

Supporting Information

Spiropyran-based polymeric micelles in aqueous solution: light-regulated reversible size alterations and catalytic characteristics

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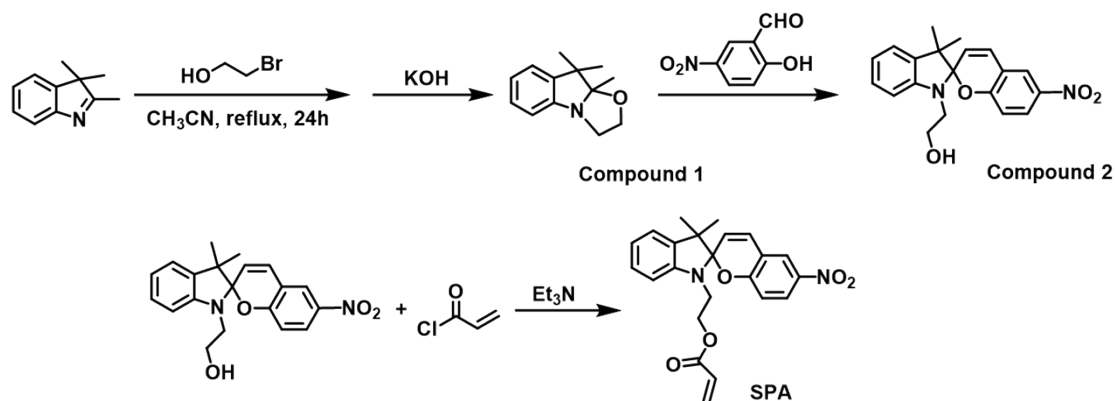
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1 Experimental Section

1.1 Preparation of SPA



The synthetic details of SPA can be found in Scheme S1. First, 2,3,3-trimethyl-1H-indole (12.6 mmol, 2.0 g) and 2-bromoethanol (15.1 mmol, 1.7 g) were refluxed in acetonitrile (25 mL) for 24 h under nitrogen atmosphere. The mixture was then washed three times with n-hexane (25 mL), and concentrated in vacuo to work up a purple-red solid (2.8 g). Next, KOH (1.17 g) aqueous solution (40 mL) was added, and the mixture was stirred for 30 minutes. The solution was extracted with ether (20 mL \times 3). The extracted ether solution was washed with deionized water (30 mL \times 3) and concentrated in vacuo to afford compound **1** as a yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.15 (td, $J = 7.6, 1.3$ Hz, 1H), 7.11 – 7.06 (m, 1H), 6.94 (td, $J = 7.4, 0.9$ Hz, 1H), 6.78 (d, $J = 7.8$ Hz, 1H), 3.88 – 3.70 (m, 2H), 3.63 – 3.48 (m, 2H), 1.45 (s, 3H), 1.41 (s, 3H), 1.20 (s, 3H).

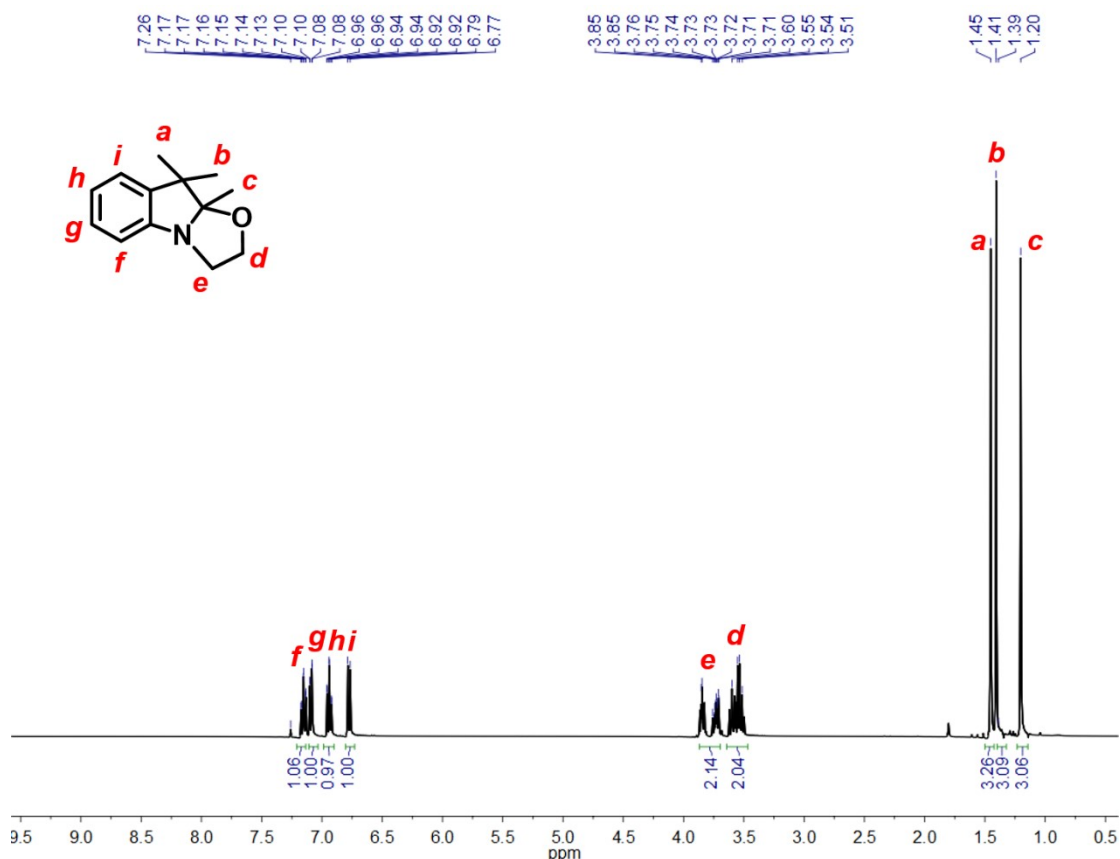


Figure S1. ^1H NMR spectrum of compound **1** (400 MHz, CDCl_3)

