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Fast Photodegradable Block Copolymer Micelles for Burst Release

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There is increasing interest in designing block copolymer (BCP) micelles of which the assembly state in aqueous solution can be controlled or disrupted by light.[1−3] This is motivated by the potential application of such BCP micelles as nanocarrier for light-triggered release of guest molecules, which offers the remote-control possibility as well as the temporal and spatial selectivity. The main established approach allowing for photocontrolled dissociation of BCP micelles is to incorporate photochromic groups onto the hydrophobic block of a BCP, whose photoreaction can increase the polarity of the block and thus shift the hydrophilic−hydrophobic balance to render the micellar association of BCP chains thermodynamically unstable.[1−3] Upon micelle dissociation, loaded hydrophobic guest can be released to aqueous medium. Recently, several groups demonstrated a new approach that is based on using a photocleavable junction linking the hydrophilic and hydrophobic blocks.[4] After micelle formation, light can be applied to break BCP chains at the junction point. It is easy to imagine that, though interesting, this approach is not ideal for light-triggered release of guest molecules loaded in the micelle core because the chain aggregation state of the latter would not be loosened due to the removal of the hydrophilic corona.

Herein we demonstrate a novel BCP design strategy. Instead of using a single photolabile junction between the two blocks, photobreakable moieties are positioned repeatedly along the hydrophobic main chain. With this design, the resulting BCP micelle possesses a photodegradable core that, upon photoreaction, can be disintegrated very quickly. The sketch in Figure 1 illustrates the difference between having just one photobreakable junction and having many such units on the main chain of the hydrophobic block. We envision that fast disintegration of the micelle core should lead to a fast release of loaded guest molecules.

Scheme 1 shows the one-pot synthesis of an amphiphilic ABA triblock copolymer of which the end block A is water-soluble poly(ethylene oxide) (PEO) and the middle block B is a hydrophobic polyurethane containing nitrobenzyl groups (PEO-*b*-PUNB-*b*-PEO). The photodegradable PUNB block was first prepared by using condensation polymerization of 2-nitro-1,3-benzenedimethanol with tolylene 2,4-diisocyanate in slight excess. It was then terminated with monomethyl ether PEO to yield the triblock copolymer of PEO-*b*-PUNB-*b*-PEO. The size exclusion chromatograph (SEC) result in Figure 2 confirms the successful coupling between PUNB and PEO. As compared with monomethyl ether PEO, the BCP sample has a larger polydispersity index (increased from 1.06 to 1.38). This is likely caused by the PUNB block formed via condensation polymerization, with which a broader distribution of molecular weights is generally associated. The possibility of having some PEO-*b*-PUNB diblock could not be ruled out, but this does not affect the core−shell micelle formation. With this BCP, fast photoinduced micelle core disintegration could be expected by having an *o*-nitrobenzyl unit linked to two methyl ester groups in each repeating unit of the micelle core-forming PUNB block. Photoinduced degradation of the BCP in dissolved state in THF was first investigated, and the result obtained with SEC is also shown in Figure 2. After irradiation of a BCP solution (3 mL, 0.1 mg/mL) with UV light (300 nm, ∼ 60 mW/cm^2), the SEC trace shows dominant low molecular weight species while a remaining polymer peak matches the elution peak of PEO, indicating a complete separation of PEO chains from PUNB as well as the severe disintegration of the hydrophobic block into low-molecular-weight species. The continuous photodegradation at a high BCP concentration in THF (10 mg/mL) was also observed from SEC measurements (Figure S4 in Supporting Information). Moreover, the photoreaction of nitrobenzyl units could be monitored from UV−vis spectra that display an increased absorption over a wide range of wavelengths (300−500 nm) as the photoreaction progresses (Figure S5 in Supporting Information). From the BCP design, a variety of degraded nitro- and nitrosobenzyl species can be expected due to the randomly occurring photocleavage reaction on the main chain of PUNB.

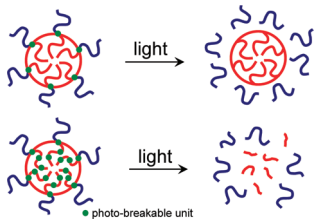

Figure 1. Schematic illustration of the difference between placing a photobreakable unit at only the block junction and repeatedly on the hydrophobic block.

