub> (2:3) afforded the product as an orange liquid (13.43 g), yield: 76.9%. <sup>1</sup>H NMR (δ, ppm, CDCl<sub>3</sub>): 7.98-7.88 (m, 4H, Ar-H); 7.53-7.49 (m, 2H, Ar-H); 7.11-7.06 (m, 2H, Ar-H); 6.69 (s, 2H, Ar-H); 6.20 (s, 1H, =CH-); 5.62 (s, 1H, =CH-); 4.17-4.14 (t, 6H, -OCH<sub>2</sub>-); 3.86-3.79 (t, 6H, -OCH<sub>2</sub>-); 3.74-3.71 (t, 6H, -OCH<sub>2</sub>-); 3.66-3.64 (t, 12H, -OCH<sub>2</sub>-); 3.55-3.53 (t, 6H, -OCH<sub>2</sub>-); 3.37 (s, 9H, -OCH<sub>3</sub>); 1.99 (s, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 18.37 (-CH<sub>3</sub>), 58.88 (-OCH<sub>3</sub>), 68.83 (Ar-CH<sub>2</sub>O-CO-), 69.67 (Ar-CH<sub>2</sub>O-Ar), 70.53, 70.67, 70.79, 71.89, 76.76, 77.05, 77.38 (-OCH<sub>2</sub>-), 107.09, 110.00, 114.98, 122.86, 124.73, 128.67, 138.22, 147.33, 152.31, 152.73 (Ar), 126.18 (CH<sub>2</sub>=), 131.74, (=C-) 161.24 (C=O). Mass spectrometry (MS) (*m/z*) [M+Na]<sup>+</sup> calcd for C<sub>45</sub>H<sub>64</sub>N<sub>2</sub>O<sub>15</sub>Na, 895.42; found, 895.705. [M+K]<sup>+</sup> calcd for C<sub>45</sub>H<sub>64</sub>N<sub>2</sub>O<sub>15</sub>K, 911.394; found, 911.687.

**Synthesis of 4-(4'-(3, 4, 5-tris (2-(2-methoxyethoxy) ethoxy) benzyloxy) phenylazo) benzyl methacrylate (MTEO<sub>2</sub>Azo).** According to the procedure of MTEO<sub>3</sub>Azo synthesis, from 4-(4'-(3, 4, 5-tris (2-(2-methoxyethoxy) ethoxy) benzyloxy) phenylazo) benzyl alcohol (16.5 g, 25 mmol), methacryloyl chloride (3.34 g, 32 mmol), NEt<sub>3</sub> (10.12 g, 100 mmol) and DMAP (0.09 g, 0.75 mmol) in THF (100 mL). MTEO<sub>2</sub>Azo was yielded as an orange liquid (13.66 g), yield: 75.2%. <sup>1</sup>H NMR (δ, ppm, CDCl<sub>3</sub>): 7.93-7.87 (m, 4H, Ar-H), 7.52-7.50 (m, 2H, Ar-H), 7.08-7.06 (m, 2H, Ar-H), 6.69 (s, 2H, Ar-H), 6.19 (s, 1H, =CH-), 5.62 (s, 1H, =CH-), 5.27 (s, 2H, -CH<sub>2</sub>O-), 5.04 (s, 2H, -CH<sub>2</sub>O-), 4.19-4.18 (t, 6H, -OCH<sub>2</sub>-), 3.87-3.81 (t, 6H, -CH<sub>2</sub>O-), 3.72-3.67 (t, 6H, -OCH<sub>2</sub>-), 3.56-3.54 (t, 6H, -CH<sub>2</sub>O-), 3.38-3.36 (s, 9H, -OCH<sub>3</sub>), 1.99 (s, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 161.09 (O=C-O), 152.91 (O-Ar), 152.52 (O-Ar), 147.01 (N-C-Ar), 138.11 (Ar-C-N), 137.80 (Ar-C-CH<sub>2</sub>), 136.23