The resulting compound **1** (7.4 mmol, 71.5 mg) was refluxed with 2-hydroxy-5-nitrobenzaldehyde (11.1 mmol, 1.9 g) in ethanol (15 mL) under nitrogen atmosphere for 5 hours. After cooling the reaction flask to room temperature, the suspension was filtered with suction and washed with ethanol to obtain a purple filter cake, which was vacuum dried overnight to obtain a purple compound **2**. ^1H NMR (400 MHz, CDCl_3) δ 8.01 (dt, $J = 6.1, 2.7$ Hz, 2H), 7.19 (td, $J = 7.7, 1.2$ Hz, 1H), 7.10 (d, $J = 7.3$ Hz, 1H), 6.90 (dd, $J = 8.6, 5.9$ Hz, 2H), 6.76 (d, $J = 8.8$ Hz, 1H), 6.67 (d, $J = 7.8$ Hz, 1H), 5.88 (d, $J = 10.4$ Hz, 1H), 3.84–3.70 (m, 2H), 3.49–3.20 (m, 2H), 1.29 (s, 3H), 1.20 (s, 3H).

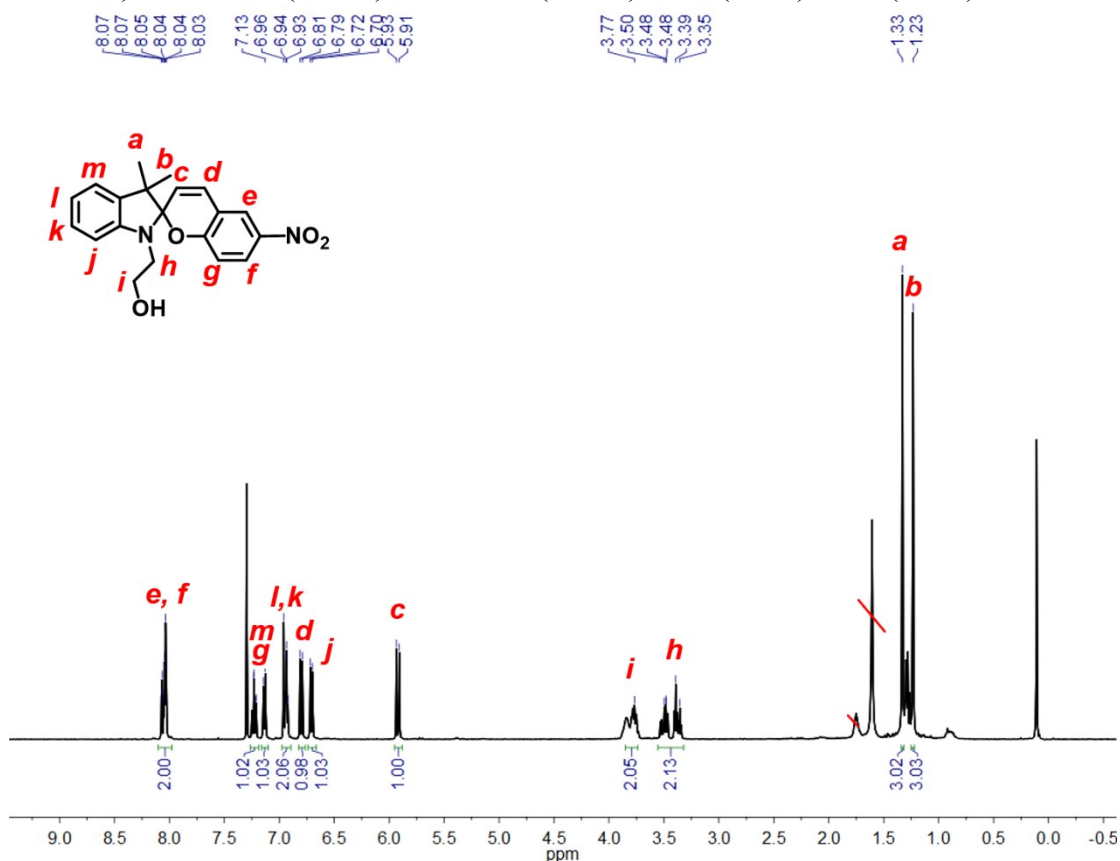


Figure S2. ^1H NMR spectrum of compound **2** (400 MHz, CDCl_3)

The obtained compound **2** (1.0 g, 3.3 mmol) and Et_3N (0.5 g, 4.9 mmol) were dissolved in anhydrous CH_2Cl_2 . Under an ice bath, acryloyl chloride (0.5 g, 4.9 mmol) in CH_2Cl_2 (10 mL) was slowly added to the reaction flask. The mixture was stirred for 30 min, then refluxed for 4 h. After the reaction, the mixture was concentrated in vacuo to obtain the crude product. The crude product was purified by column chromatography to give SPA as a purple solid. ^1H NMR (400 MHz, CDCl_3) δ 8.17–7.80 (m, 2H), 7.21 (td, $J = 7.7, 1.0$ Hz, 1H), 7.09 (d, $J = 7.2$ Hz, 1H), 6.90 (dd, $J = 8.9, 5.3$ Hz, 2H), 6.75 (d, $J = 8.6$ Hz, 1H), 6.69 (d, $J = 7.8$ Hz, 1H), 6.37 (dt, $J = 14.8, 7.4$ Hz, 1H), 6.11–5.99 (m, 1H), 5.90–5.79 (m, 2H), 4.31 (t, $J = 6.3$ Hz, 2H), 3.62–3.35 (m, 2H), 1.28 (s, 3H), 1.16 (s, 3H).