The fast photodegradation of the PUNB block indeed leads to fast disintegration of the BCP micelle in solution. We first carried out the experiment with BCP micelles in a mixed solvent of dioxane/water (1:1) where the photodegraded molecular species are soluble, which made it possible to monitor the micelle disintegration process through dynamic light scattering (DLS) measurements. In this experiment, micelles were prepared by dissolving the BCP in dioxane (0.2 mg/mL), followed first by slow addition of water (35% in volume with respect to dioxane) and then fast addition of water (dioxane/water, 1:1). Figure 3a shows the change in the scattering intensity of the micellar solution (1 mL) upon UV irradiation (300 nm, 250 mW/cm^2). The intensity of scattered light drops after only 10 s of UV exposure and changes little after 30 s of irradiation even though the photoreaction continues as revealed by the UV−vis spectra (Figure S6 in Supporting Information). This result suggests that the BCP micelles could be disrupted quickly as the PUNB block is broken into pieces upon cleavage of *o*-nitrobenzyl moieties. Figure 3b shows the change in the volume-averaged size distribution before and after 180 s UV irradiation of the solution. The BCP micelles (hydrodynamic diameter D_H ∼ 60 nm) are transformed into smaller species of various sizes after the short time irradiation. The situation after irradiation is understandable because, as mentioned above, the photodegradation of the PUNB block is expected to generate various species including PEO chains. The fast disintegration of BCP micelles is also observable on AFM.

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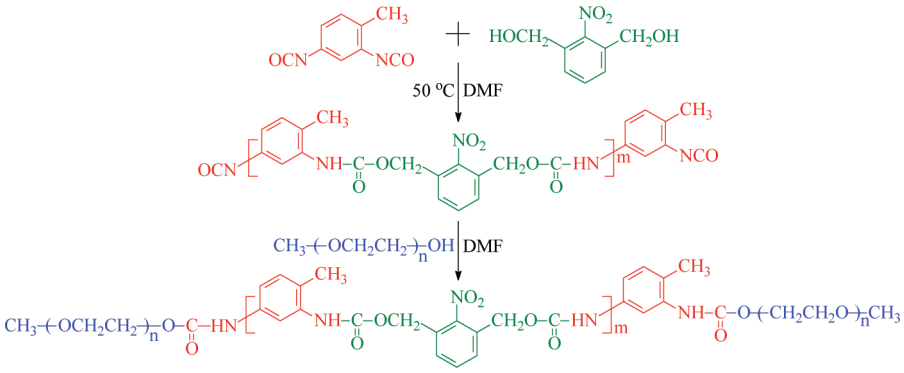
Scheme 1. Synthetic Route to the Triblock Copolymer of PEO-*b*-PUNB-*b*-PEO



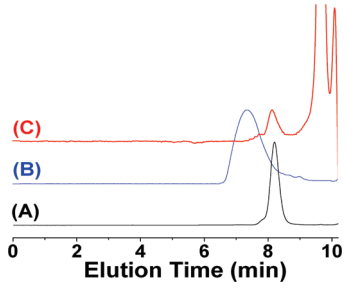


Figure 2. Size exclusion chromatograph (SEC) traces of (a) monomethyl ether PEO, (b) triblock copolymer of PEO-*b*-PUNB-*b*-PEO, and (c) PEO-*b*-PUNB-*b*-PEO triblock copolymer in THF after 1 h UV irradiation for photodegradation (3 mL, 0.1 mg/mL, 1 h exposure to 300 nm, 60 mW/cm^2).

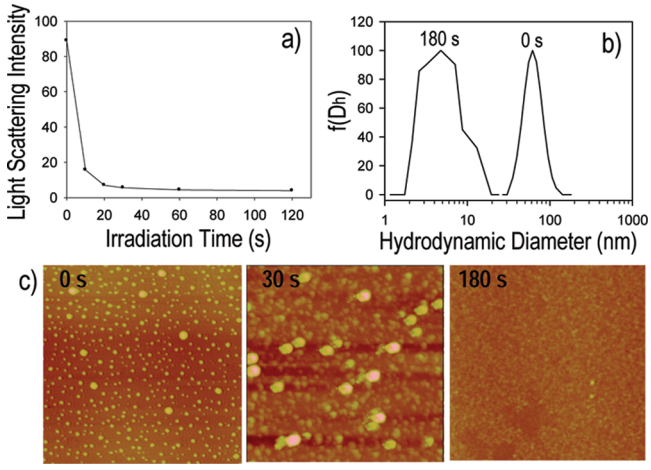


Figure 3. (a) Scattering intensity (measured at 90°) for BCP micelles in a mixed solvent (dioxane/water, 1/1) recorded after UV irradiation for various times (300 nm, 250 mW/cm^2, solution volume 1 mL). (b) Volume-averaged distribution of hydrodynamic diameters for the micelle solution before and after 180 s UV irradiation. (c) AFM height images of the micelle solution cast on mica before and after UV irradiation (30 and 180 s) (image area: 2 μm × 2 μm).

Figure 3c shows the height images of the sample cast from the solution before and after UV irradiation. The micelles ($D_H \sim 49$ nm from the cast sample) appear to be swollen and deformed after 30 s of irradiation. It is likely that at this short time of photoreaction BCP chains remain aggregated, but the degraded micelle core becomes more solvated prior to actual disintegration. After 3 min irradiation, clear micellar aggregates can no longer be observed.

