

Supporting Information

Light-Driven Sequential Shape Transformation of Block Copolymer Particle through Three-Dimensional Confined Self-Assembly

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Table of Contents

1. General Information	S3
2. Experimental methods	S4
2.1 Synthesis of azo-containing bromoalkene (AzoxBr)	S4
2.2 Synthesis of 6-bromohexyloxy azobenzene (Azo6Br).....	S4
2.3 Fabrication of PS _{102k} - <i>b</i> -P2VP _{97k} (AzoxBr) Particles.	S5
2.4 Sequential Shape Transformation of PS- <i>b</i> -P2VP(AzoxBr) Particles.....	S6
2.5 Evaluation of the <i>In Vitro</i> Release of Drug-loaded Particles.	S6
3. Characterization results	S7

Fig S2. UV absorption spectra of AzoxBr aqueous solution with different alkyl chain length.

Fig S3. DLS result of PS-*b*-P2VP(Azo6Br)_{0.4} particle with different UV irradiation time.

Fig S4. SAXS result of PS-*b*-P2VP (Azo6Br)_{0.4} particle with different UV irradiation time.

Fig S5. TEM image showing the PS-*b*-P2VP(Azo6Br)_{0.2} particles under 365 nm UV irradiation for different times.

Fig S6. TEM image showing the PS-*b*-P2VP(Azo6Br)_{0.6} particles under 365 nm UV irradiation for different times.

Fig S7. TEM image showing the PS-*b*-P2VP(Azo6Br)_{0.8} particles under 365 nm UV irradiation for different times.

Fig S8. TEM image showing the effect of solvent absorption annealing and temperature on the structure of PS-*b*-P2VP(Azo6Br)_{0.4} particle.

Fig S9. TEM and SEM images showing the PS-*b*-P2VP(Azo4Br)_{0.4} particles under UV irradiation for different times.

Fig S10. TEM and SEM images showing the PS-*b*-P2VP(Azo8Br)_{0.4} particles under UV irradiation for different times.

Fig S11. TEM image of the NR-loaded BCPs and UV absorption spectra of NR-loaded BCP particles with or without UV light stimulus.

Table S1. Mass fraction of AzoxBr (m_{AzoxBr}) and corresponding molar ratio of AzoxBr to

the 2VP units.

Table S2. Summary of D_{PS} , D_{P2VP} , L , S and aspect ratio (AR) values (average \pm standard deviation) for particle batches with $m_{AzoxBr} = 0, 0.2, 0.4, 0.6$ and 0.8 .

4. ReferencesS14

1. General Information

Diblock copolymers PS_{102k}-*b*-P2VP_{97k} (the subscripts are the M_n of the blocks) with dispersity (D) = 1.12 was purchased from Polymer Source Inc., Canada. 1,4-dibromobutane, 1,6-dibromohexane, 1,8-dibromooctane, 1,12-dibromododecane, 4-hydroxyazobenzene (AzoH), trimethylamine (TMA, 28 wt%), cetyltrimethylammonium bromide (CTAB), and Nile Red (NR) were purchased from Aladdin Chemistry. Sodium hydroxid (NaOH), magnesium sulfate (MgSO₄), anhydrous ethanol, tetrahydrofuran (THF), dichloromethane and choroform (CHCl₃) were obtained from Sinopharm Chemical Reagent Co., Ltd. Poly (vinyl alcohol) (PVA, average M_w :13k-23k g/mol) was provided by Sigma-Aldrich. Deionized water (Millipore, 18 M Ω /cm) was used for all experiments. All of the reagents were used as received without further purification.

Molecular structure of AzoxBr, were characterized by ¹H NMR and ¹³C NMR spectrometer (Bruker Advance 500 MHz spectrometer) with CDCl₃-*d*₆ as the solvent. The morphology of the BCP particles were characterized by transmission electron microscopy (TEM, Hitachi HT-7700) and field emission scanning electron microscopy (FE-SEM, ZEISS SUPRATM 55). The samples were prepared by drop-casting of particle dispersion and dried on the silicon wafer and copper grid for SEM and TEM, respectively. P2VP domains were selectively stained by iodine vapor before TEM

characterization. Energy dispersive X-ray spectroscopy (EDS, X-MAXn65 T, Oxford) was used to clarify the location of iodine or bromine atoms in PS-*b*-P2VP(AzoxBr) particles. Synchrotron radiation small-angle X-ray scattering (SAXS) of copolymer solutions (0.01 wt%) was measured on the BL19U2 beamline of SSRF (Shanghai, China) using an incident X-ray with a wavelength of 1.03 Å. The solution sample was pumped into a quartz capillary ($\Phi = 2$ mm) cell by a Hamiltonton syringe pump (Hamilton Robotics Inc., Bonaduz, GR, Switzerland). The release behavior of NR-loaded BCP particles were also observed by confocal laser scanning microscopy (CLSM) (Zeiss LSM 900) and Hitachi UH -5300 spectrometer.

