

Supporting information for:

Photodegradable poly(ester amide)s for indirect light-triggered release of paclitaxel

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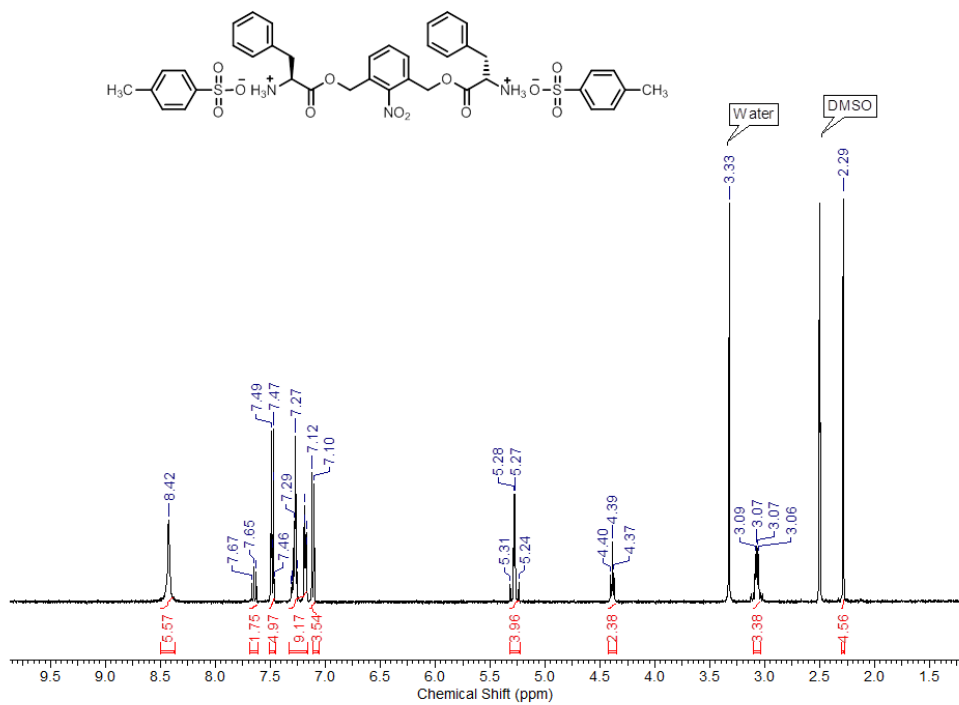


Figure S1. ^1H NMR spectrum of monomer **3** (400 MHz, $\text{DMSO-}d_6$).

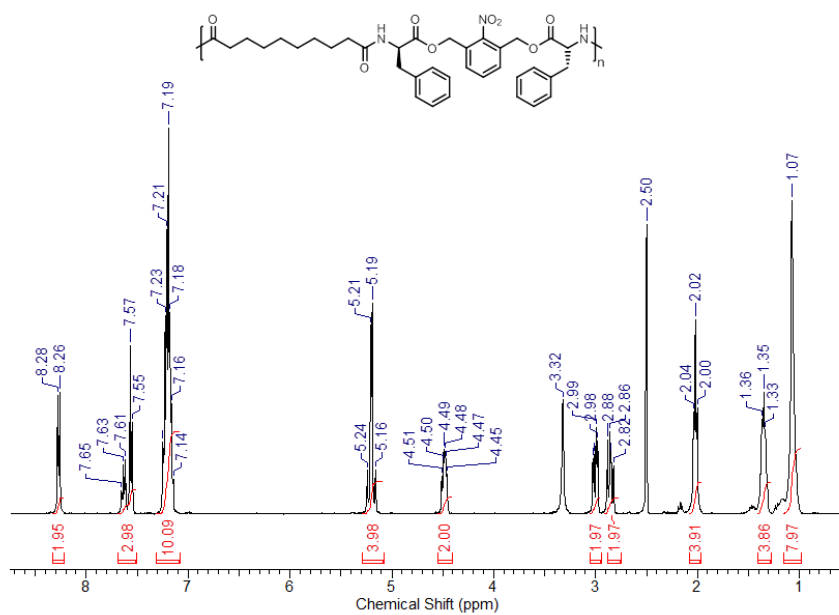


Figure S2. ^1H NMR spectrum of polymer **5** (400 MHz, $\text{DMSO-}d_6$).