We then investigated the release in aqueous solution of a model hydrophobic guest, Nile Red (NR), loaded in the BCP micelle upon photoinduced disintegration of the micelle core. Both NR and the BCP were dissolved in THF (0.5 mg/mL, NR to BCP ratio: 1:6); water was added to induce the micelle formation and the concomitant NR encapsulation by the micelle core; THF was removed by evaporation and nonsolubilized NR was filtered by microfiltration (0.2 μm pore filter). The final BCP concentration was adjusted to 0.2 mg/mL. Figure 4a shows the fluorescence emission spectra of NR loaded in the BCP micelle before and after short time UV irradiation (up to 60 s). Figure 4b shows the plots of normalized fluorescence vs time for the solution without UV irradiation and subjected to various times of irradiation. It is seen that the emission intensity remains constant over time in the absence of irradiation, indicating stable encapsulation of the dye in a hydrophobic environment. By contrast, the emission intensity drops by more than 70% after only 10 s of irradiation! AFM observation further confirmed the fast disintegration of NR-loaded micelles in aqueous solution. Figure 5 shows the height images recorded by casting the solution on mica before and after 60 s of irradiation. Prior to irradiation, the micelles had a uniform size of $D_H \sim 41$ nm (smaller than those in the mixed solvent), while after exposure to UV light, much larger aggregates of various sizes were observed, indicating the changing assembly state of the micelles caused by a short time of irradiation. The observed rate of fluorescence quenching is very fast, indicating burst release of loaded NR into an aqueous medium. Here we emphasize that the release of loaded NR means that NR molecules initially confined in a hydrophobic micelle core are brought into contact with water molecules. This can happen as a result of either photoinduced micelle core dissociation or swelling or, in the present case, disintegration. In the context of photocontrolled drug delivery applications, after being 'transported" to a target, hydrophobic drug molecules generally need to enter into an aqueous medium and have a chance to interact with biomolecules. We also carried out a control test by dissolving both NR and the BCP in THF or a THF/water mixture and found no fluorescence change after UV irradiation under the same condition, ensuring that the fast drop of NR fluorescence in Figure 4 is not caused by photodegraded PUNB block but by quenching by water molecules (Figure.S7 in Supporting Information). The results thus confirm the design hypothesis; that is, burst release could be achieved by fast disintegration of BCP micelle core. We mention that light-triggered burst release from polymer nanoparticles prepared by emulsification was reported recently by Fomina et al. using self-immolative monomers.[5] It would be interesting to apply the concept of self-immolative polymers[6] to prepare BCP micelles whose core degradation can be activated by removing a small number of trigger units and compare them with the fast photodegradable BCP micelles demonstrated in the present study.

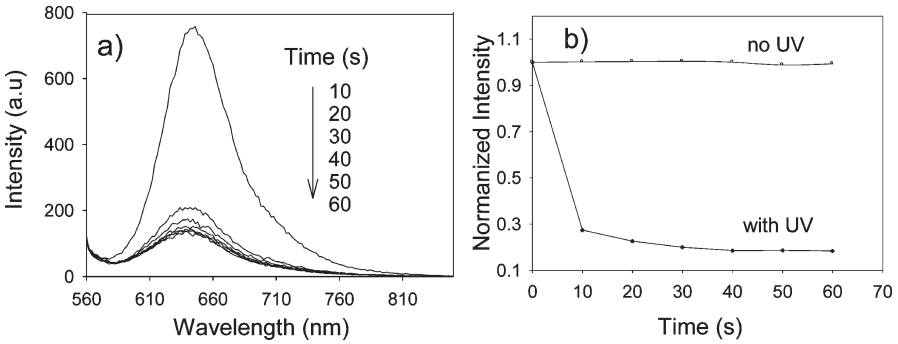


Figure 4. (a) Fluorescence emission spectra of Nile Red-loaded micelles in aqueous solution (λ_{ex} = 550 nm) recorded before and after UV irradiation for different times (300 nm, 250 mW/cm^2, solution volume 0.7 mL). (b) Normalized fluorescence emission intensity vs time for the Nile Red-loaded micelle solution with and without the UV irradiation.

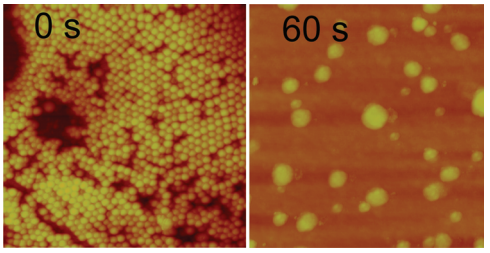


Figure 5. AFM height images of micelles obtained by casting an aqueous solution of Nile Red-loaded micelles on mica before and after 60 s UV irradiation (300 nm, 250 mW/cm^2, solution volume 0.7 mL). Image area: 1 μm × 1 μm.