(CH<sub>2</sub>=C-CH<sub>3</sub>), 131.69 (Ar-C), 128.28 (Ar-C), 126.32 (O-Ar), 124.98 (Ar-C), 122.73 (Ar-C), 114.82 (Ar-C), 110.26 (CH<sub>2</sub>=C-), 106.96 (Ar-C), 72.67 (Ar-CH<sub>2</sub>-O), 71.86 (O-CH<sub>2</sub>-CH<sub>2</sub>), 70.60 (O-CH<sub>2</sub>-CH<sub>2</sub>), 69.69 (CH<sub>2</sub>-CH<sub>2</sub>-O), 68.63 (CH<sub>2</sub>-CH<sub>2</sub>-O), 66.35 (Ar-CH<sub>2</sub>-O), 58.80 (CH<sub>3</sub>-O-), 18.12 (CH<sub>3</sub>-C=). MS (*m/z*) [M+Na]<sup>+</sup> Calcd for C<sub>39</sub>H<sub>52</sub>N<sub>2</sub>O<sub>12</sub>Na, 763.34; Found, 763.347; [M + K]<sup>+</sup> Calcd for C<sub>39</sub>H<sub>52</sub>N<sub>2</sub>O<sub>12</sub>K, 779.34; Found, 779.334.

**Polymerization.** All polymers were obtained by conventional solution radical polymerization (see Scheme 1). A typical polymerization procedure was carried out as follows: for example, the monomer MTEO<sub>3</sub>Azo (0.5 g, 0.57 mmol), 0.02 g mL<sup>-1</sup> of AIBN (470 μL) in THF solution and dry THF (4.6 mL) were transferred into a polymerization tube. After three freeze-pump-thaw cycles, the tube was sealed off under vacuum. Polymerization was carried out at 70 °C for 21 h. The tube was then opened, and the reaction mixture was diluted with THF (6 mL), and then reprecipitated in ether. After purification, the polymers were dried to a constant weight.

**Preparation of Micellar Aggregates.** Micellar aggregates of MTEO<sub>3</sub>Azo, MTEO<sub>2</sub>Azo and PTEO<sub>3</sub>Azo were prepared by using 1.0 mg mL<sup>-1</sup> of aqueous solution of the samples, respectively. To investigate the effects of irradiation, these solutions, placed in a quartz cell, were exposed to UV light for 1 h, respectively. To prepare samples for scanning (SEM) observations, one drop of the diluted solution was cast on a silicon wafer and heated to their LCSTs. The samples cast for SEM observation, before and after light illumination, were quenched immediately after casting with liquid nitrogen and then freeze-dried (-50 °C).<sup>S3, S4</sup>

#### 4. Supporting Reference

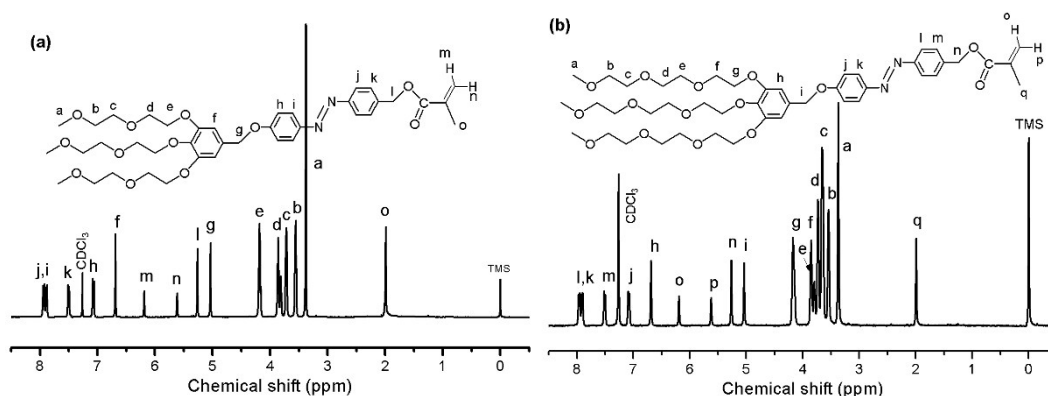
(S1) M. J. N. Junk, Wen. Li, A. D. Schlüter, G. Wegner, H. W. Spiess, A. F. Zhang and D. Hinderberger, *Angew. Chem. Int. Ed.*, 2010, **49**, 5683.

(S2) X. Q. Shen, H. W. Liu, Y. S. Li and S. Y. Liu, *Macromolecules*, 2008, **41**, 2421.

