Supporting Information for

Concise Synthesis of Light/Temperature/pH/CO_2-Quadruple Responsive Azobenzene Functionalized Homopolymer for Reversible Photopatterning

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Characterization

NMR spectrum were performed on Bruker Avance III 400MHz Nuclear Magnetic Resonance Spectrometer. FTIR spectrum were measured by a Nicolet IR200 FT-IR spectrometer. An Agilent PL-GPC50 instrument was used to carry out molecular weight and polydispersity index (eluent: THF; standard sample: polystyrene; chromatographic column: PLMIXED-C, 5 μm, 7.5 × 50 mm; detector: differential refraction detector; flow rate: 1.0 mL/min). The UCST, LCST and UV/vis absorption spectrum were tested on a UH-4150 UV-vis spectrophotometer. TEM was observed by a FEI TECNAI G2 F20 (accelerating voltage: 200 kV). NanoBrook Omni laser light scattering spectrometer was used to the analysis of dynamic light scattering (DLS). Intensity of 365 nm UV lamp: 90 W/cm^2, intensity of 430 nm blue light lamp: 30 W/cm^2.

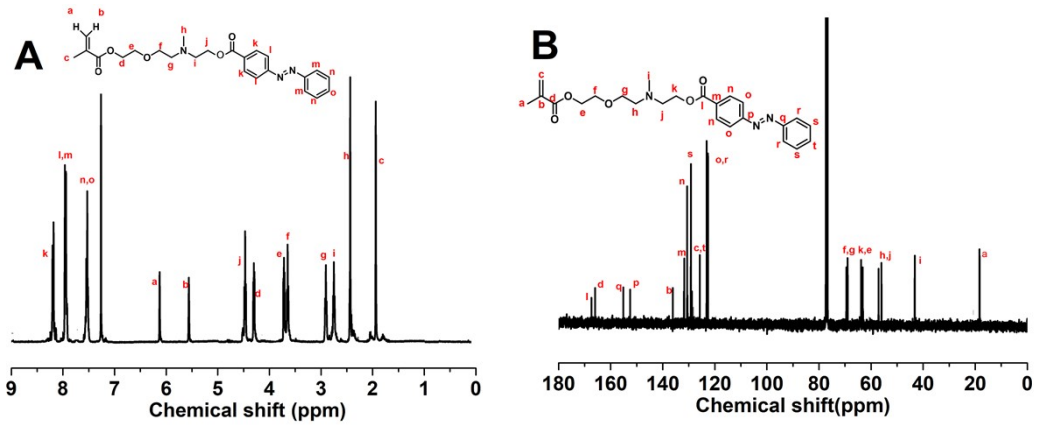


Figure S1. The ^{1}H NMR spectra (A) and ^{13}C NMR spectra (B) of Azo-N-EOMA in $CDCl_3$.

(E)-2-((2-(2-(methacryloyloxy) ethoxy)ethyl) (methyl)amino)ethyl 4-(phenyldiazenyl)benzoate (Azo-N-EOMA) (78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 - 8.15 (d, J = 8.4 Hz, 2H) , 7.95 (dd, J = 8.2, 1.7 Hz, 4H), 7.55 - 7.50 (m, 3H), 6.12(s, 1H), 5.58 - 5.53 (m, 1H), 4.46 (t, J=5.9 Hz, 2H), 4.29 (t, J = 5.8 Hz, 2H), 3.74 - 3.69 (m, 2H), 3.64 (t, J = 5.6 Hz, 2H), 2.89 (t, J=5.7 Hz, 2H), 2.75 (t, J= 5.7 Hz, 2H), 2.42 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ167.4, 166.0, 155.1, 152.7, 136.1, 131.8, 130.6, 129.2, 125.2, 123.1, 122.8, 69.5, 69.1, 63.8, 63.2, 57.2, 56.0, 43.2, 18.2.