In summary, we designed, synthesized, and investigated a novel photosensitive ABA triblock copolymer. The results demonstrated a new amphiphilic BCP design strategy for the preparation of fast light-breakable micelles. It consists in positioning a photocleavable unit repeatedly on the main chain of the hydrophobic block. This approach differs from those based on either light-changeable hydrophilic−hydrophobic balance or the use of a single photocleavable junction linking the constituting hydrophilic and hydrophobic blocks. We showed that with this type of BCP micelles undergoing fast photoinduced disintegration of micelle core, light-triggered burst release of loaded hydrophobic guest molecules in aqueous solution could be achieved. This progress is of fundamental interest because the approach is general and can easily be applied to design BCPs with photocleavable groups other than *o*-nitrobenzyl. Although UV light was utilized in this proof-of-principle study, light of longer wavelengths, which is more suitable for biomedical applications, could activate the same photoreaction and thus the same fast disintegration of BCP micelles through two-photon absorption of the photocleavable *o*-nitrobenzyl moieties on the main chain.[2d] By using coumarin-based photocleavable units, two-photon absorption allows the use of near-infrared light (NIR) at wavelengths ~800 nm.[2g]

Acknowledgment. We acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and le Fonds québécois de la recherche sur la nature et les technologies of Québec (FQRNT). Y.Z. is a member of the FQRNT-funded Center for Self-Assembled Chemical Structures.

Supporting Information Available: Details of block copolymer synthesis and more characterization results using ^{1}H NMR, UV−vis, fluorescence, and SEC. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Zhao, Y. *J. Mater. Chem.* **2009**, *19*, 4887–4895. (b) Schumers, J.-M.; Fustin, C.-A.; Gohy, J.-F. *Macromol. Rapid Commun.* **2010**, *31*, 1588–1607. (c) Wang, B. Y.; Xu, H.; Zhang, X. *Adv. Mater.* **2009**, *21*, 2849–2864.

(2) (a) Wang, G.; Tong, X.; Zhao, Y. *Macromolecules* **2004**, *37*, 8911–8917. (b) Tong, X.; Wang, G.; Soldera, A.; Zhao, Y. *J. Phys. Chem. B* **2005**, *109*, 20281–20287. (c) Jiang, J.; Tong, X.; Zhao, Y. *J. Am. Chem. Soc.* **2005**, *127*, 8290–8291. (d) Jiang, J.; Tong, X.; Morris, D.; Zhao, Y. *Macromolecules* **2006**, *39*, 4633–4640. (e) Jiang, J.; Qi, B.; Lepage, M.; Zhao, Y. *Macromolecules* **2007**, *40*, 790–792. (f) Babin, J.; Lepage, M.; Zhao, Y. *Macromolecules* **2008**, *41*, 1246–1253. (g) Babin, J.; Pelletier, M.; Lepage, M.; Allard, J. F.; Morris, D.; Zhao, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 3329–3332.

(3) (a) Lee, H.; Wu, W.; Oh, J. K.; Mueller, L.; Sherwood, G.; Peteanu, L.; Kowalewski, T.; Matyjaszewski, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 2453–2457. (b) Zou, J.; Guan, B.; Liao, X. J.; Jiang, M.; Tao, F. G. *Macromolecules* **2009**, *42*, 7465–7473. (c) Goodwin, A. P.; Mynar, J. L.; Ma, Y.; Fleming, G. R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2005**, *127*, 9952–9953. (d) Wang, Y.; Han, P.; Xu, H.; Wang, Z.; Zhang, X.; Kabanove, A. *Langmuir* **2010**, *26*, 709–715. (e) Su, W.; Luo, Y. H.; Yan, Q.; Wu, S.; Han, K.; Zhang, Q. J.; Gong, Y. Q.; Li, Y. M. *Macromol. Rapid Commun.* **2007**, *28*, 1251–1256. (f) Barrio, J. D.; Oriol, L.; Sánchez, C.; Serrano, J. L.; Cicco, A. D.; Keller, P.; Li, M.-H. *J. Am. Chem. Soc.* **2010**, *132*, 3762–3769. (g) Feng, Z.; Lin, L.; Yan, Z.; Yu, Y. *Macromol. Rapid Commun.* **2010**, *31*, 640–644. (h) Jiang, X.; Lavender, C. A.; Woodcock, J. W.; Zhao, B. *Macromolecules* **2008**, *41*, 2632–2643. (i) Jochum, F. D.; Theato, P. *Chem. Commun.* **2010**, *46*, 6717–6719.

(4) (a) Kang, M.; Moon, B. *Macromolecules* **2009**, *42*, 455–458. (b) Schumers, J. M.; Gohy, J. F.; Fustin, C. A. *Polym. Chem.* **2010**, *1*, 161–163. (c) Katz, J. S.; Zhong, S.; Ricart, B. G.; Pochan, D.; J.; Hammer, D. A.; Burdick, J. A. *J. Am. Chem. Soc.* **2010**, *132*, 3654–3655.

(5) Fomina, N.; McFearin, C.; Sermsakdi, M.; Edigin, O.; Almutairi, A. *J. Am. Chem. Soc.* **2010**, *132*, 9540–9542.