2. Experimental methods

2.1 Synthesis of azo-containing bromoalkene (AzoxBr)

Azobenzene-containing bromoalkene additives, denoted as AzoxBr (x represents the hydrophobic alkyl chain length, $x = 4,6,8,12$), were synthesized through alkylation with dibromoalkane following by the previous report.^{1,2} ^1H NMR and ^{13}C NMR spectra for AzoxBr confirm the successful syntheses of the azo-containing additives. Here, Azo6Br was selected as an example to describe the synthesis procedure. The detailed synthesis route is shown in Fig S1a.

2.2 Synthesis of 6-bromohexyloxy azobenzene (Azo6Br).

4-hydroxyazobenzene (1.386 g, 7.0 mmol) was dissolved in anhydrous ethanol (25 mL) containing NaOH (200 mg, 5.0 mmol) and the mixture was stirred for 30 min. Anhydrous ethanol (10.8 mL) containing 1,6-dibromohexane (5.124 g, 21.0 mmol) was slowly added (30 min) and the mixture was heated at reflux for two days. The solvent was evaporated under vacuum. The remaining solid was dissolved in dichloromethane

(10 mL) and extractions were performed with NaOH solution (1M, 2×4 mL) and pure water (2×4 mL). The organic phase was dried with MgSO₄ and concentrated. Yield: 70% (orange powder). ¹H NMR (Fig S1b) and ¹³C NMR (Fig S1c) are used to characterize the product of Azo6Br. All the protons or carbon atoms and their corresponding signals are clearly labeled in the following NMR spectra. ¹H NMR (400MHz, CDCl₃-d₆, 298K), δ ppm: 7.91 (2H, Ar-H), 7.89-7.85 (2H, Ar-H), 7.50 (2H, Ar-H), 7.46-7.41 (2H, Ar-H), 7.00 (H, Ar-H), 4.05 (2H, CH₂O), 3.42 (2H, CH₂Br), 1.88 (8H, CH₂). ¹³C NMR (400MHz, CDCl₃-d₆, 298K), δ ppm: 161.76 (Ar-C), 1152.88 (Ar-C), 147.03 (Ar-C), 130.48 (Ar-C), 129.17 (Ar-C), 124.93 (Ar-C), 122.68 (Ar-C), 114.84 (Ar-C), 68.22 (OCH₂), 33.79 (CH₂), 32.65 (CH₂), 29.17 (CH₂), 28.06 (CH₂), 27.44 (CH₂Br).

Other azo-containing additives with different hydrophobic alkyl chain length (Azo4Br, Azo8Br, Azo12Br) were synthesized using the similar method mentioned above.

2.3 Fabrication of PS_{102k}-*b*-P2VP_{97k}(AzoxBr) Particles.

The emulsion-solvent evaporation method was applied to prepare the polymer particles. The pristine PS-*b*-P2VP or PS-*b*-P2VP(AzoxBr) were first dissolved in chloroform at a concentration of 1 wt%. In the preparation of NR-loaded BCP particles, 0.1 mg/mL of Nile red (NR, J&K chemical) was added into the solution. Subsequently, the solution (0.15 mL) was emulsified with 1.0 mL of aqueous solution containing CTAB and PVA (1 wt %, CTAB/PVA = 1:4 w/w) with a homogenizer. To produce PS-*b*-P2VP(AzoxBr) particles, a mixture of PS-*b*-P2VP and AzoxBr with a mass fraction

ranging from 0.20 to 0.80 were dissolved in chloroform and stirred for 4 h prior to emulsification. The chloroform was slowly evaporated by stirring the emulsions in an open vial at room temperature. After complete evaporation of chloroform, the formed polymer particles were separated by centrifugation (1000 rpm, 6 min) to remove the remaining surfactant.