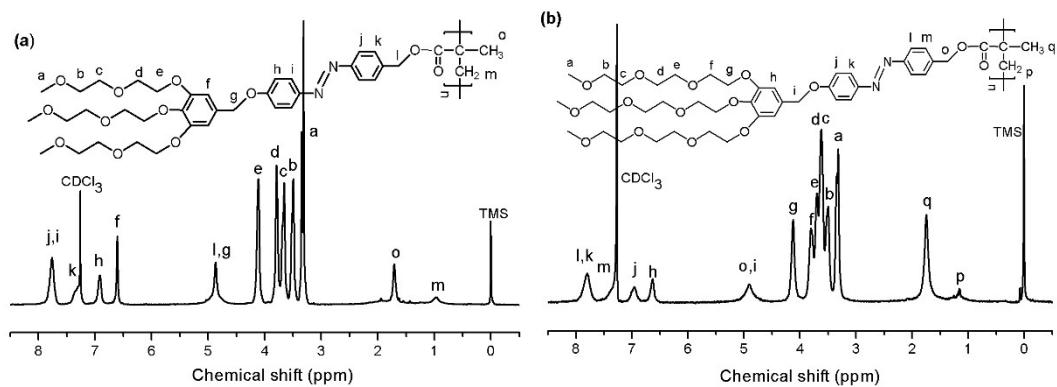
(S3) G. Wang, X. Tong and Y. Zhao, *Macromolecules*, 2004, **37**, 8911.

(S4) L. Zhang and A Eisenberg, *Macromolecules*, 2000, **33**, 2561.

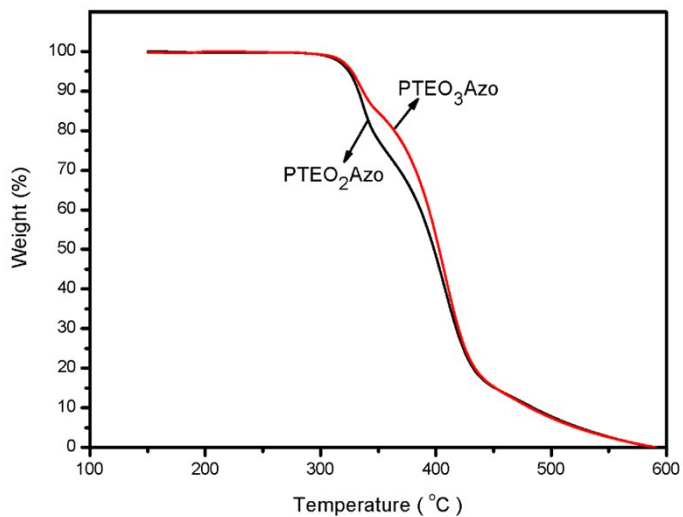
## 5. Supporting Figures



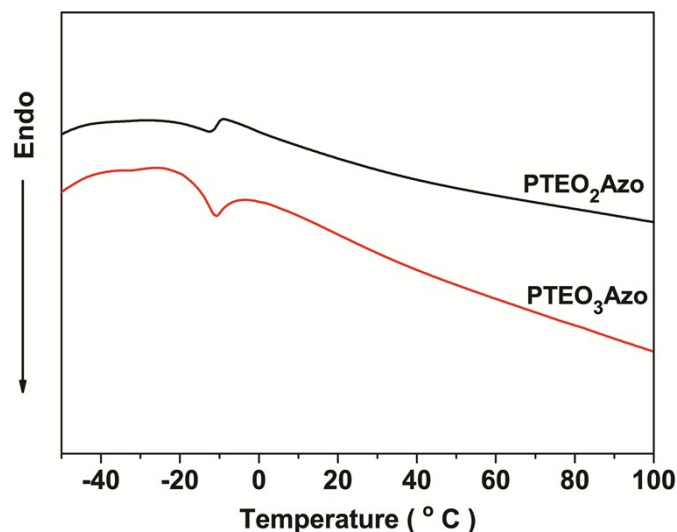
**Figure S1.**  $^1\text{H}$ NMR spectra of MTEO<sub>2</sub>Azo (a) and MTEO<sub>3</sub>Azo (b) in CDCl<sub>3</sub>-d.



**Figure S2.**  $^1\text{H}$ NMR spectra of PTEO<sub>2</sub>Azo (a) and PTEO<sub>3</sub>Azo (b) in CDCl<sub>3</sub>-d.



**Figure S3.** TGA curve of the polymers (PTEO<sub>2</sub>Azo and PTEO<sub>3</sub>Azo) at a heating rate of 20 °C min<sup>-1</sup> under N<sub>2</sub>.