(6) (a) Sagi, A.; Weinstain, R.; Karton, N.; Shabat, D. *J. Am. Chem. Soc.* **2008**, *130*, 5434–5435. (b) DeWit, M. A.; Gillies, E. R. *J. Am. Chem. Soc.* **2009**, *131*, 18327–18334. (c) Esser-Kahn, A. P.; Sottos, N. R.; White, S. R.; Moore, J. S. *J. Am. Chem. Soc.* **2010**, *132*, 10266–10268.

Supporting Information

Fast-Photodegradable Block Copolymer Micelles for Burst Release

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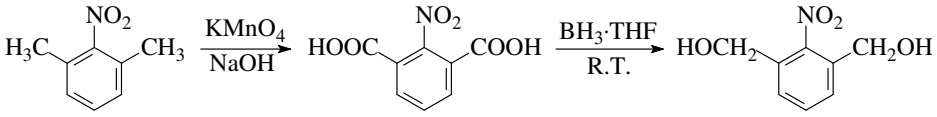
1. Synthesis

Materials. Tetrahydrofuran (THF, 99%) was refluxed with sodium and a small amount of benzophenone and distilled prior to use. 1,3-Dimethyl-2-nitrobenzene (99%), potassium permanganate ($KMnO_4$, ≥99.0%), borane tetrahydrofuran complex solution (1.0 M, in THF), anhydrous *N*,*N*-dimethylformamide (99.8%) and tolylene 2,4-diisocyanate (95%) were purchased from Aldrich and used directly. Poly(ethylene oxide) monomethyl ether (M_n=2000 g/mol) was purchased from Aldrich and dried by azeotropic distillation using anhydrous toluene.

Characterizations. ^{1}H NMR spectra were recorded on a Bruker 300MHz spectrometer using deuterated chloroform as solvent and tetramethylsilane as internal standard. The spectra were used to determine the number-average molecular weights (M_n) of triblock copolymer PEO-*b*-PUNB-*b*-PEO. A Waters size exclusion chromatograph (SEC) instrument, equipped with a Waters 410 differential refractometer detector and a Waters 996 photodiode array detector, was also utilized to measure the M_n, M_w (weight-average molecular weight) and the polydispersity index (PDI) using polystyrene (PS) standards. The SEC measurements were conduced at 35 ^{o}C using one column (Waters Styragel HR4E, 7.8 mm × 300 mm, 5 μm beads) and THF eluent (flow rate: 1.0 mL min^{-1}). UV-vis spectra were recorded with a Varian 50 Bio spectrophotometer. Tapping-mode atomic force microscopy (AFM, Nanoscope IV) was used to examine the BCP micelles solution-cast on mica plate, followed by removing solvent with a filter paper. Dynamic light scattering (DLS) experiments were carried out using a Brookhaven goniometer (BI-200) equipped with an avalanche photodiode detector (Brookhaven, BI-APD), a digital correlator (Brookhaven, TurboCorr) that calculates the photon intensity autocorrelation function $g^2(t)$ and a helium-neon laser (λ = 632.8 nm). The hydrodynamic diameter (D_H) values of the micelles were obtained by a cumulant and CONTIN analysis. The UV irradiation beam was generated by a spot curing system (Novacure 2100) combined with an interference filter for the used 300 nm wavelength (10 nm bandwidth, Oriel), with the beam intensity measured with a powermeter (Oriel).

Synthesis of 2-nitro-1,3-benzenedicarboxylic acid. The synthetic procedure for 2-nitro-1,3-benzenedimethanol is shown in Scheme S1. 2-Nitro-1,3-benzenedicarboxylic acid was firstly synthesized according to a literature method. A stirred mixture of 1,3-dimethyl-2-nitrobenzene (15.8 g, 0.105 mol), water (800 mL) and sodium hydroxide (6.4 g, 0.16 mol) was heated to 95 ºC, then KMnO4 (66 g, 0.418 mol) was added in portions over a period of 3 hrs. The resulting mixture was refluxed for another 20 h, cooled and filtered; the filtrate was acidified with concentrated HCl and the precipitate was collected, dried and its structure was verified by ^{1}H NMR spectroscopy (Figure S1).



Scheme S1. Synthesis for 2-nitro-1,3-benzenedimethanol.

Synthesis of 2-nitro-1,3-benzenedimethanol.