2.4 Sequential Shape Transformation of PS-*b*-P2VP(AzoxBr) Particles.

The sequential shape transformation of PS-*b*-P2VP(AzoxBr) particles was achieved by UV stimulus. The distance between the light source and the sample is 10 cm. In this process, solvent-adsorption annealing is used to facilitate the mobility of the BCP chains. An open vial containing the particle suspension (1 mL) in water was placed inside a larger vial containing chloroform (5 mL) to produce a chloroform-saturated atmosphere and irradiated at 365 nm UV light (WFH-203B, 6W) for different times (0-3 h). Then, the absorbed chloroform was completely removed for 24 h. The resulting solution was washed by repeated centrifugation at 13000 rpm for 3 min to remove any remaining surfactants.

2.5 Evaluation of the *In Vitro* Release of Drug-loaded Particles.

NR-loaded PS-*b*-P2VP(AzoxBr) particles were prepared as mentioned above. The amount of released NR was determined from the UV absorbance at 530 nm by comparing with the calibrated absorption curve of NR in water. The calibration curve of NR in micelle solution was obtained through linear fitting, this is, $y = -0.0041x + 0.00727$ ($x = 0.007 - 0.3$ mg/mL, $R^2 = 0.99$), as shown in Fig S11. The release experiments were conducted in triplicate and the average results were used. For

comparison, the release behavior of PS-*b*-P2VP(AzoxBr) particle without UV light irradiation was also conducted.

3. Characterization results

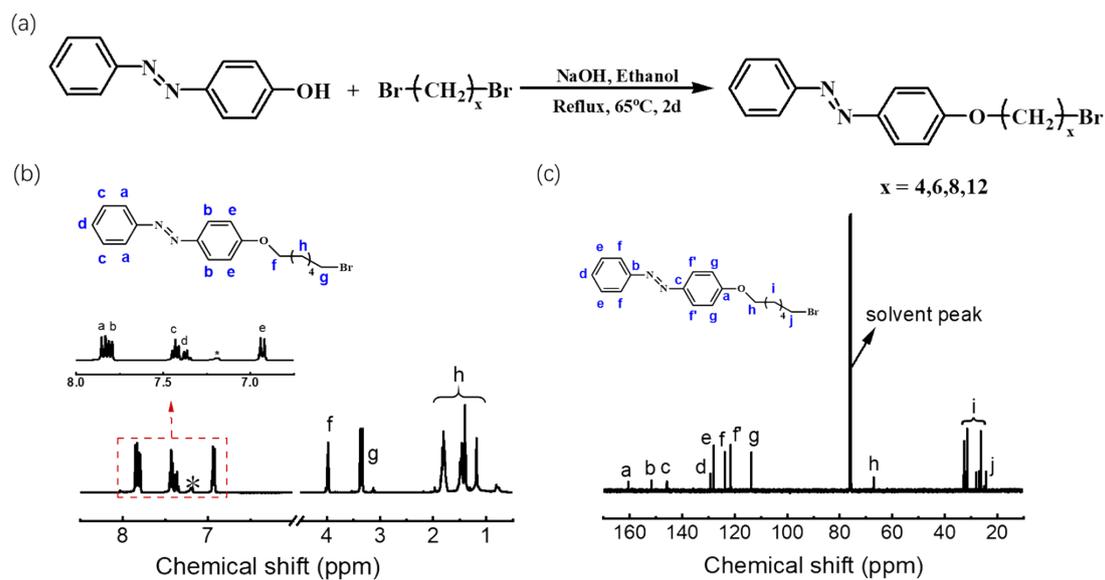


Fig S1. (a) Synthesis of AzoxBr with different hydrophobic alkyl chain length. (b) ^1H NMR and (c) ^{13}C NMR spectrum of Azo6Br in CDCl_3-d_6 .