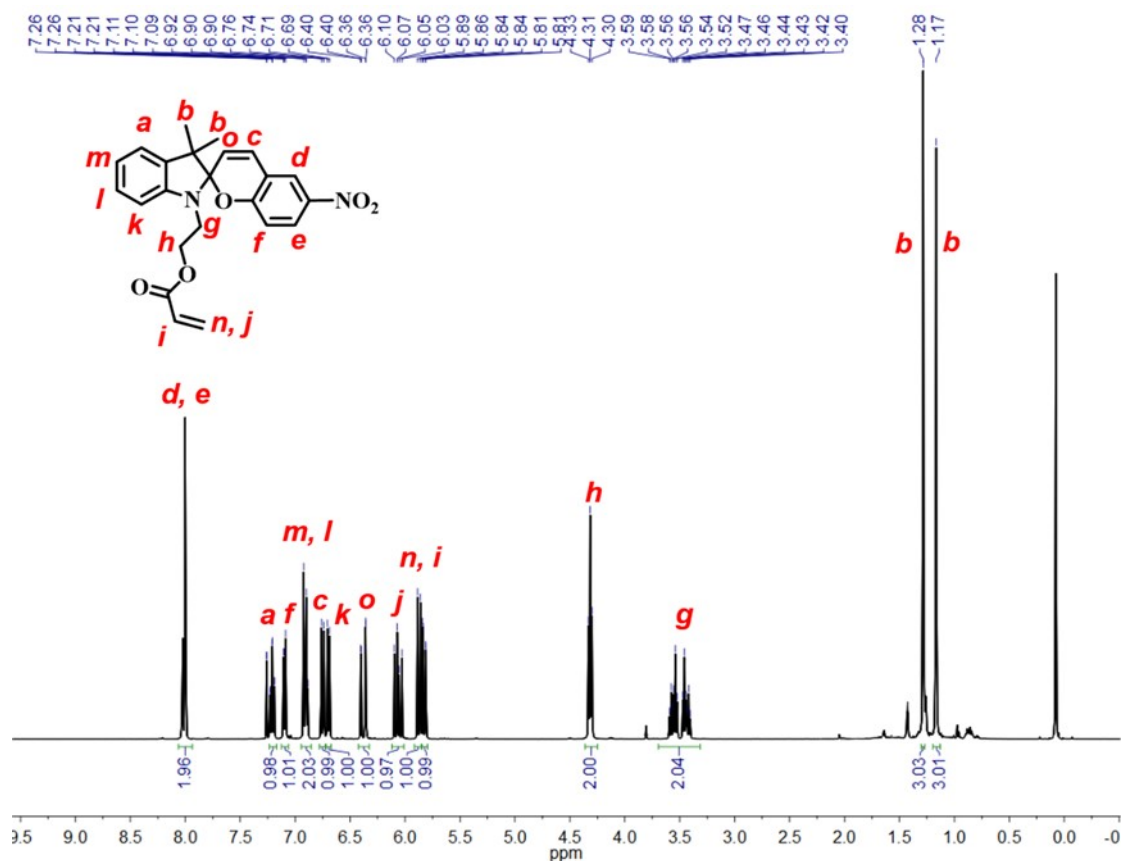


Figure S3. ^1H NMR spectrum of SPA (400 MHz, CDCl_3)

1.2 Synthesis of $\text{P}(\text{MMA}_{14})\text{-NHS}$

$$DP_{\text{MMA}} = \frac{g}{4} * \frac{a}{3} = \frac{4}{4} * \frac{42.03}{3} \approx 14 \quad (\text{Eq. S1})$$