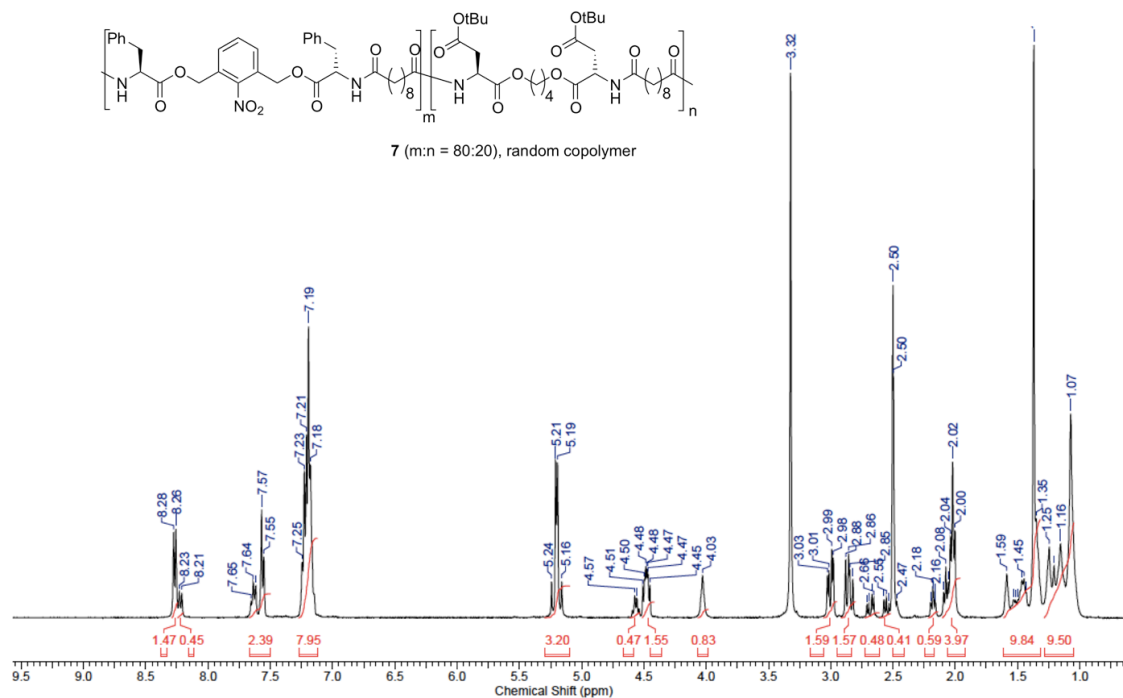


Figure S3. ^1H NMR spectrum of polymer **7** (400 MHz, $\text{DMSO-}d_6$). Incorporation of monomers **3:6** in an 80:20 ratio is confirmed by the relative integrations of the peaks corresponding to the methylene groups of the nitrobenzyl ester of **3** (5.20 ppm, integration = 3.2) and the methylene groups of the aliphatic ester of the L-aspartic acid monomer **6** (4.03 ppm, integration = 0.8).