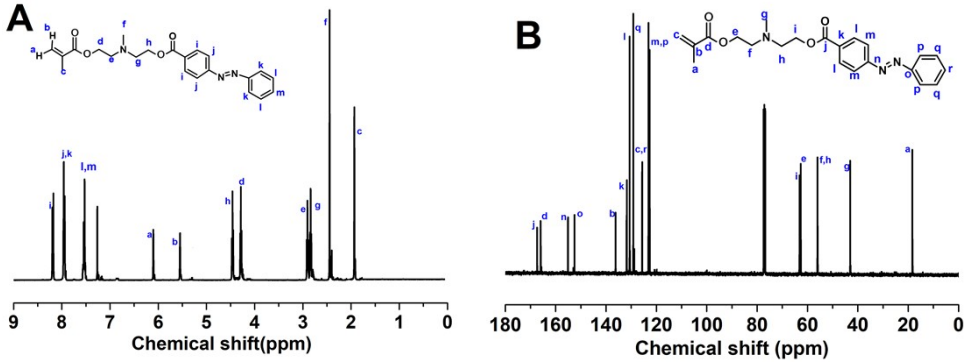


Figure S2. The ^{1}H NMR spectra (A) and ^{13}C NMR spectra (B) of Azo-N-MA in $CDCl_3$.

(E)-2-((2-(methacryloyloxy) ethyl) (methyl)amino)ethyl 4-(phenyldiazenyl)benzoate (Azo-N-MA) (83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 -

8.15 (d, *J* = 8.6 Hz, 2H) , 7.95(dd, *J* = 8.2, 1.7 Hz, 4H), 7.55 - 7.50 (m, 3H), 6.12(s, 1H), 5.58 - 5.53 (m, 1H), 4.46 (t, *J*=5.8 Hz, 2H), 4.29 (t, *J* = 5.8 Hz, 2H), 2.89 (t, *J*=5.8 Hz, 2H), 2.75 (t, *J*= 5.8 Hz, 2H), 2.42 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ167.2, 165.9, 155.2, 152.7, 136.0, 132.3, 130.9, 129.2, 125.5, 123.0, 122.9, 62.9, 62.2, 56.1, 56.0, 43.1, 18.3.

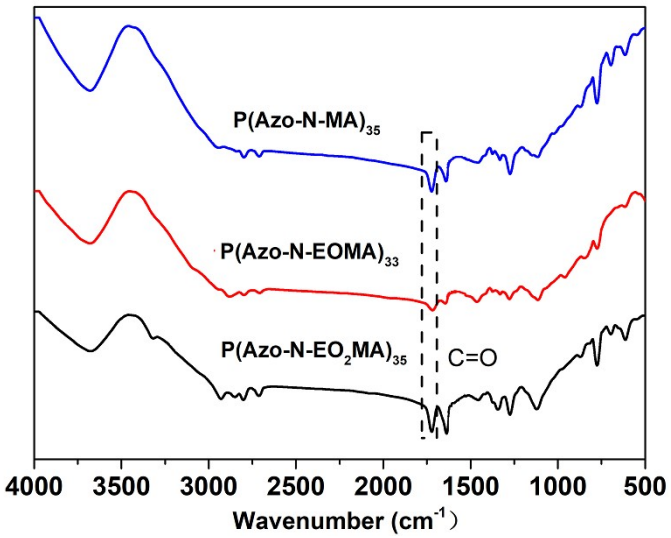
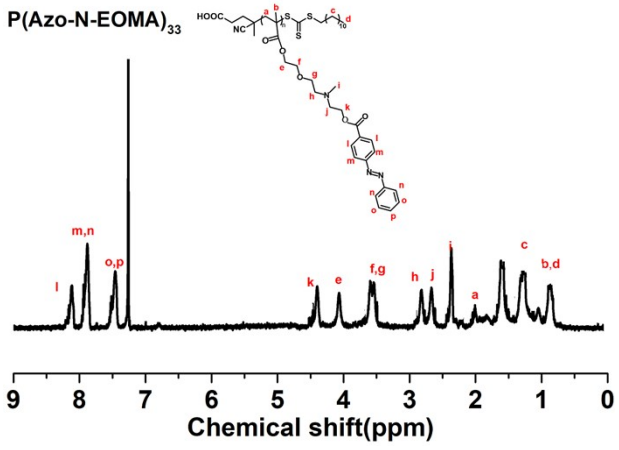


Figure S3. The FT-IR spectra of P(Azo-N-EO_2MA)$_{35}$, P(Azo-N-EOMA)$_{33}$ and P(Azo-N-MA)$_{35}$.