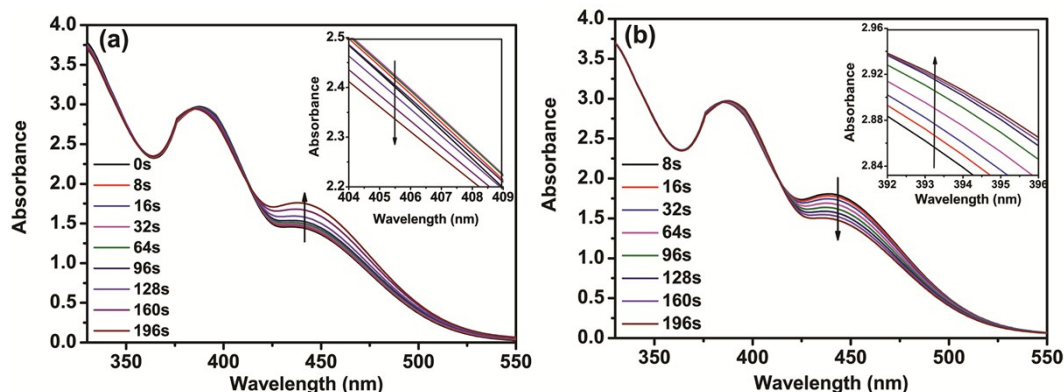


**Figure S4.** DSC curves of the polymers (PTEO<sub>2</sub>Azo and PTEO<sub>3</sub>Azo) during the second heating at a rate of 10 °C min<sup>-1</sup>.

**Table S1.** Composition and Molecular Weight for polymers PTE<sub>n</sub>Azo (n=2, 3)

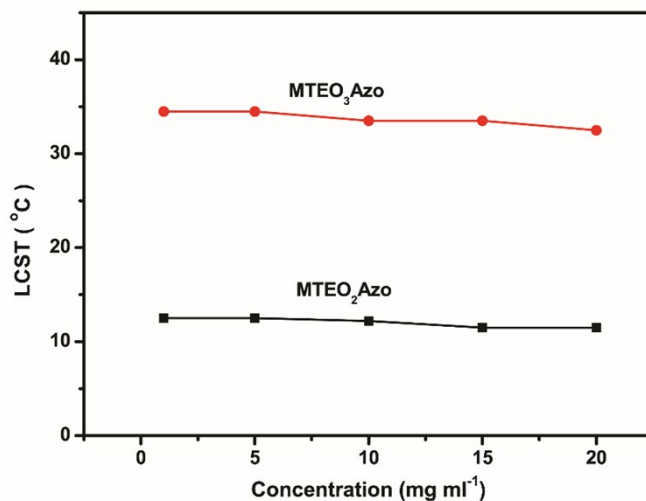
Sample	$M_n^a$ ( $\times 10^{-4}$ )	PDI <sup>a</sup>	$T_d^b$ (°C)	$T_g^c$ (°C)	LCST <sup>Vis</sup> (°C) <sup>d</sup>		LCST <sup>UV</sup> (°C) <sup>e</sup>	
					Heating	Cooling	Heating	Cooling
MTEO <sub>2</sub> Azo	—	—	—	—	12.5	11.5	6.2	5.8
MTEO <sub>3</sub> Azo	—	—	—	—	34.5	34.5	31.5	30.5
PTEO <sub>2</sub> Azo	2.19	1.57	324	-12.4	—	—	—	—
PTEO <sub>3</sub> Azo	2.14	1.31	327	-10.8	55.8	55.7	47.6	50.5

<sup>a</sup>The  $M_n$  and PDI of polymers were measured by gel permeation chromatography (GPC), using PS as standards and DMF as the eluent. <sup>b</sup>The decomposition temperature at 5% weight loss were measured by TGA at a heating rate of 20 °C min<sup>-1</sup> under N<sub>2</sub>. <sup>c</sup>The glass transition temperatures were measured by DSC at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere during the second heating process. <sup>d</sup>The transmittance of the aqueous sample solutions (1.0 mg mL<sup>-1</sup>) were measured by UV-Vis at 600 nm. The LCST was defined as the temperature at 50% transmittance of solutions. <sup>e</sup>UV irradiation was carried out with a 365 nm UV LED (FUWO, FUV-6BK 160mW cm<sup>-2</sup>).