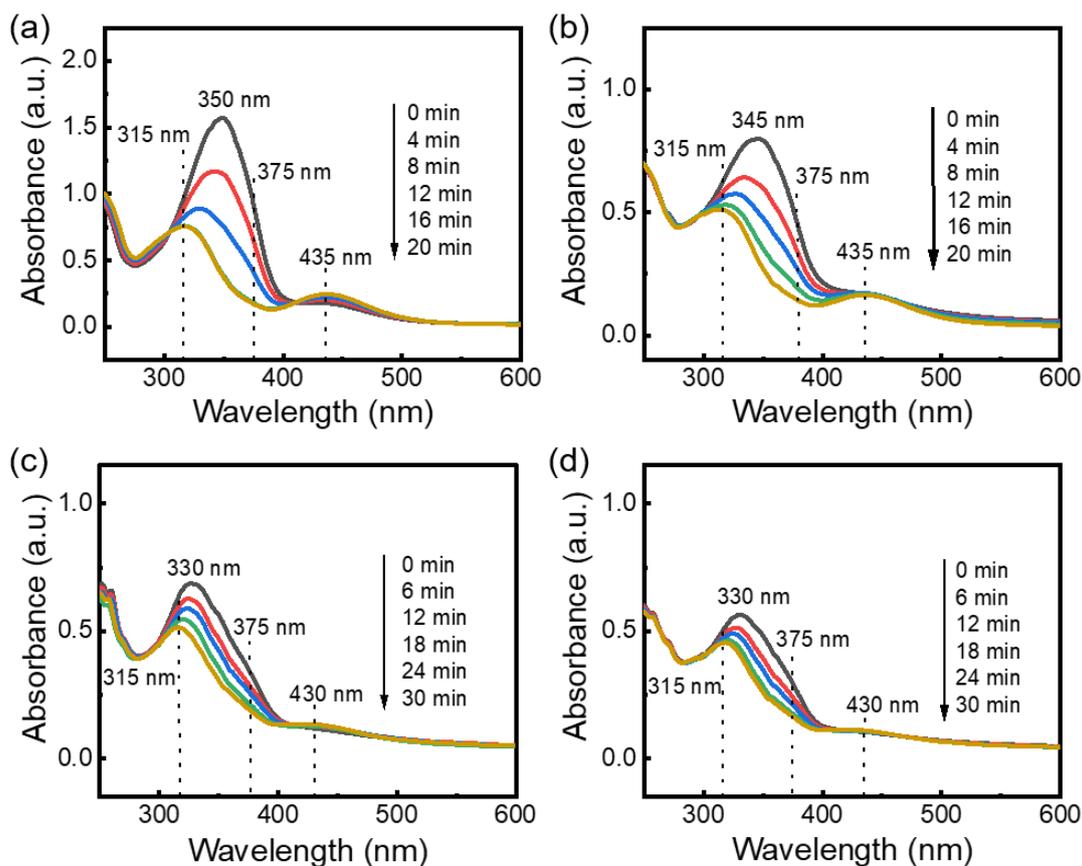


Fig S2. UV absorption spectra of AzoxBr aqueous solution (0.01 mg/mL) under 365 nm light irradiation: (a) Azo4Br, (b) Azo6Br, (c) Azo8Br, and (d) Azo12Br.

As depicted in Fig S2a, for Azo4Br additive, the typical maximum absorption wavelength at 350 nm was a result of the π - π^* transition in the *trans*-isomer. After continuous UV irradiation (365 nm), the absorbance strength at 350 nm decreased, while two new peaks at 315 nm and 435 nm appeared due to the n - π^* transition of the *cis*-isomer.³⁻⁵ Similar results could be observed for AzoxBr additives with different alkyl chain length (Fig S2b-d).

Table S1. Mass fraction of AzoxBr (m_{AzoxBr}) and corresponding molar ratio of AzoxBr to the 2VP units.

Polymer Particle	Feed mass fraction (m_{AzoxBr})	Ratio of AzoxBr relative to the 2VP units
PS- <i>b</i> -P2VP	0	0
PS- <i>b</i> -P2VP(Azo4Br) _{0.2}	0.2	0.16
PS- <i>b</i> -P2VP(Azo4Br) _{0.4}	0.4	0.43
PS- <i>b</i> -P2VP(Azo4Br) _{0.6}	0.6	0.97
PS- <i>b</i> -P2VP(Azo4Br) _{0.8}	0.8	2.59
PS- <i>b</i> -P2VP(Azo6Br) _{0.2}	0.2	0.15
PS- <i>b</i> -P2VP(Azo6Br) _{0.4}	0.4	0.40
PS- <i>b</i> -P2VP(Azo6Br) _{0.6}	0.6	0.90
PS- <i>b</i> -P2VP(Azo6Br) _{0.8}	0.8	2.39
PS- <i>b</i> -P2VP(Azo8Br) _{0.2}	0.2	0.14
PS- <i>b</i> -P2VP(Azo8Br) _{0.4}	0.4	0.37
PS- <i>b</i> -P2VP(Azo8Br) _{0.6}	0.6	0.83
PS- <i>b</i> -P2VP(Azo8Br) _{0.8}	0.8	2.22
PS- <i>b</i> -P2VP(Azo12Br) _{0.2}	0.2	0.12
PS- <i>b</i> -P2VP(Azo12Br) _{0.4}	0.4	0.32
PS- <i>b</i> -P2VP(Azo12Br) _{0.6}	0.6	0.73
PS- <i>b</i> -P2VP(Azo12Br) _{0.8}	0.8	1.94

Table S2. Summary of D_{PS} , D_{P2VP} , L , S and aspect ratio (AR) values (average \pm standard deviation) for particle batches with $m_{AzoxBr} = 0, 0.2, 0.4, 0.6$ and 0.8 .