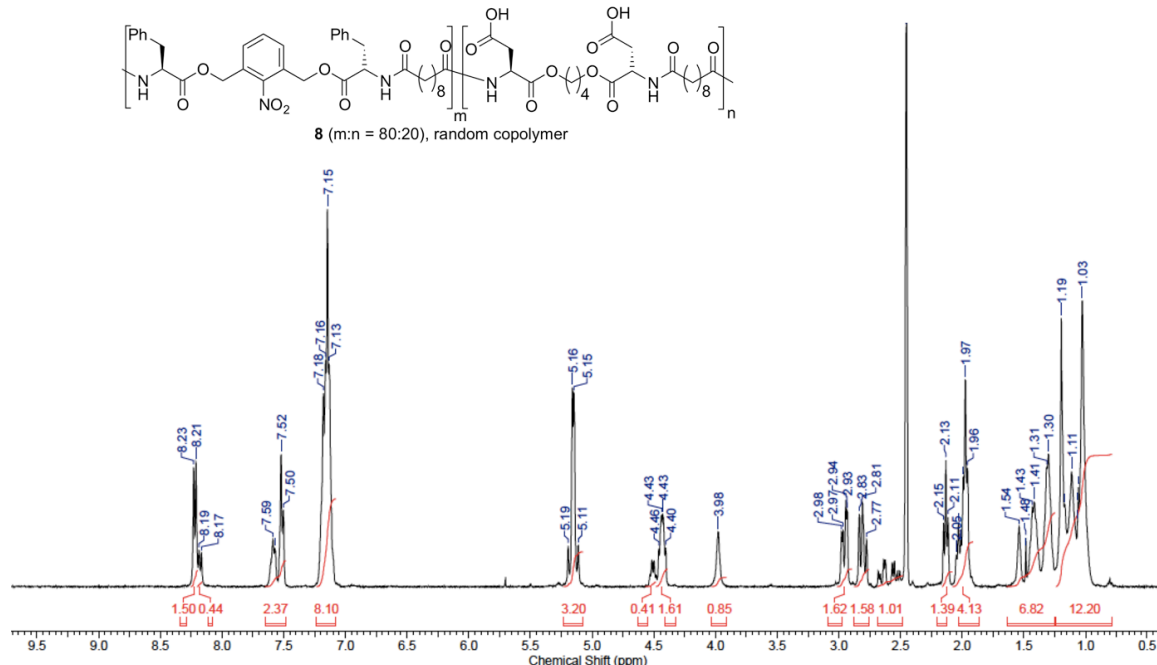


Figure S4. ^1H NMR spectrum of polymer **8** (400 MHz, $\text{DMSO-}d_6$). Cleavage of the *t*-butyl ester is confirmed by absence of the large peak at 1.37 ppm otherwise seen in the spectrum of **7**, corresponding to the *t*-butyl ester and is consistent with similar chemistry reported by our group (*J. Polym. Sci. Part A: Polym. Chem.*, 2009, **47**, 3757).