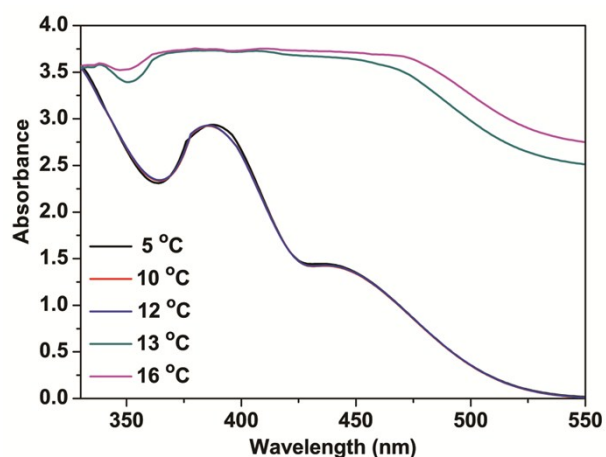




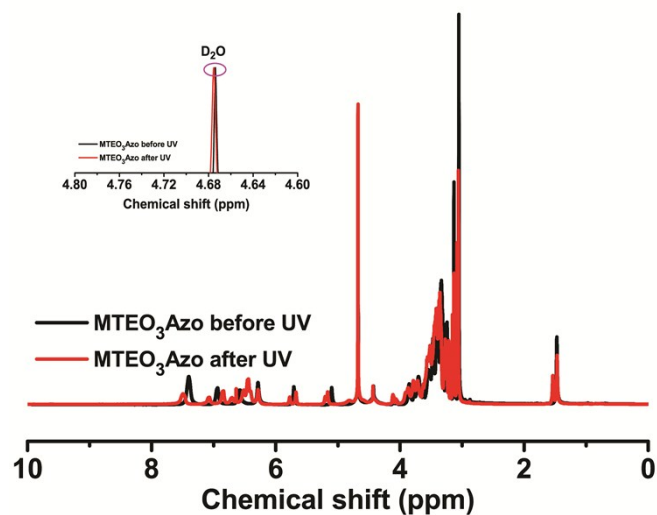
**Figure S5.** Time-dependent UV-vis absorption spectra recorded at room temperature for 1.0 mg mL<sup>-1</sup> aqueous solutions of (a) MTEO<sub>2</sub>Azo upon UV irradiation (365 nm) and (b) MTEO<sub>2</sub>Azo upon vis irradiation (470 nm) for varying time durations (0-196s).



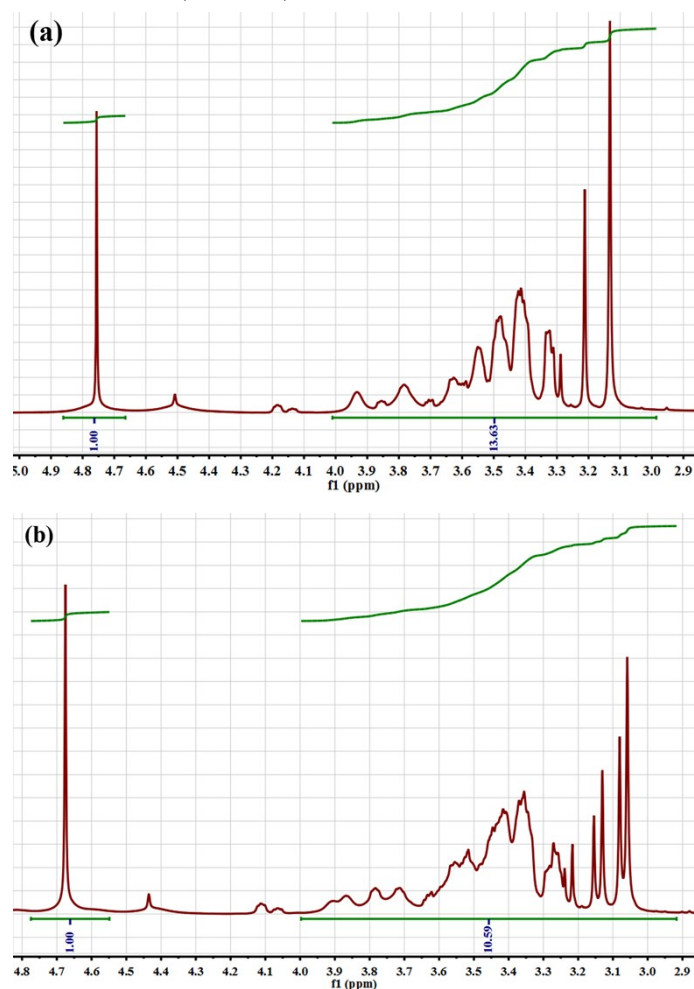
**Figure S6.** Cloud points (LCST) of MTEO<sub>2</sub>Azo and MTEO<sub>3</sub>Azo aqueous solutions as a function of concentration ranging from 1.0 mg ml<sup>-1</sup> to 20.0 mg ml<sup>-1</sup>.