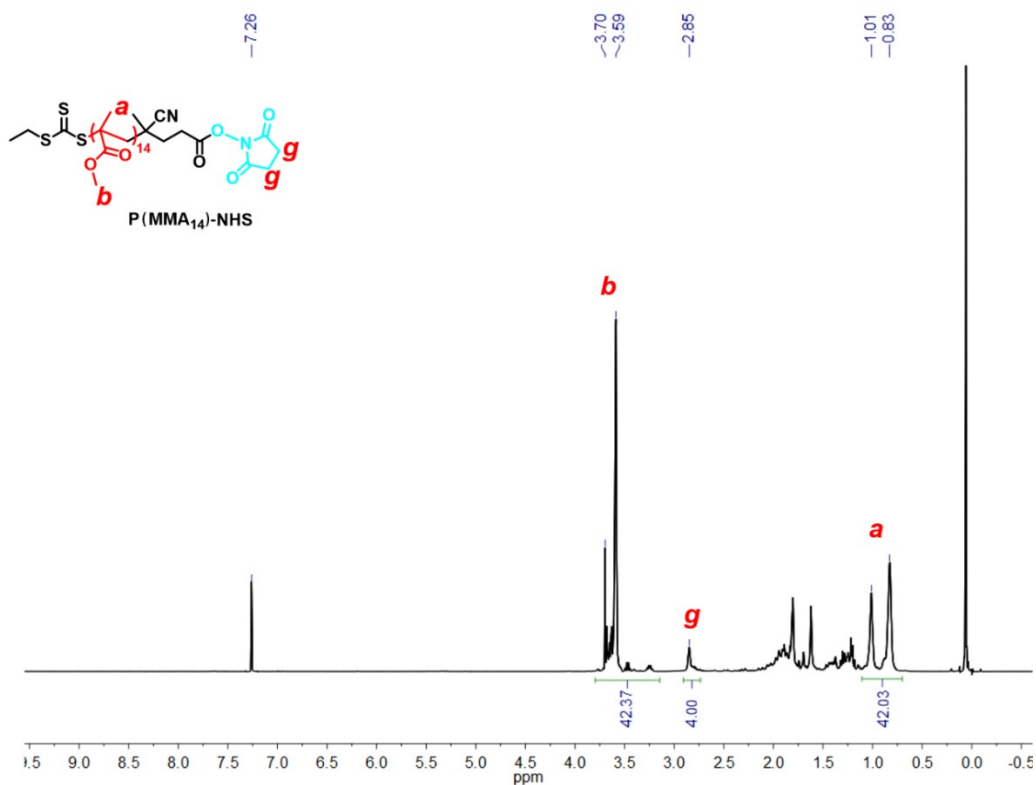


Figure S4. ^1H NMR spectrum of $\text{P}(\text{MMA}_{14})\text{-NHS}$ (400 MHz, CDCl_3)

1.3 Synthesis of P(SPA₁₀-*b*-MMA₁₄)-NHS

$$DP_{SPA} = \frac{k}{14 * 3} * \frac{c}{2} = \frac{42}{3 * 14} * \frac{22.69}{2} \approx 10 \quad (\text{Eq. S2})$$

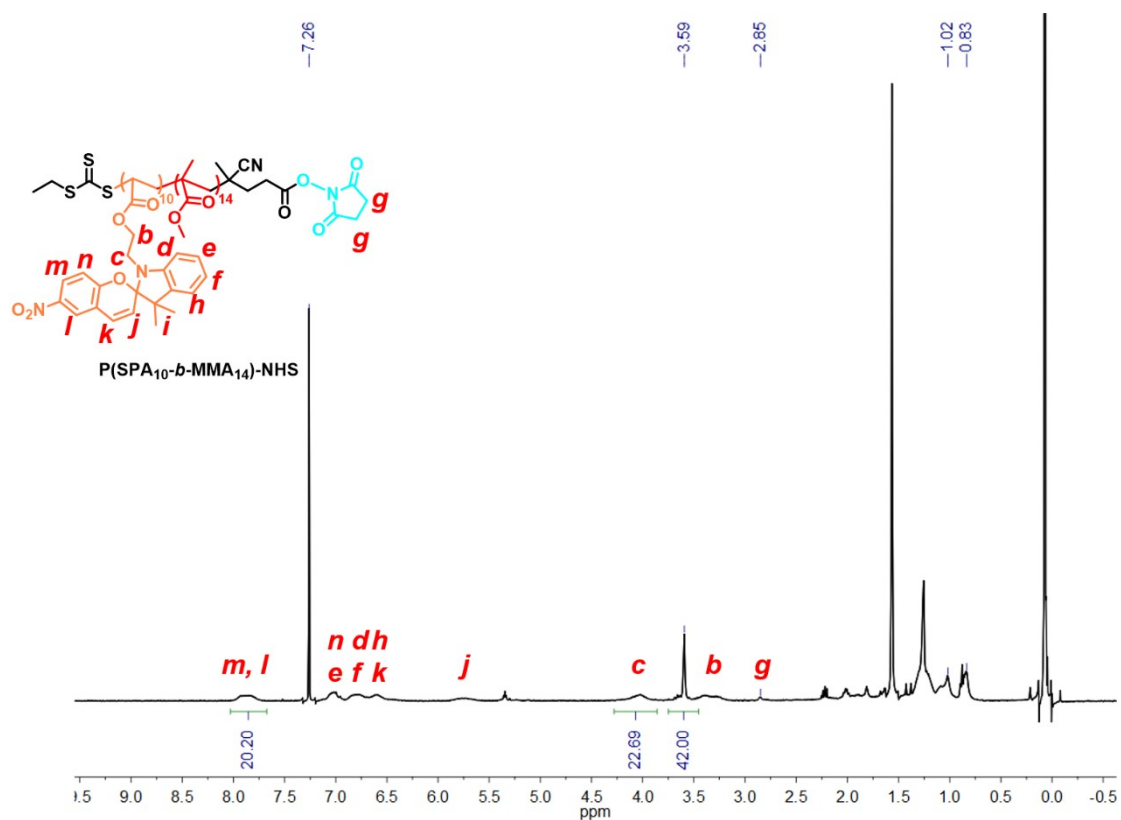


Figure S5. ¹H NMR spectrum of P(SPA₁₀-*b*-MMA₁₄)-NHS (400 MHz, CDCl₃)

1.4 Synthesis of P(OEGMA₅₁-*b*-SPA₁₀-*b*-MMA₁₄)-NHS (1)

$$Conv. = \frac{b - b'}{b} = \frac{72.72 - 10.53}{72.72} \approx 85.5\% , DP_{OEGMA} \approx 85.5\% \times 60 \approx 51 \quad (\text{Eq. S3})$$