Polymer Particle	D_{PS} (nm)	D_{P2VP} (nm)	L (nm)	S (nm)	AR
PS- <i>b</i> -P2VP	34.3 \pm 5.9	30.9 \pm 5.5	1710.9 \pm 225.8	1005.7 \pm 61.0	1.71 \pm 0.30
PS- <i>b</i> -P2VP(Azo4Br) _{0.2}	42.2 \pm 3.1	39.1 \pm 4.2	2230.9 \pm 394.4	903.5 \pm 151.3	2.47 \pm 0.20
PS- <i>b</i> -P2VP(Azo4Br) _{0.4}	44.2 \pm 5.4	42.1 \pm 2.9	2307.2 \pm 519.7	782.4 \pm 256.7	3.01 \pm 0.24
PS- <i>b</i> -P2VP(Azo4Br) _{0.6}	46.1 \pm 4.3	45.6 \pm 3.8	1186.3 \pm 322.7	438.5 \pm 94.1	2.68 \pm 0.11
PS- <i>b</i> -P2VP(Azo4Br) _{0.8}	52.2 \pm 4.3	48.4 \pm 2.3	851.6 \pm 456.6	284.2 \pm 128.7	2.95 \pm 0.17
PS- <i>b</i> -P2VP(Azo6Br) _{0.2}	44.1 \pm 3.8	41.0 \pm 5.2	1441.9 \pm 215.4	596.1 \pm 86.8	2.42 \pm 0.01
PS- <i>b</i> -P2VP(Azo6Br) _{0.4}	46.8 \pm 4.2	44.7 \pm 3.2	2287.9 \pm 619.6	643.5 \pm 215.2	3.58 \pm 0.20
PS- <i>b</i> -P2VP(Azo6Br) _{0.6}	48.4 \pm 7.3	46.4 \pm 2.4	1118.7 \pm 332.3	363.5 \pm 91.0	3.05 \pm 0.16
PS- <i>b</i> -P2VP(Azo6Br) _{0.8}	56.7 \pm 5.8	46.0 \pm 6.7	506.6 \pm 44.1	184.1 \pm 17.3	2.76 \pm 0.15
PS- <i>b</i> -P2VP(Azo8Br) _{0.2}	48.1 \pm 6.9	44.6 \pm 3.5	1041.7 \pm 41.5	377.2 \pm 30.3	2.74 \pm 0.15
PS- <i>b</i> -P2VP(Azo8Br) _{0.4}	53.3 \pm 5.5	46.4 \pm 4.0	687.9 \pm 51.8	226.8 \pm 21.9	3.03 \pm 0.12

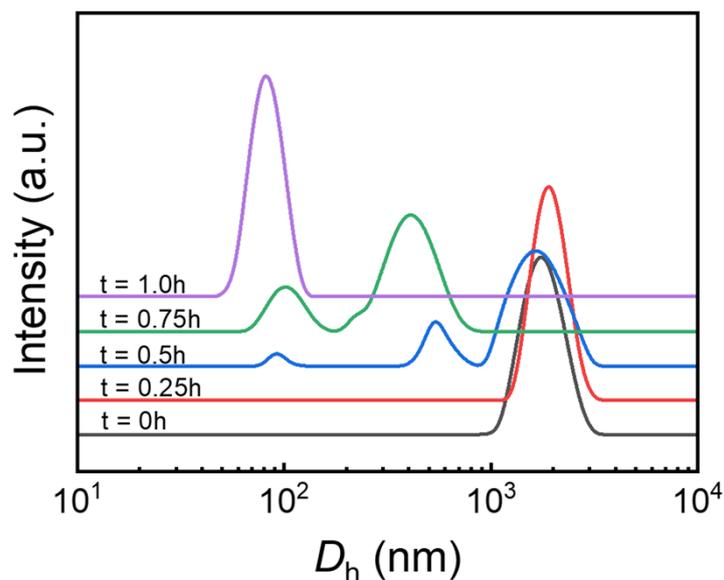


Fig S3. DLS results of the PS-*b*-P2VP(Azo6Br)_{0.4} particle irradiated by UV light at different times.