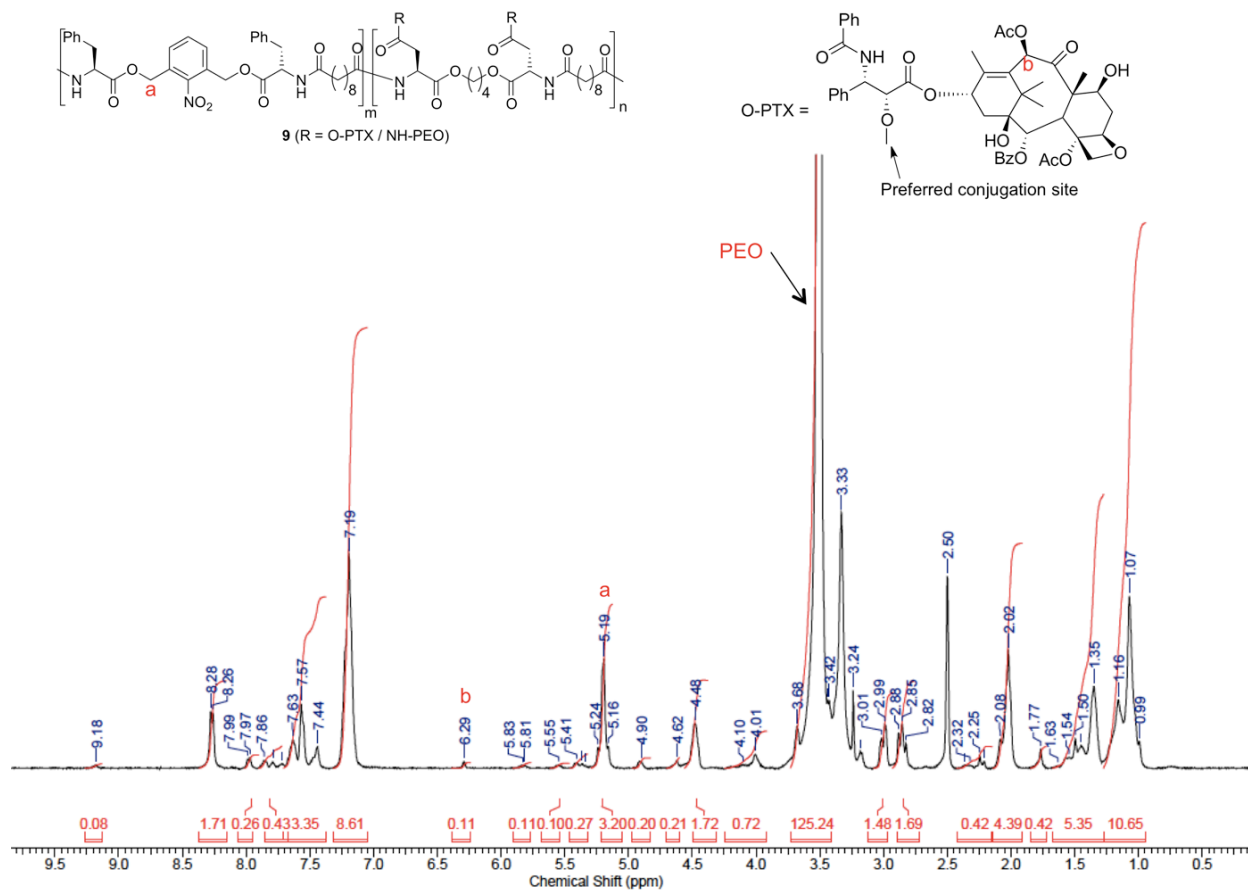


Figure S5. ¹H NMR spectrum of polymer **9** (400 MHz, DMSO-*d*₆). The amount of conjugated PTX was calculated based on the relative integrations of the peak corresponding to the proton labeled "b" on PTX at 6.29 ppm and the peak corresponding to the benzylic methylene protons labeled "a" on the photodegradable monomer unit at 5.16-5.24 ppm. The PEO content was calculated based on the relative integrations of the PEO peak and that of "a". Peak "b" was assigned based on comparison with literature spectra of PTX ester conjugates (Deutsch, H. M.; Glinski, J. A.; Hernandez, M.; Haugwitz, R. D.; Narayanan, V. L.; Suffness, M.; Zalkow, L. H., *J. Med. Chem.* **1989**, 32 (4), 788-792).