A solution of 2-nitro-1,3-benzenedicarboxylic acid (8.0 g, 38 mmol) in 50 mL anhydrous THF was cooled to 0 ^{o}C in the presence of N_2, and then 1.0 M borane-tetrahydrofuran (200 mL) was added

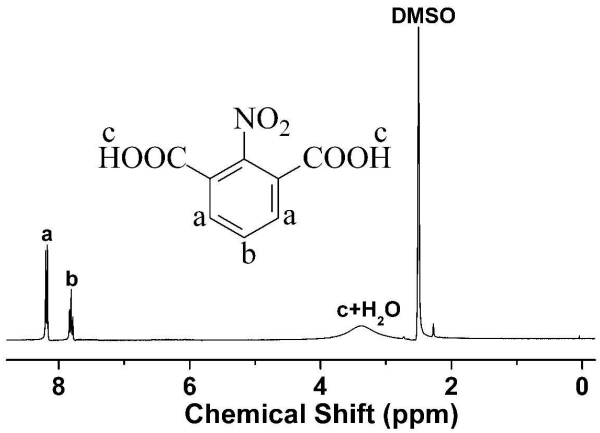


Figure S1. The ^{1}H NMR spectrum of 2-nitro-1,3-benzenedicarboxylic acid.

dropwise over about 1 h. The reaction mixture was allowed to warm slowly to room temperature and stirred for another 48 h. Methanol (40 mL) was then added into the reaction system slowly by syringe, the mixture filtered and the filtrate evaporated with a rotary evaporator. The residue was redissolved in ethyl acetate and washed with water (3×100 mL). The organic layer was dried with anhydrous $MgSO_4$ overnight before the solvent was removed on a rotary evaporator. The resulting yellow solid was further purified by silica gel chromatography (hexane:ethyl acetate=1:1) to obtain 2-nitro-1,3-benzenedimethanol (4.5 g, 65% yield). Its structure was confirmed by ^{1}H NMR spectroscopy (Figure S2).

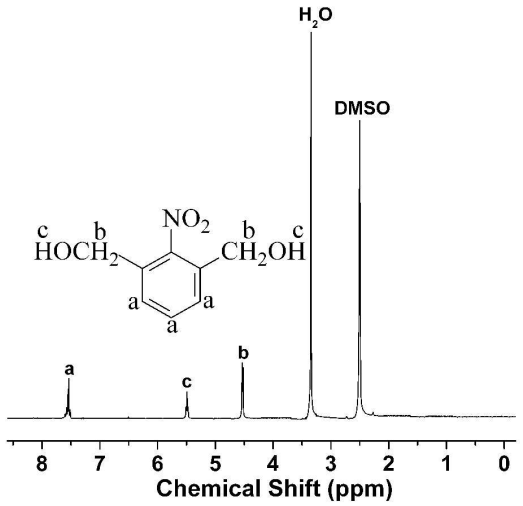


Figure S2. The ^{1}H NMR spectrum of 2-nitro-1,3-benzenedimethanol.

Synthesis of PEO-*b*-PUNB-*b*-PEO triblock copolymer.

The PEO-*b*-PUNB-*b*-PEO triblock was synthesized via a one-pot procedure. The central PUNB block was obtained by condensation polymerization of 2-nitro-1,3-benzenedimethanol with tolylene 2,4-diisocyanate in slight excess and it was terminated with poly(ethylene oxide) monomethyl ether. The detailed polymerization procedure is as follows. In a 25 mL two-necked flask, 2-nitro-1,3-benzenedimethanol (0.38 g, 2.08 mmol) was dissolved in 4.0 mL of anhydrous DMF in the presence of N_2. The reaction flask was quickly covered with aluminum foil to avoid the sunlight. Tolylene 2,4-diisocyanate (0.39 g, 2.25 mmol) dissolved into 1.0 mL of anhydrous DMF was then added into the flask by syringe in the presence of N_2. The reaction flask was finally immersed into an oil bath thermostated at 50 ^{o}C. After polymerization for 12 h, poly(ethylene oxide) monomethyl ether (0.26 g, 0.13 mmol) dissolved into 2.0 mL of anhydrous DMF was injected into the reaction flask under N_2 and the reaction continued for another 24 h. Afterward, the polymer solution was directly added dropwise into diethyl ether, the polymer precipitated was collected by filtration. The obtained yellow powder was further purified twice by adding its THF solution in diethyl ether for precipitation. After filtration, the lightly yellow PEO-*b*-PUNB-*b*-PEO triblock was collected and dried under vacuum overnight (0.88 g, yield 86%). The triblock copolymer was firstly characterized with size exclusion chromatograph (SEC) with polystyrene (PS) standards and THF eluent in comparison with PEO monomethyl ether, yielding M_n=15100 g/mol and PDI=1.38 as compared to the 2000 g/mol PEO with PDI=1.06. In order to estimate the composition of the triblock copolymer, ^{1}H NMR spectrum was measured and shown in Figure S3. Knowing the molecular weight of PEO, the molecular weight of PEO-*b*-PUNB-*b*-PEO was determined by comparing the integrals of peak *g* at δ=5.20-5.30 ppm (from PUNB) and peak *b* at δ=3.60-3.70 ppm (from PEO), yielding $M_{n,NMR}$=14000 g/mol, the degree of polymerization of PUNB being 28.