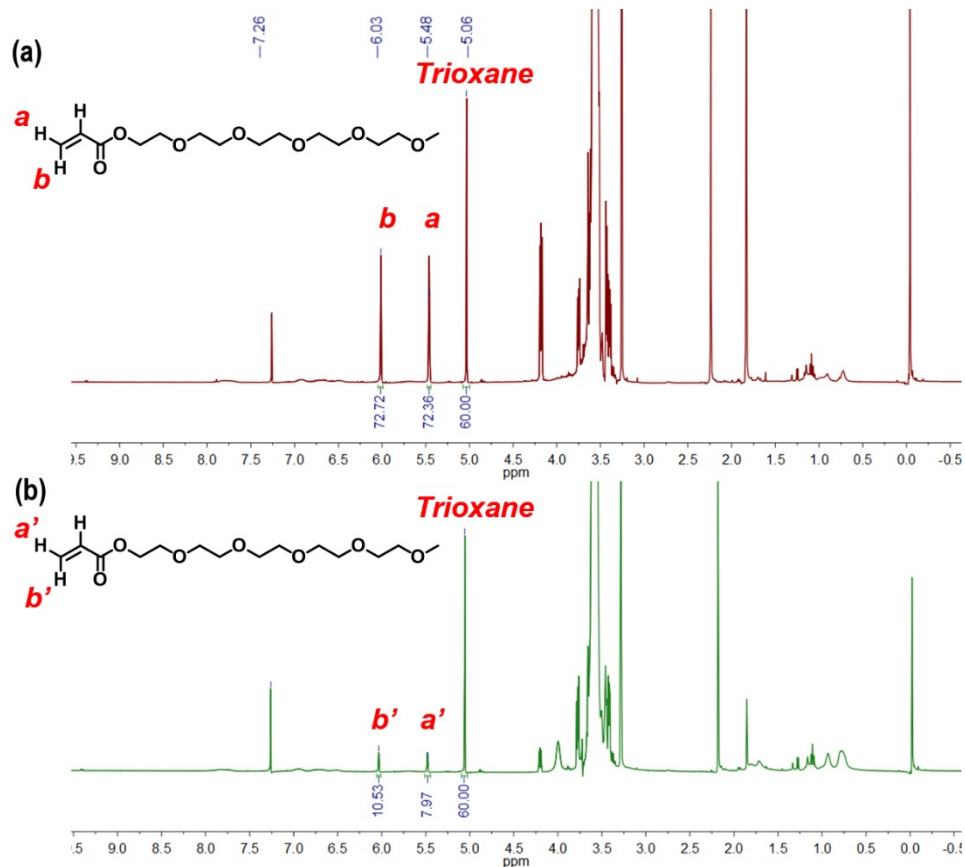


Figure S6. (a) ¹H NMR spectrum of the mixture before the reaction (400 MHz, CDCl₃) with 10 equiv. of s-trioxane as the internal standard and 60 equiv. of OEGMA added before the reaction. (b) Unpurified ¹H NMR spectrum after the reaction. (400 MHz, CDCl₃)

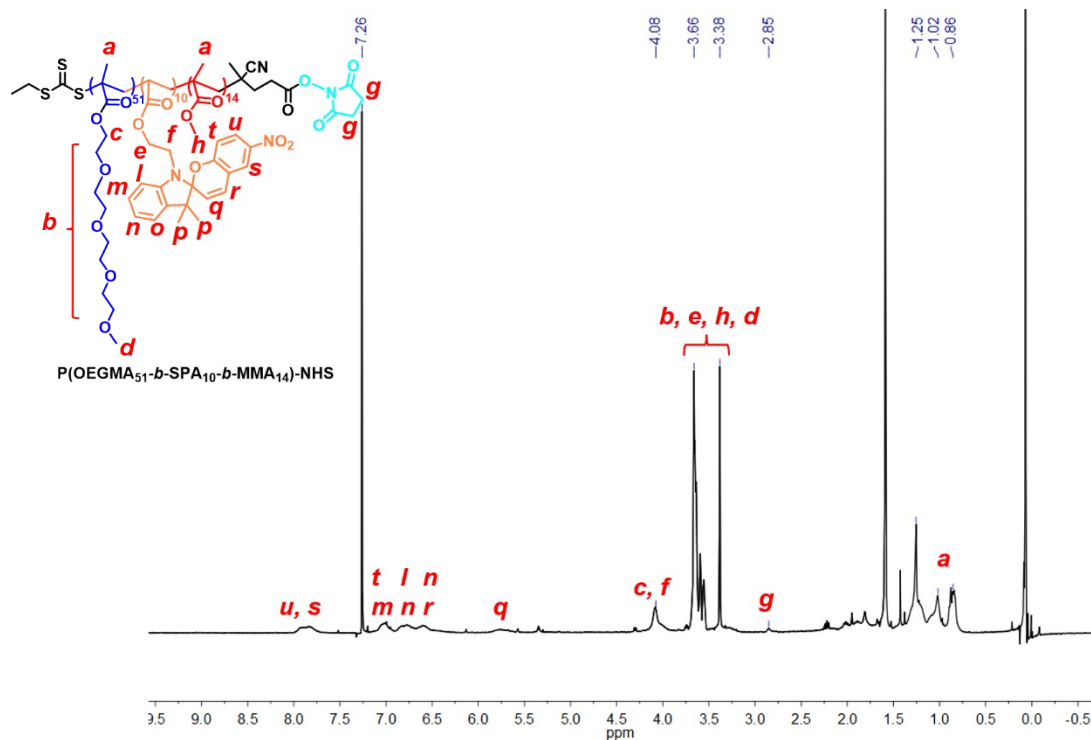


Figure S7. ¹H NMR spectrum of P(OEGMA₅₁-b-SPA₁₀-b-MMA₁₄)-NHS (400 MHz, CDCl₃)

1.5 Synthesis of P(OEGMA₅₆-b-MMA₁₄)-NHS

P(MMA₁₄)-NHS (100 mg, 0.057 mmol), OEGMA (498.2 mg, 3.4 mmol), trioxane (51.17 mg, 0.57 mmol) and AIBN (1.4 mg, 0.008 mmol) were dissolved in 1,4-dioxane (5 mL). and transferred to a 25 mL ampule. The solution was degassed by three freeze-pump-thaw cycles, then the ampule was refilled with nitrogen and sealed. RAFT polymerization was carried out at 70 °C overnight. The reaction was exposed to air and the temperature was lowered to 0 °C to quench the reaction. The diblock copolymer was obtained by precipitation in cold petroleum ether. DP_{OEGMA} = 56.