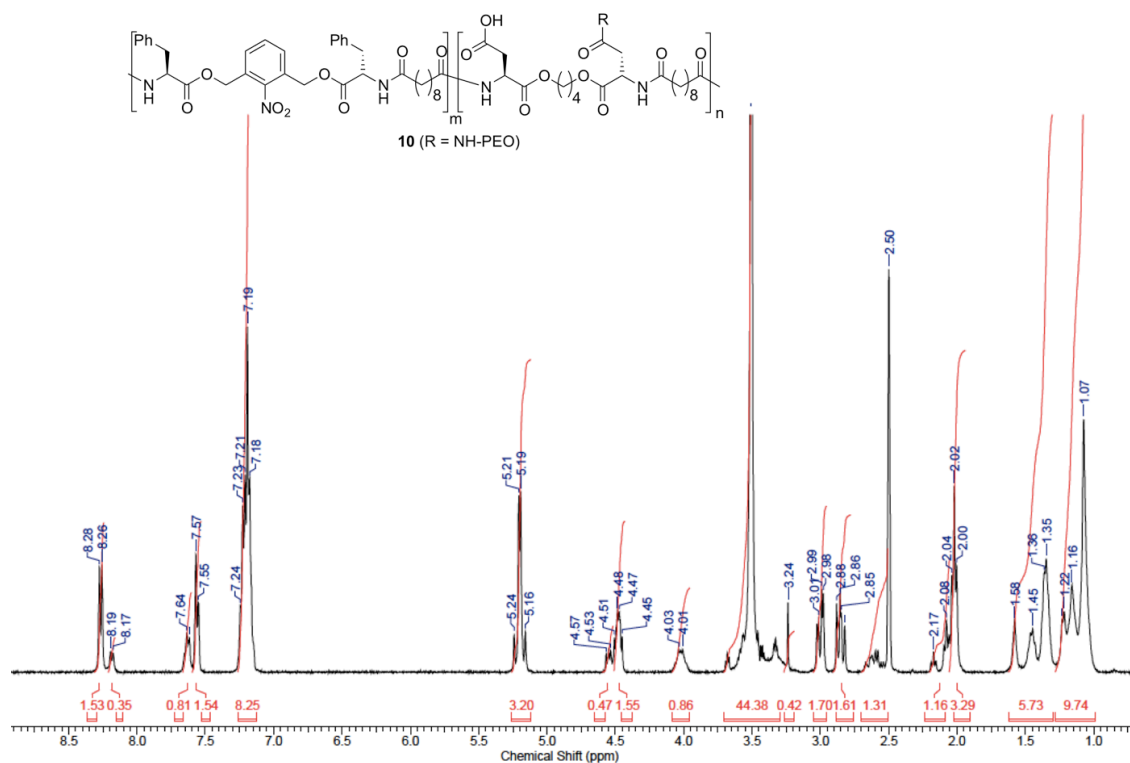


Figure S6. ^1H NMR spectrum of polymer **10** (400 MHz, $\text{DMSO-}d_6$).

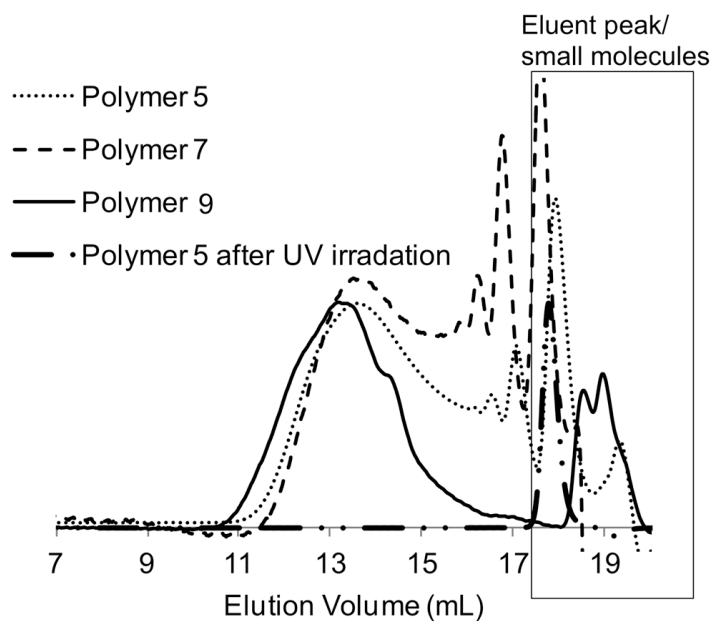


Figure S7. SEC traces for polymer **5**, **7**, **9**, and photodegraded polymer **5**. As the peaks for polymers **5** and **7** are not baseline separated from the eluent peak, they were processed using a flat baseline and dropped verticals.