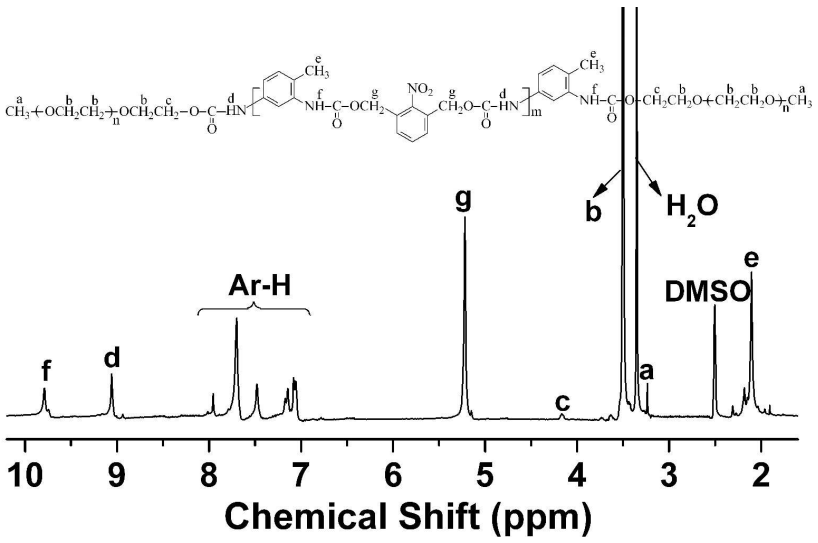


Figure S3. The ^{1}H NMR spectrum of PEO-*b*-PUNB-*b*-PEO triblock copolymer (in DMSO-d6).

2. Photodegradation of PEO-*b*-PUNB-*b*-PEO as Revealed by SEC Measurements

The continuous photodegradation of PEO-*b*-PUNB-*b*-PEO upon UV irradiation was monitored by means of SEC using a THF solution at a high BCP concentration of 10 mg/mL (required for the SEC

measurements). The results are shown in Figure S4. As the UV irradiation goes on, more and more species of decreased molecular weights are formed, shifting the elution peaks to longer elution times.

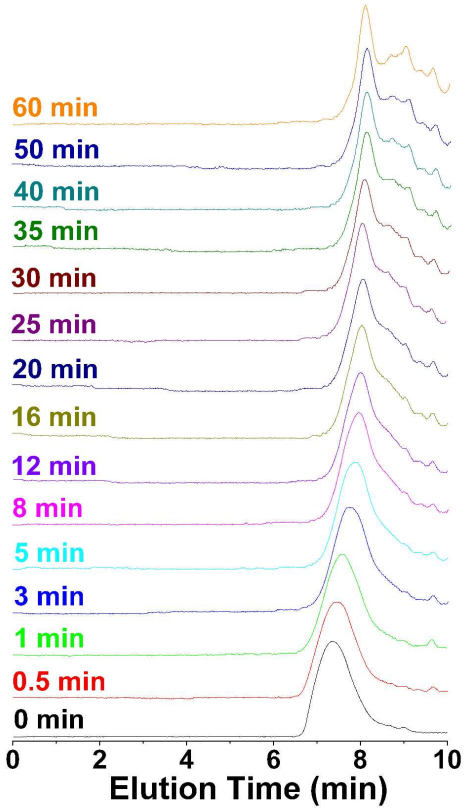


Figure S4. SEC traces of PEO-*b*-PUNB-*b*-PEO in THF (10 mg/mL) recorded as a function of UV irradiation time (300 nm, 50 mW.cm^{-2}).

3. Photoreaction of PEO-*b*-PUNB-*b*-PEO as Revealed by UV-vis Spectra

Figures S5 and S6 show the UV-vis spectra of BCP dissolved in THF and BCP micelles in aqueous solution upon UV irradiation, respectively. In both cases, the spectral changes indicate the photodegradation of the PUNB block. From the BCP design, it is expected that the randomly occurred photocleavage of nitrobenzyl moieties on the main chain could generate species of various sizes and contain nitrosobenzyl and residual nitrobenzyl units. This accounts for the increased absorption over a wide range of wavelengths between ~ 300-500 nm as the photoreaction progresses. It is interesting to notice that due to the large number of nitrobenzyl units on the hydrophobic main chain, it is not necessary to degrade the PUNB block onto small species to break the micelle core. The micelle core can be disintegrated quickly, after a few cleavages on each chain, while the photoreaction continues on all species still bearing nitrobenzyl groups. This explains why the fluorescence quenching of Nile Red can occur shortly upon UV irradiation, while the photoreaction proceeds continuously over a longer period of time.