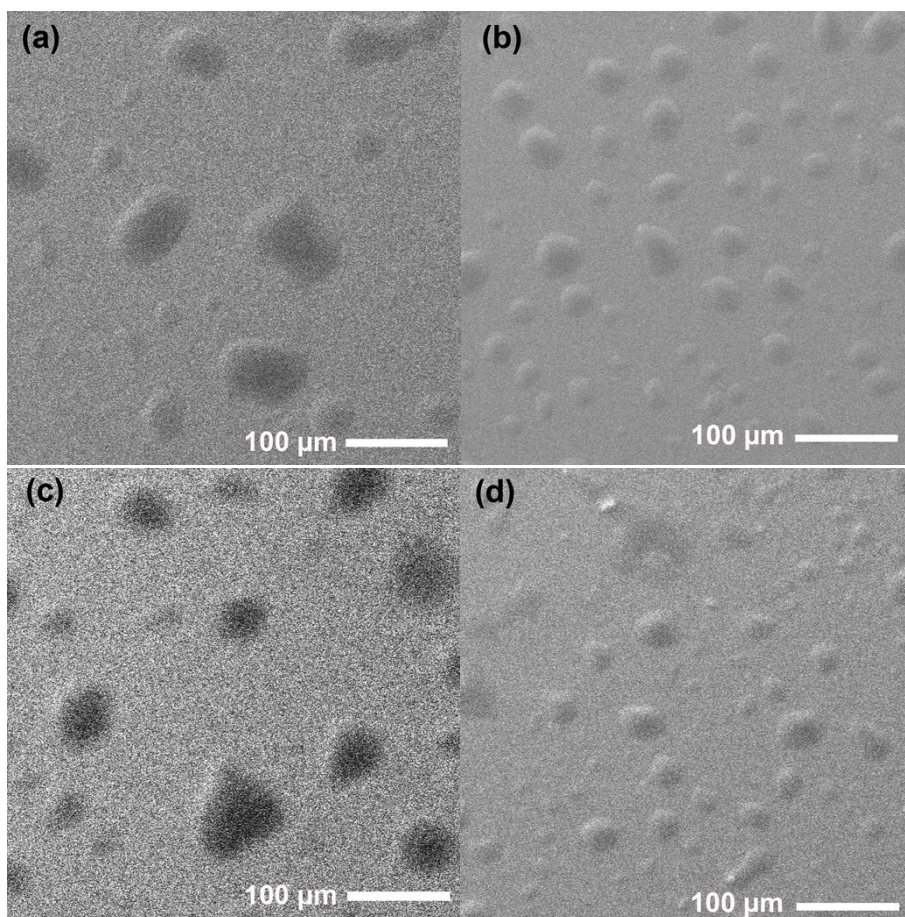
**Figure S7.** Temperature-dependent UV-vis absorption spectra recorded in the temperature range 10-15 °C for 1.0 mg ml<sup>-1</sup> aqueous solutions of MTEO<sub>2</sub>Azo (LCST=12.5 °C).



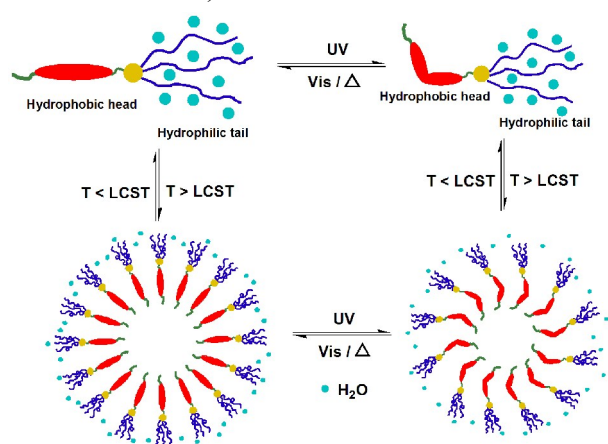
**Figure S8.** Light irradiation dependence of the  $^1\text{H}$  NMR spectral areas of the ethylene oxide units of the monomer  $\text{MTEO}_3\text{Azo}$  2% (w/v) in  $\text{D}_2\text{O}$  before UV irradiation (365 nm) and after UV irradiation (365 nm).