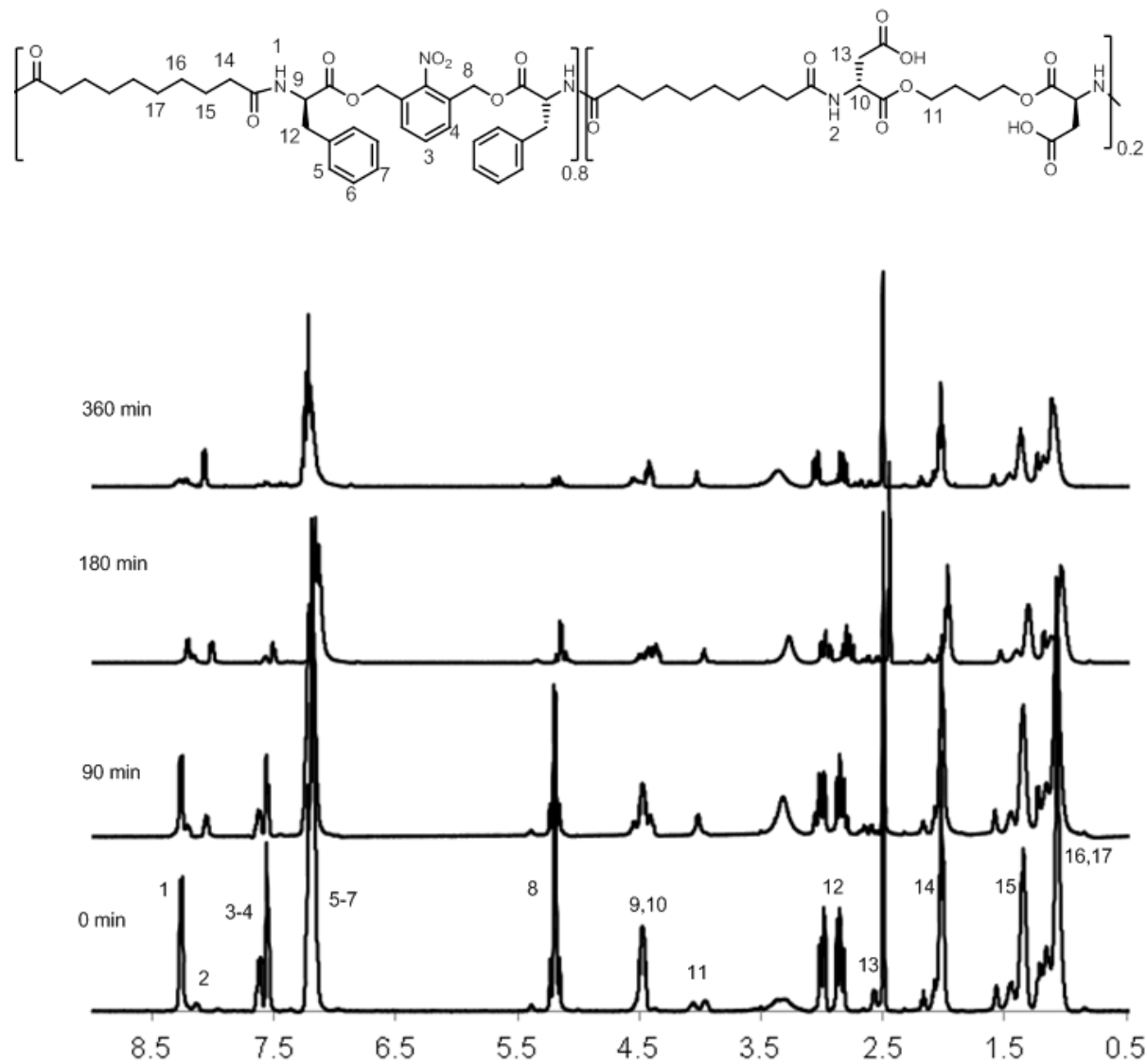


Figure S8. Evolution of ^1H NMR spectra during the photolysis of a 7.5 mg/mL sample of functional polymer **8**, confirming that the photodegradation occurs as for polymer **5** (DMSO- d_6 , 400 MHz).