As shown in Fig S3, upon irradiated for 0.25 h, the particle size increases from 1.7 to 2.2 μm , which is associated with the structural elongation of the ellipsoidal particles. After 0.5 h and 0.75 h irradiation, accordion-like particles generate and gradually disassemble into spheres. Finally, dispersed spherical particles with average size of 78 nm are observed after irradiating for 1 h, indicating the complete disassembly of the particles.

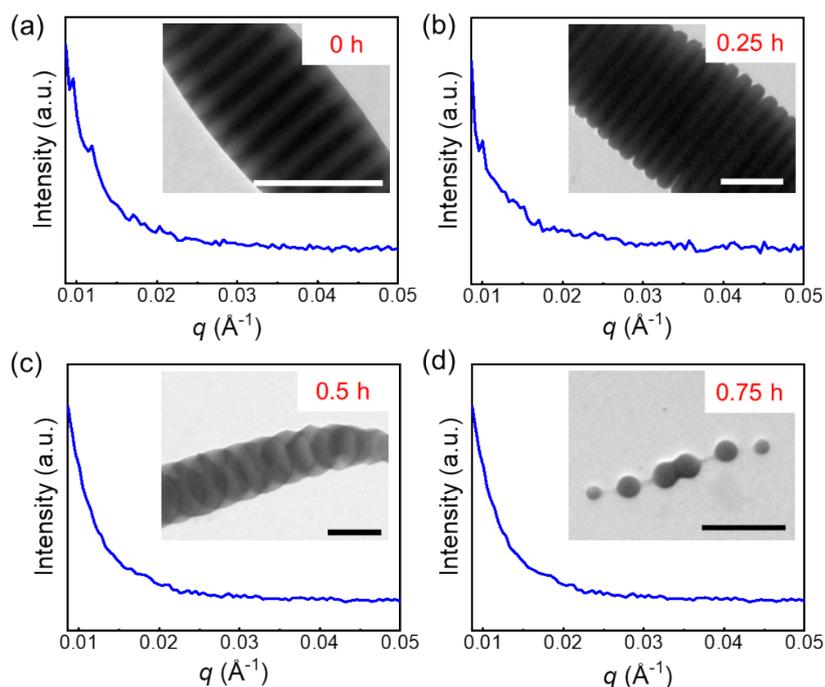


Fig S4. SAXS results of the PS-*b*-P2VP(Azo6Br)_{0.4} irradiated at 365nm UV light for different times. Insets in (a–c) are the representative TEM images. Scale bar: 500 nm. The P2VP domains are stained by I₂ vapor for TEM observation.

To illustrate the structural transition of the particles, synchrotron radiation SAXS of BCP particles upon irradiating with different times is detected. As shown in Fig S4a, two distinct scattering peaks are presented from the SAXS pattern, indicating lamellar morphology of the particle. Upon irradiation for 0.25 h, only one correlation peak appears and the peak position changes, implying that the inner sequence structure of BCP particle is different from the primitive structure (Fig S4b). The reason is that parts of *trans*-azo groups have turned to *cis*-azo, enhancing the interactions with water. Furtherly, the scattering peak disappears upon 1 h irradiation (Fig S4c,d), suggesting that the inner sequence structure has been disrupted at this time. That is, the PS-*b*-P2VP(Azo6Br) particle has completely disassembled.

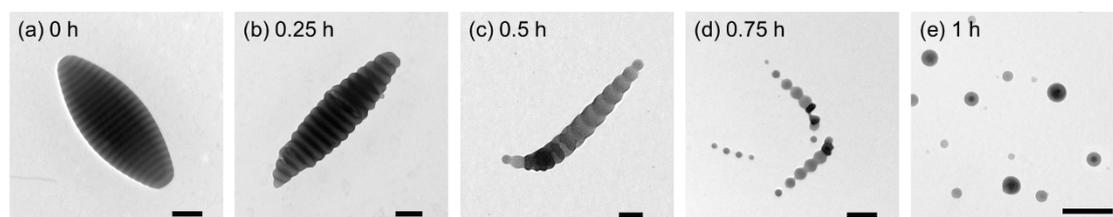


Fig S5. TEM images showing the PS-*b*-P2VP(Azo6Br)_{0.2} particles irradiated at 365nm uv light for different times: (a) 0, (b) 0.25, (c) 0.5, (d) 0.75, and (e) 1.0 h. Scale bar: 200 nm. The P2VP domains are stained by I₂ vapor for TEM observation.