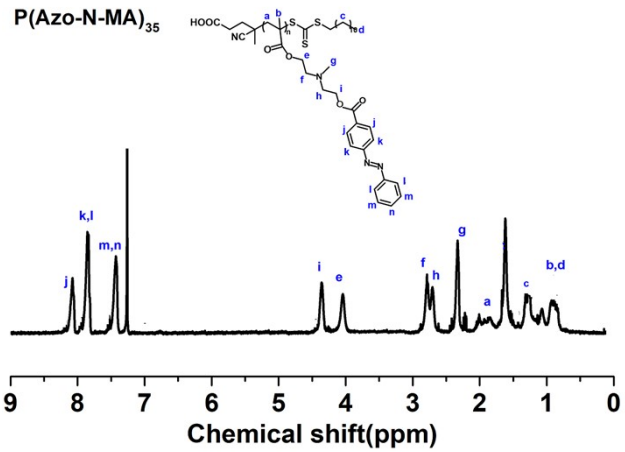


Figure S4. The ^{1}H NMR spectra of P(Azo-N-EO$_2$MA)$_{33}$ and P(Azo-N-MA)$_{35}$.

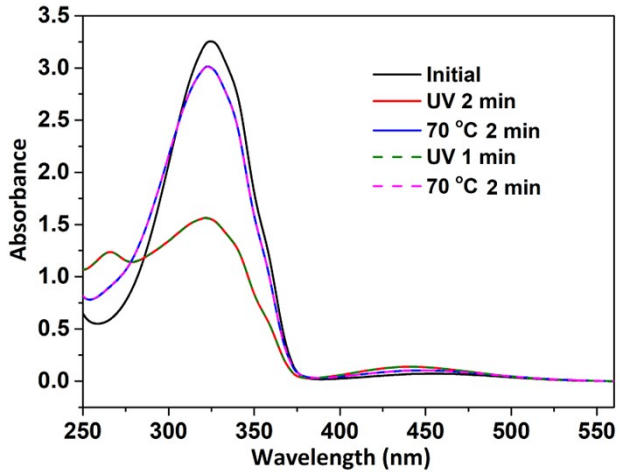


Figure S5 UV/vis absorption spectra of P(Azo-N-EO$_2$MA)$_{35}$ in THF solution (0.1 mg/mL) under UV/heating.

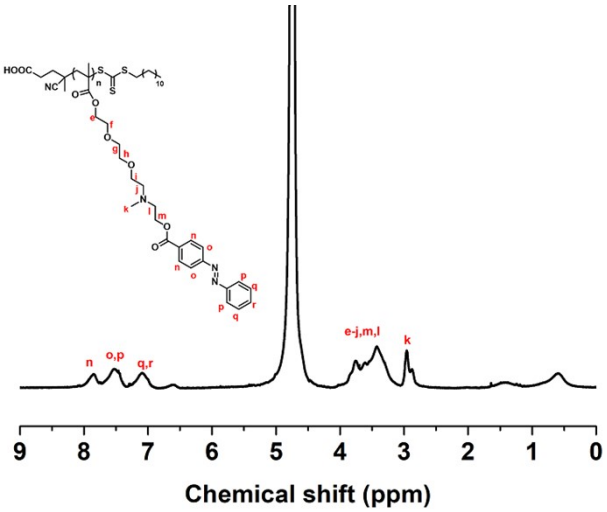


Figure S6 ^{1}H NMR spectra of P(Azo-N-EO$_2$MA)$_{35}$ in D$_2$O (C = 5 mg/mL, pH = 4).

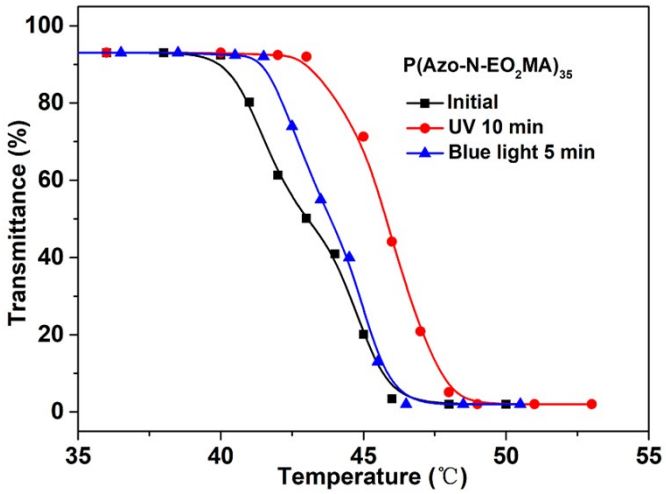


Figure S7 The effect of the irradiation of UV/blue light on the LCST of P(Azo-N-$EO_2MA)_{35}$.