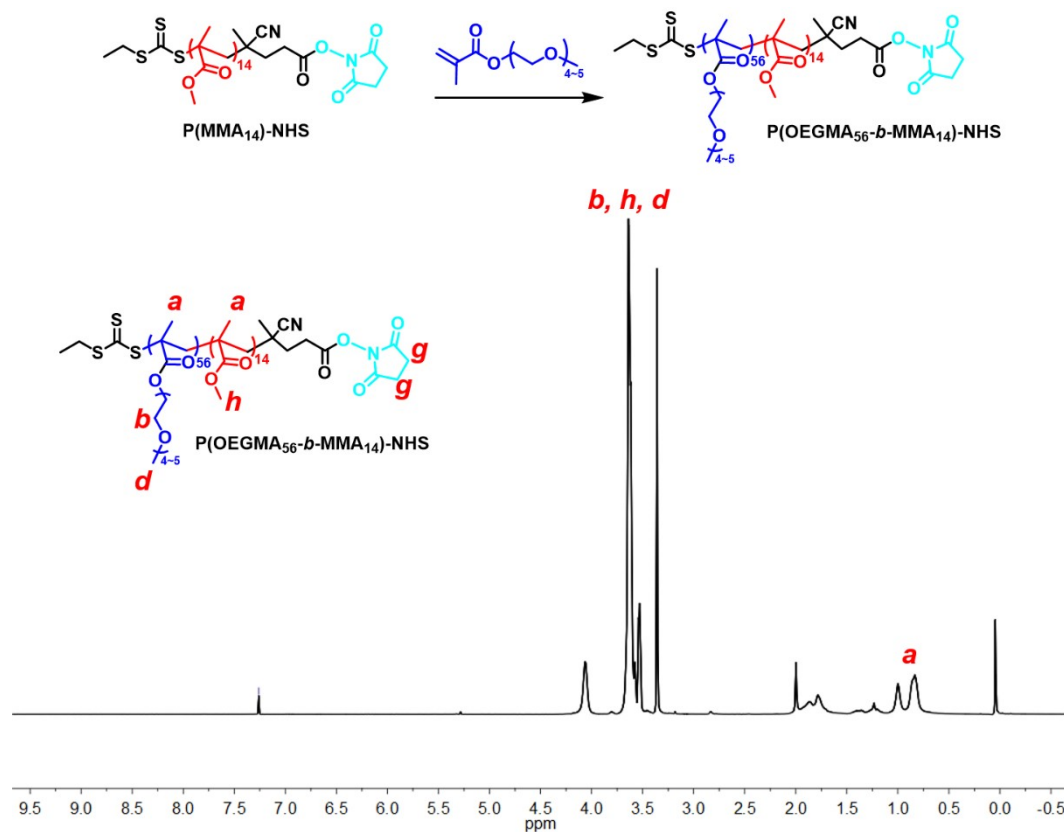


Figure S8. ¹H NMR spectrum of P(OEGMA₅₆-*b*-MMA₁₄)-NHS (400 MHz, CDCl₃)

2 SEC curves

The molecular weights were measured by size exclusion chromatography (SEC) using a waters breeze polymer labs SEC system in THF at 30 °C (1.0 mL/min). (Number average molecular weights (M_n) were determined by size exclusion chromatography in THF)

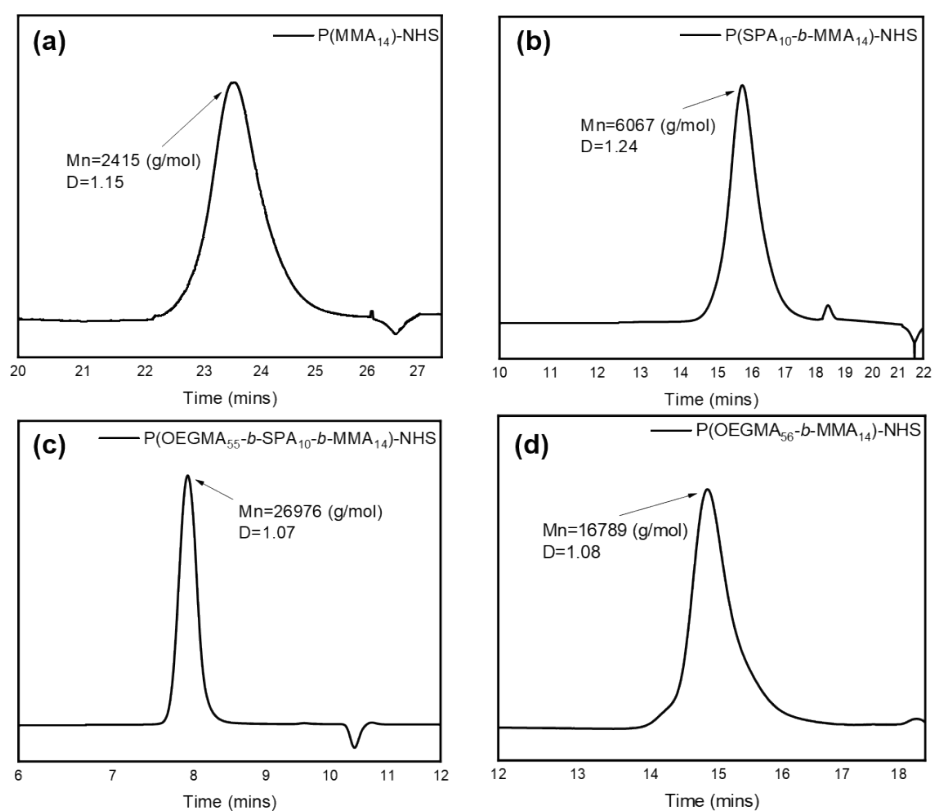


Figure S9. SEC traces of (a) P(MMA₁₄)-NHS; (b) P(SPA₁₀-*b*-MMA₁₄)-NHS; (c) P(OEGMA₅₁-*b*-SPA₁₀-*b*-MMA₁₄)-NHS; (d) P(OEGMA₅₁-*b*-MMA₁₄)-NHS.