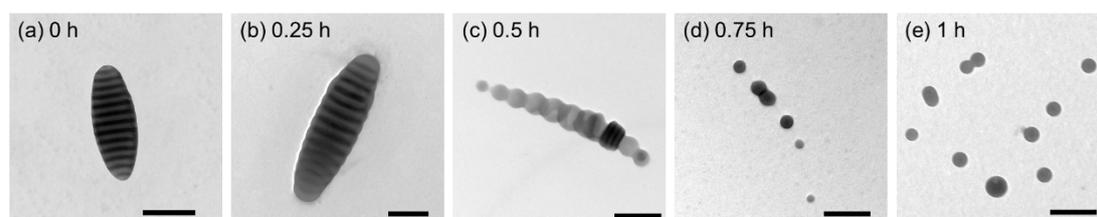


Fig S6. TEM images showing the PS-*b*-P2VP(Azo6Br)_{0.6} particles irradiated by 365nm UV light for different times: (a) 0, (b) 0.25, (c) 0.5, (d) 0.75, and (e) 1.0 h. Scale bar:

200 nm. The P2VP domains are stained by I₂ vapor for TEM observation.

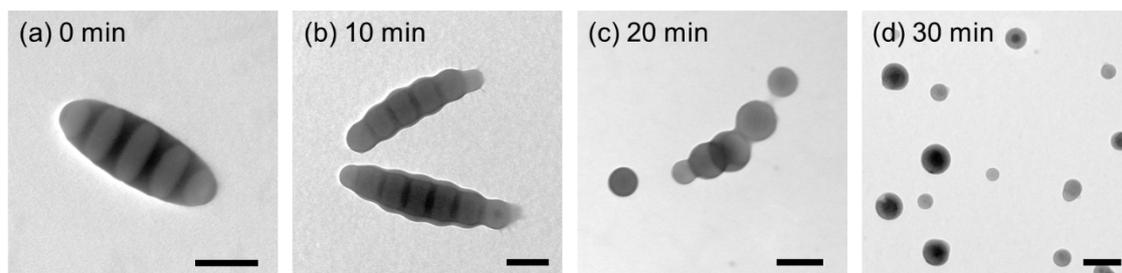


Fig S7. TEM images showing the PS-*b*-P2VP(Azo6Br)_{0.8} particles irradiated by 365nm UV light for different times: (a) 0, (b) 10, (c,) 20, and (d) 30 min. Scale bar: 200 nm. The P2VP domains are stained by I₂ vapor for TEM observation.

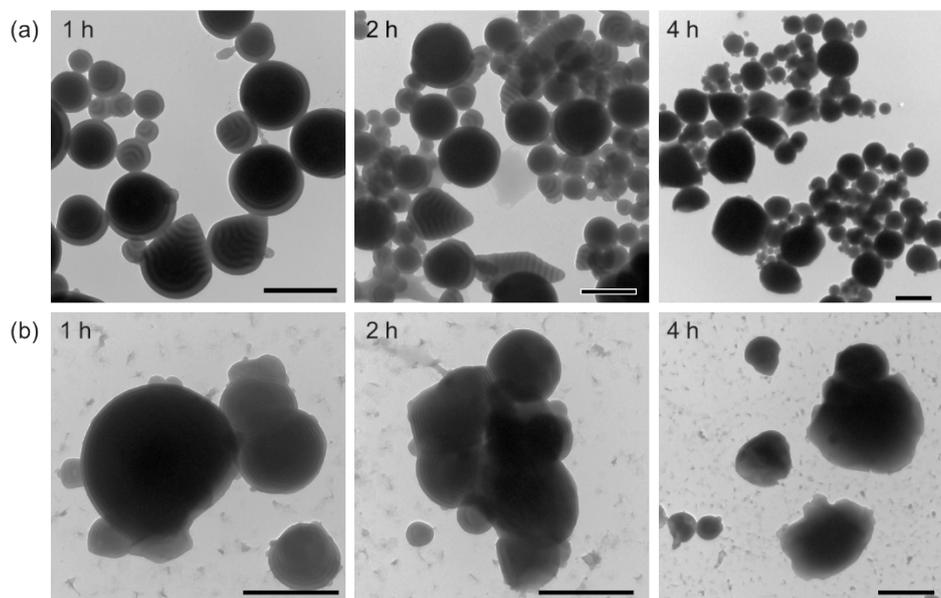


Fig S8. TEM images shows the effects of solvent absorption annealing process and temperature (35 °C) on the shape of the PS-*b*-P2VP(AzoxBr) particles without light irradiation. Scale bar is 1.0 μm for all the images. The P2VP domains are stained by I₂ vapor for TEM observation.