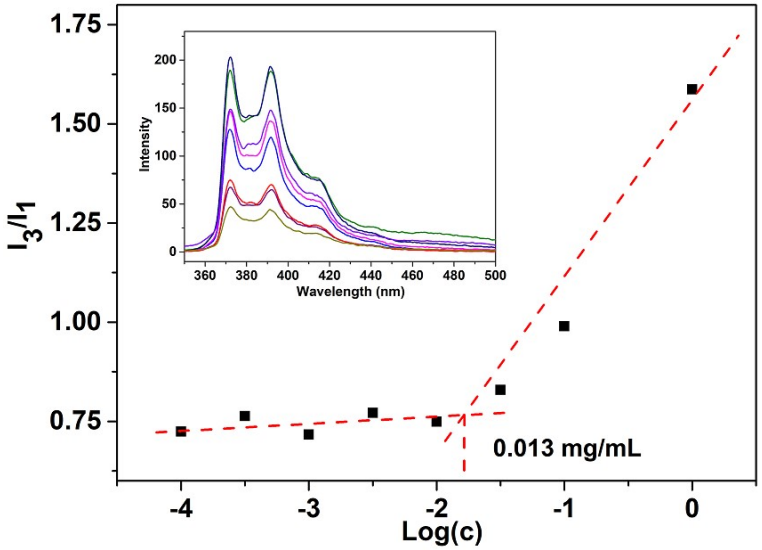


Figure S8 Fluorescence spectra of P(Azo-N-$EO_2MA)_{35}$ in water with pyrene and plots of I_3/I_1 vs concentration for P(Azo-N-$EO_2MA)_{35}$ in deionized water with different concentrations (from 0.0001 to 1 mg/mL).

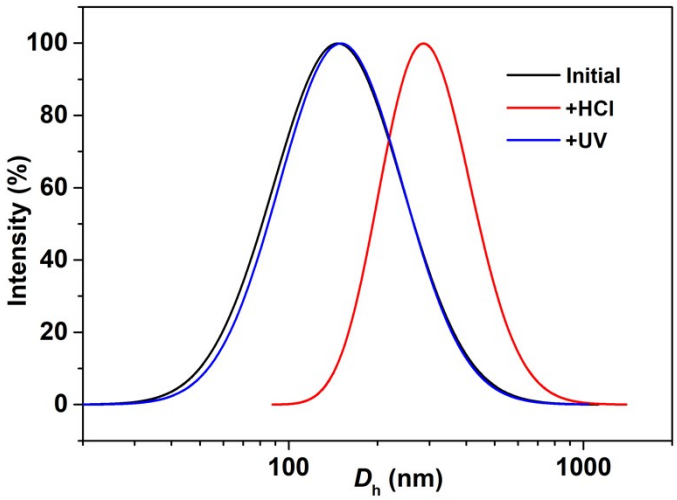


Figure S9 The D_h of micelles of P(Azo-N-$EO_2MA)_{35}$, after treated with HCl and after irradiation of UV.

Table S1. Summary of LCST-type CP (°C), UCST-type CP (°C) and Critical pH of homopolymers.

	pH=3		pH=5 (LCST, °C)			pH=7		BuOH/H_2O (UCST, °C)			Critial pH		
	A[a]	U[b]	A	U	B[c]	A	U	A	U	B	A	U	B
P(Azo-N-$EO_2MA)_{35}$	S[d]	S	43	46	43.5	I	I	34	25	32	4.65	5.0	4.73
P(Azo-N-$EOMA)_{33}$	S	S	38	42	38.5	I	I	66	56	63	3.8	4.2	3.9
P(Azo-N-$MA)_{35}$	I[e]	I	I	I	I	I	I	I	I	I	I	I	I

[a]A is the initial state of the solution; [b]U is the solution under UV radiation for 10 min; [c]B is the solution under blue light radiation for 5 min; [d]S represents the sample being soluble; [e]I represents the sample being insoluble.