3 DLS and color comparison of diblock copolymers before and after UV.

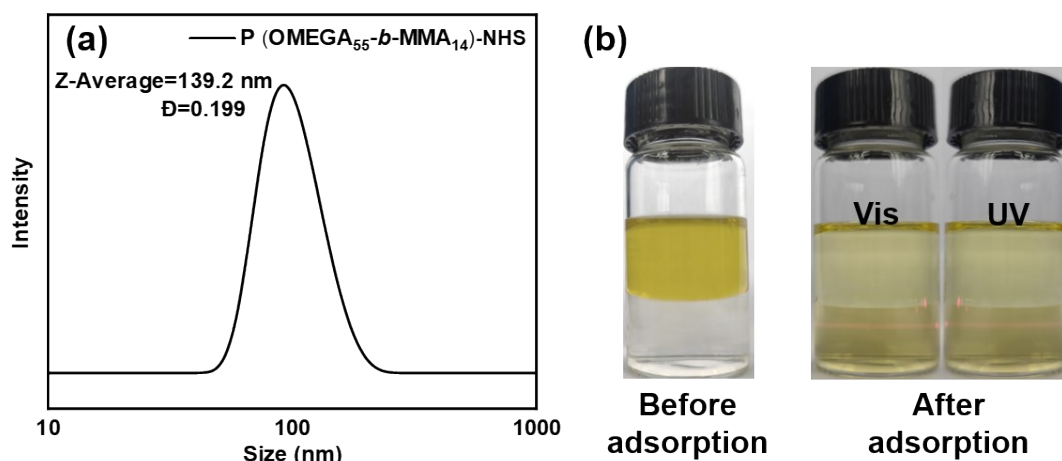


Figure S10. (a) DLS curve of P(OEGMA₅₆-*b*-MMA₁₄)-NHS; (b) before and after adsorption of methyl red (0.03 mg/mL) by micelles from P(OEGMA₅₆-*b*-MMA₁₄)-NHS under visible light and UV light

4 Dye removal rate.

$$\text{Dye removal rate} = \frac{\text{Absorbance}_{\text{Before adsorption}} - \text{Absorbance}_{\text{After adsorption}}}{\text{Absorbance}_{\text{Before adsorption}}} * 100\% \quad (\text{Eq. S4})$$

5 Synthesis of P(OEGMA₅₁-*b*-SPA₁₀-*b*-MMA₁₄)-TREN-Boc and P(OEGMA₅₁-*b*-SPA₁₀-*b*-MMA₁₄)-NHS.

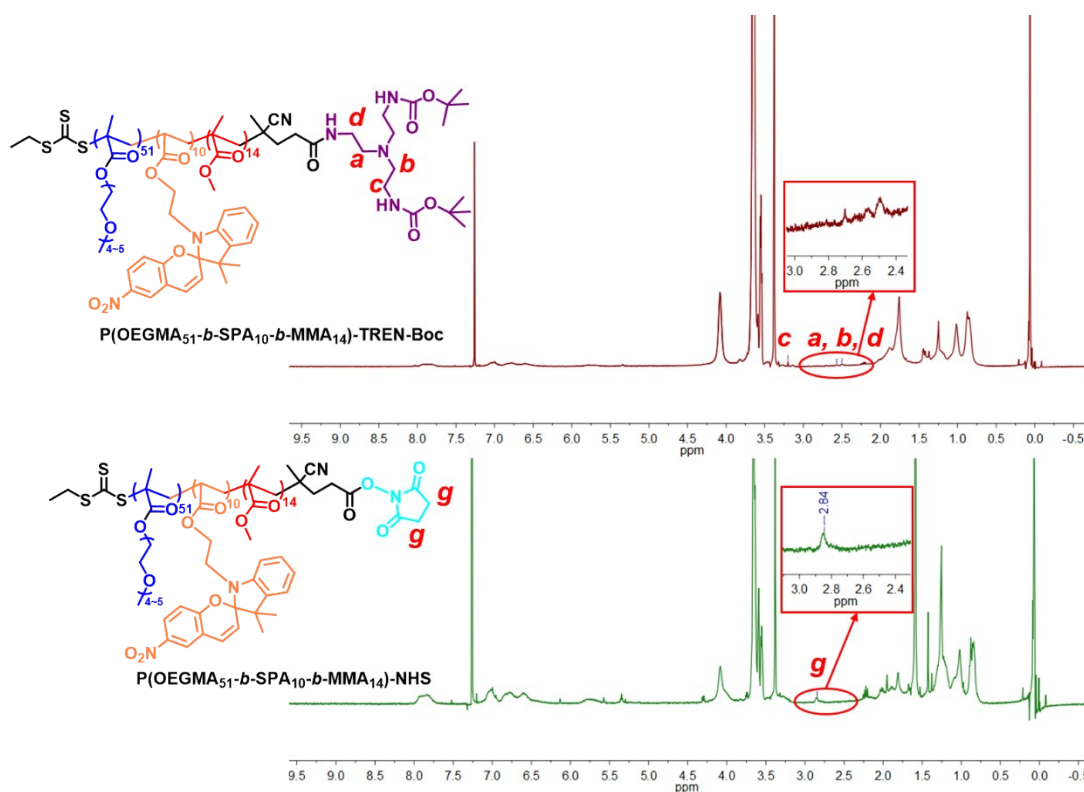


Figure S11. Comparison of ¹H NMR spectra before and after introduction of TREN-Boc (400 MHz, CDCl₃)