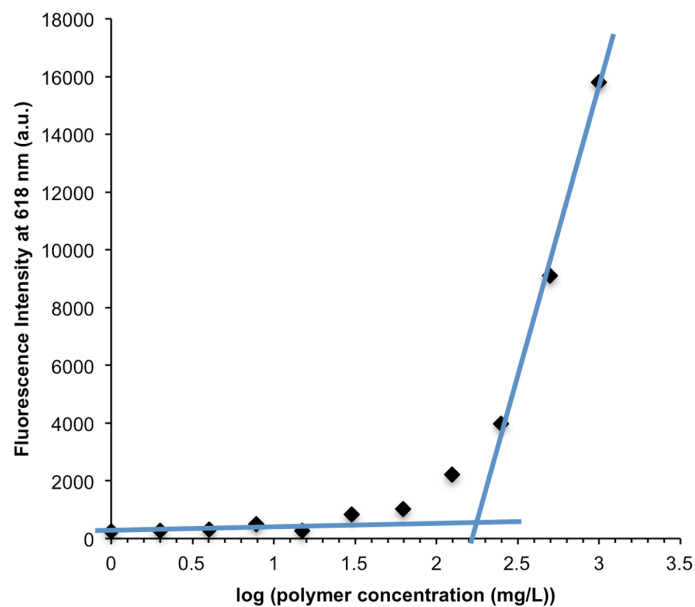


Figure S9. Determination of the critical aggregation concentration (CAC) for micelles formed from polymer **9**. Micelles were prepared as described in the experimental section. Nile Red (0.94 mg, 3.0 μmol) was dissolved in 9 mL of CH_2Cl_2 and 0.1 mL of this solution was added to a series of vials. The CH_2Cl_2 was removed under a stream of nitrogen. A series of concentrations of the micelle suspension ranging from 2 mg/L to 1000 mg/L was prepared by serial two-fold dilutions. The micelle suspensions were added to the vials containing Nile Red and were allowed to equilibrate with stirring overnight. The fluorescence spectra were obtained on a QM-4 SE spectrometer from Photon Technology International (PTI), equipped with double excitation and emission monochromators. An excitation wavelength of 550 nm was used for Nile Red and the emission spectra were recorded from 565 to 700 nm. The emission intensity at 618 nm was recorded for each micelle concentration. The CAC was determined as the concentration at the intercept of the lines for the two linear regions of the above graph.

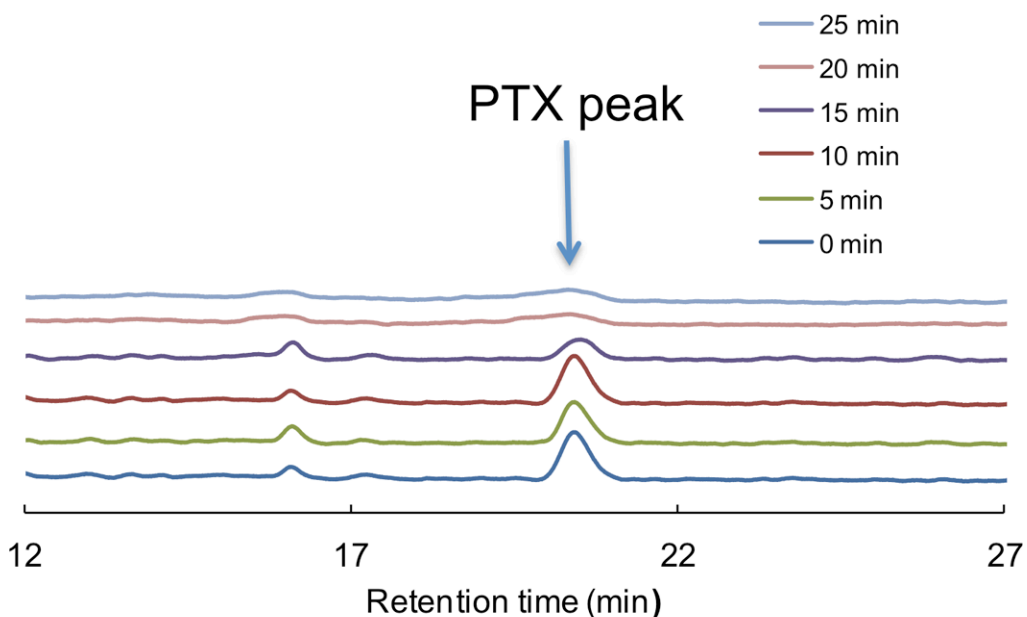


Figure S10. Evolution of HPLC traces for PTX irradiated with UV light for various time intervals. No significant changes were observed up to 10 min.