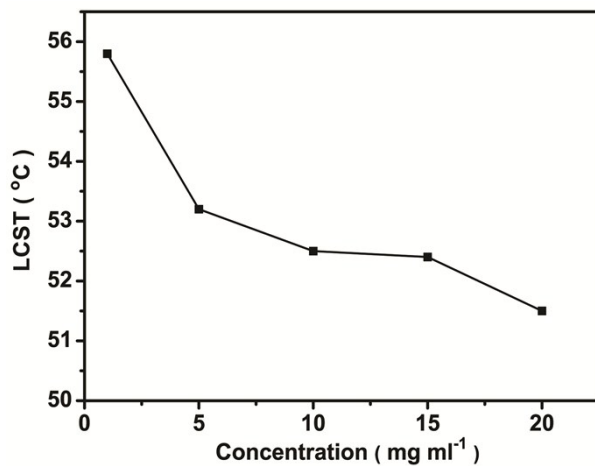
**Figure S9.** Light irradiation dependence of the  $^1\text{H}$  NMR spectral areas of the ethylene oxide units of the monomer  $\text{MTEO}_3\text{Azo}$  2% (w/v) in  $\text{D}_2\text{O}$  (a) before UV irradiation (365 nm) and (b) after UV irradiation (365 nm).



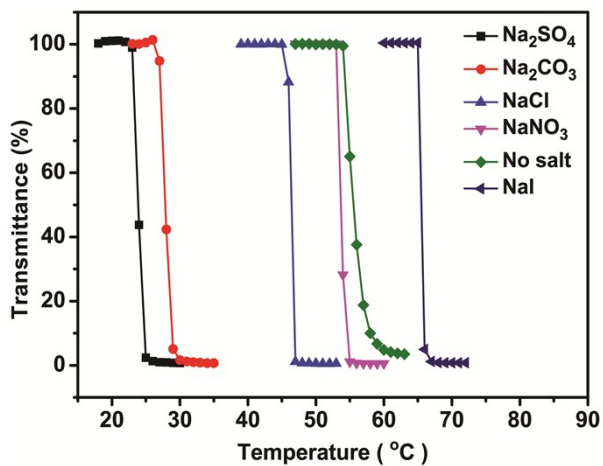
**Figure S10.** SEM images for (a) MTEO<sub>3</sub>Azo (before irradiation) and (b) MTEO<sub>3</sub>Azo (after UV light irradiation); SEM images for (c) MTEO<sub>2</sub>Azo (before irradiation) and (d) MTEO<sub>2</sub>Azo (after UV light irradiation). The initial monomers concentration was 1.0 mg mL<sup>-1</sup>. (Magnification: 200×)



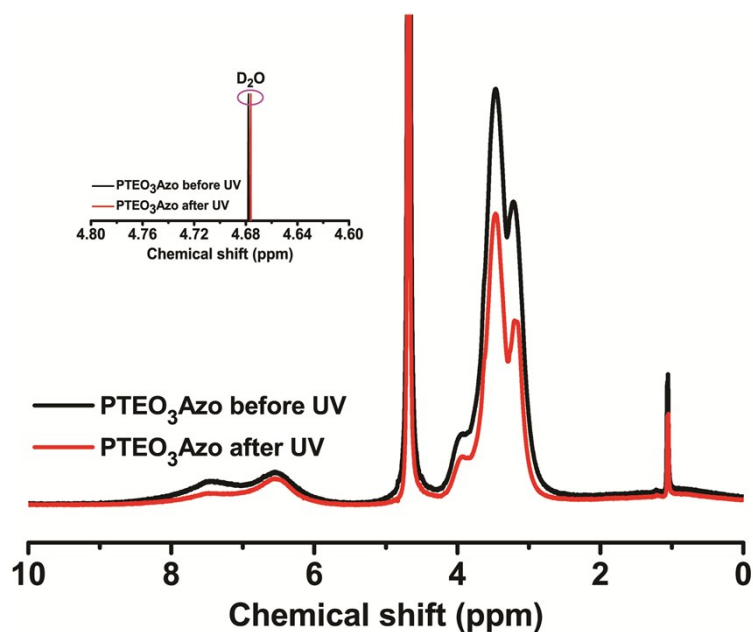
**Figure S11.** Schematic representation of the proposed thermo- and photoinduced morphological changes of the monomers (MTEO<sub>2</sub>Azo and MTEO<sub>3</sub>Azo) micelle aggregates.