6 Synthesis of P(OEGMA₅₁-*b*-SPA₁₀-*b*-MMA₁₄)-TREN (2)

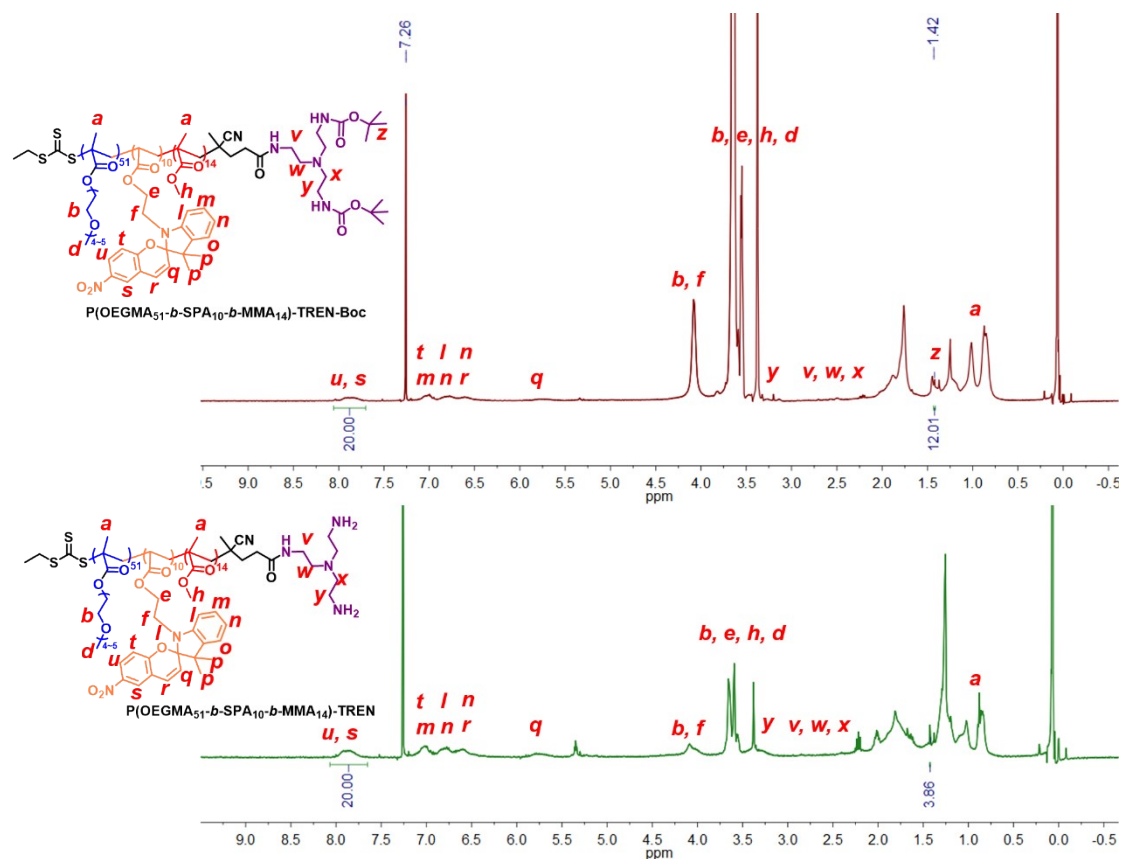


Figure S12. ¹H NMR spectra before and after the removal of N-Boc. (400 MHz, CDCl₃)

7 TEM images of self-assemblies of Catalytic Nanomicelles

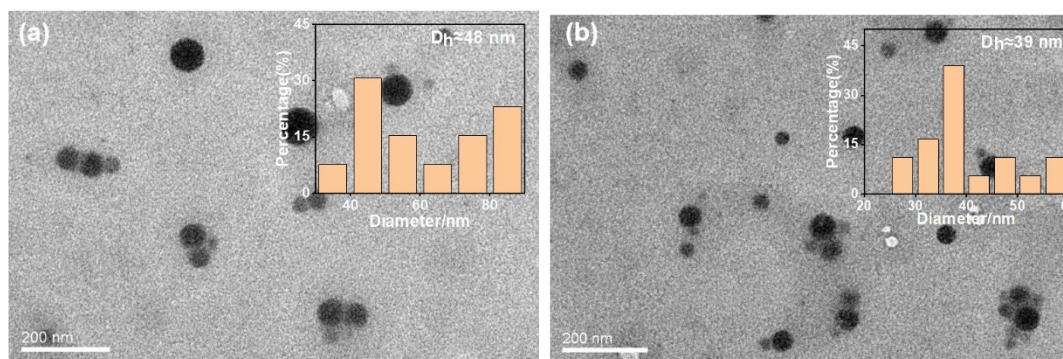


Figure S13. TEM images of self-assemblies of Catalytic Nanomicelles: (a) P(OEGMA₅₁-*b*-SPA₁₀-*b*-MMA₁₄)-TREN under visible light; (b) P(OEGMA₅₁-*b*-SPA₁₀-*b*-MMA₁₄)-TREN under UV irradiation.