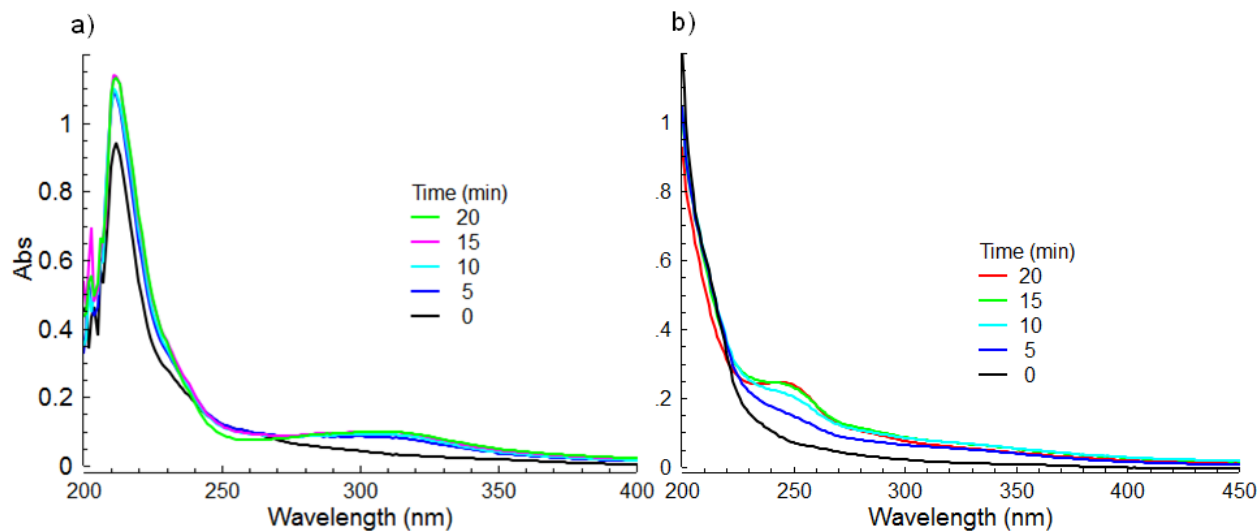


Figure S11. UV-vis spectra of micelles formed from polymer **9** following photoirradiation for different time periods in a) dioxane (4 $\mu\text{g/mL}$) and b) water (4 $\mu\text{g/mL}$).

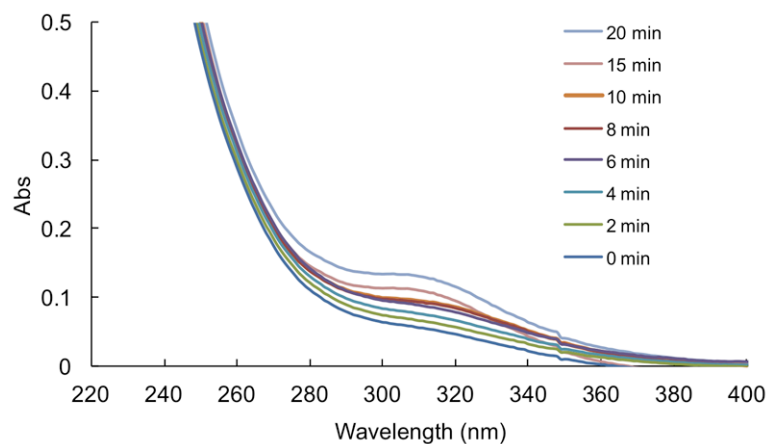


Figure S12. Photodegradation of micelles formed from polymer **9** at a concentration of 1.5 mg/mL in water. At each time point, 100 μ L of the aqueous suspension was removed, diluted into dioxane and a UV-vis spectrum was obtained.