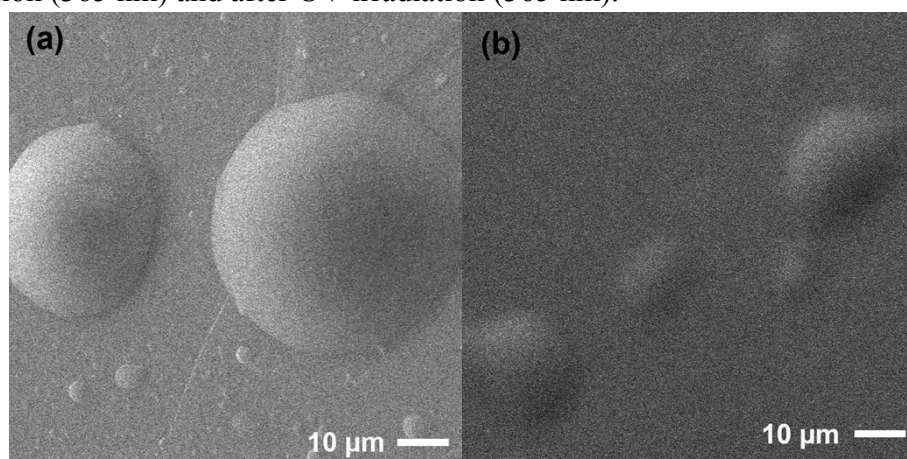
**Figure S12.** Concentration-dependent cloud points (LCST) recorded at a wavelength of 600 nm for the polymer PTEO<sub>3</sub>Azo aqueous solution.



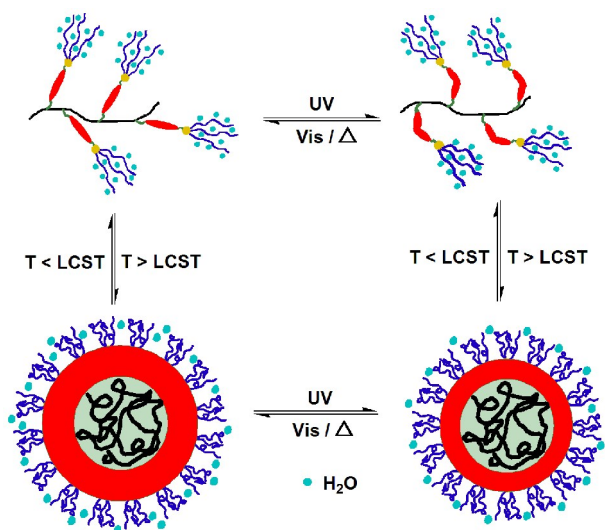
**Figure S13.** Temperature-dependent optical transmittance recorded at a wavelength of 600 nm for the PTEO<sub>3</sub>Azo aqueous solution (1.0 mg ml<sup>-1</sup>) for varying the type of salts (0.5M).



**Figure S14.** Light irradiation dependence of the  $^1\text{H}$  NMR spectral areas of the ethylene oxide units of the polymer  $\text{PTEO}_3\text{Azo}$  2% (w/v) in  $\text{D}_2\text{O}$  before UV irradiation (365 nm) and after UV irradiation (365 nm).



**Figure S15.** SEM images for (a)  $\text{PTEO}_3\text{Azo}$  (before irradiation) and (b)  $\text{PTEO}_3\text{Azo}$  (after UV light irradiation). The initial polymer concentration was  $1.0 \text{ mg mL}^{-1}$ . (Magnification:  $1000\times$ )



**Figure S16.** Schematic representation of the proposed thermo- and photoinduced morphological changes of PTEO<sub>3</sub>Azo micelles.