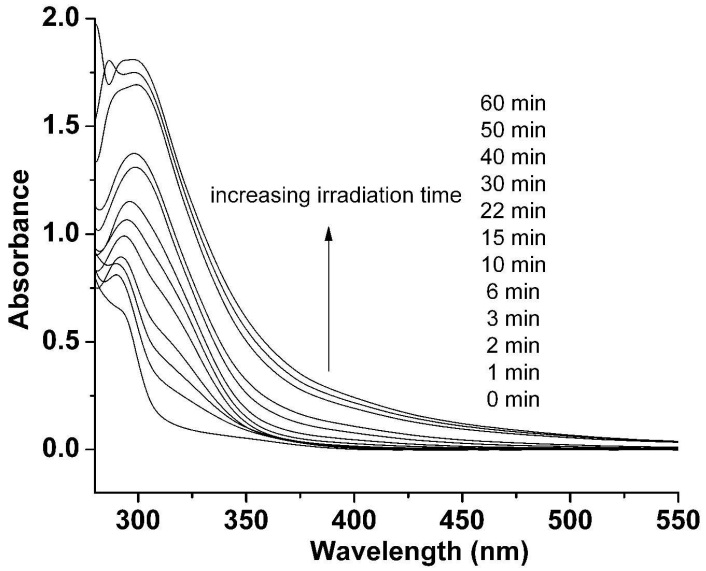


Figure S5. UV-vis spectra of PEO-*b*-PUNB-*b*-PEO dissolved in THF (0.06 mg/mL) and subjected to UV irradiation (300 nm, 50 mW/cm^2, solution volume 3 mL).

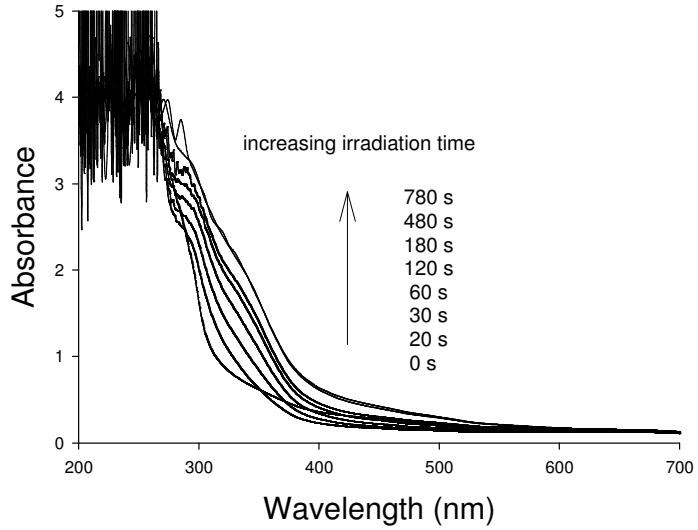


Figure S6. UV-vis spectra of PEO-*b*-PUNB-*b*-PEO micelles in aqueous solution (0.2 mg/mL) and subjected to UV irradiation (300 nm, 250 mW/cm^2, solution volume 0.7 mL).

4. Fluorescence of Nile Red in a THF Solution of PEO-*b*-PUNB-*b*-PEO Subjected to Photodegradation

Figure S7 shows the result of a control test. Nile Red was dissolved with the BCP in either THF or a mixture of THF/water (5:1, v/v), and the solution was subjected to UV irradiation under the same conditions as for Nile Red-loaded BCP micelles in aqueous solution. No fluorescence change was observed after 60 s UV irradiation. This result indicates that photodegraded species could not quench the fluorescence emission of Nile Red.

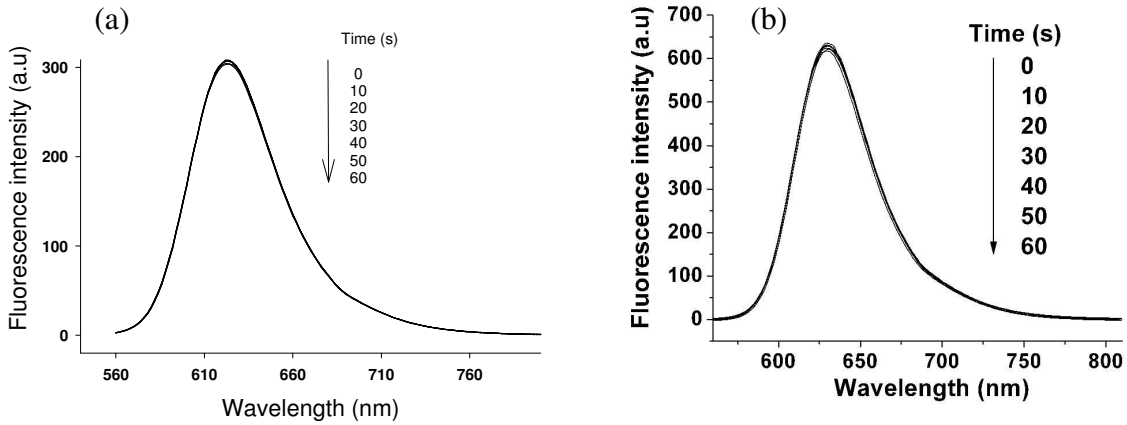


Figure S7. Fluorescence emission spectra (λ_{ex}=550 nm) of Nile Red dissolved with PEO-*b*-PUNB-*b*-PEO (0.2 mg/mL) in (a) THF and (b) THF/water (5:1, v/v) under UV irradiation (300 nm, 250 mW/cm^2, solution volume 0.7 mL).