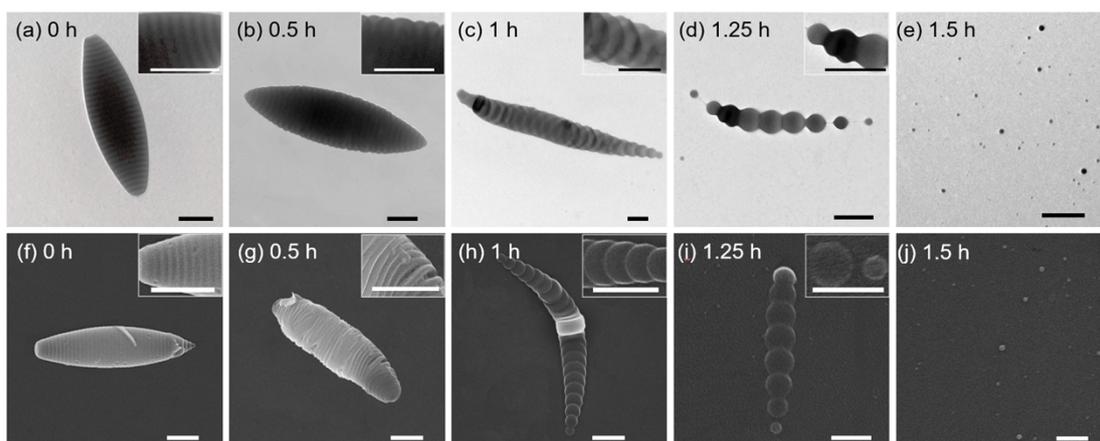


Fig S9. (a-e) TEM and (f-j) SEM images showing the PS-*b*-P2VP(Azo4Br)_{0.4} particles irradiated by 365nm UV light for different times: (a, f) 0, (b, g) 0.5, (c, h) 1, (d, i) 1.25, and (e, j) 1.0 h. Scale bar: 500 nm. The P2VP domains are stained by I₂ vapor for TEM observation.

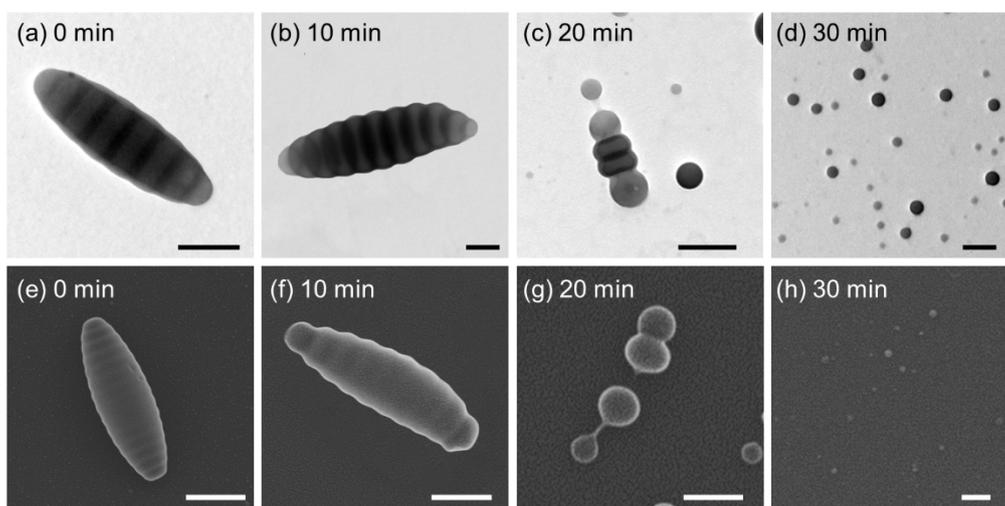


Fig S10. (a-d) TEM and (e-h) SEM images showing the PS-*b*-P2VP(Azo8Br)_{0.4} particles irradiated by 365nm UV light for different times: (a, e) 0, (b, f) 10, (c, g) 20, and (d, h) 30 min. Scale bar: 200 nm. The P2VP domains are stained by I₂ vapor for TEM observation.

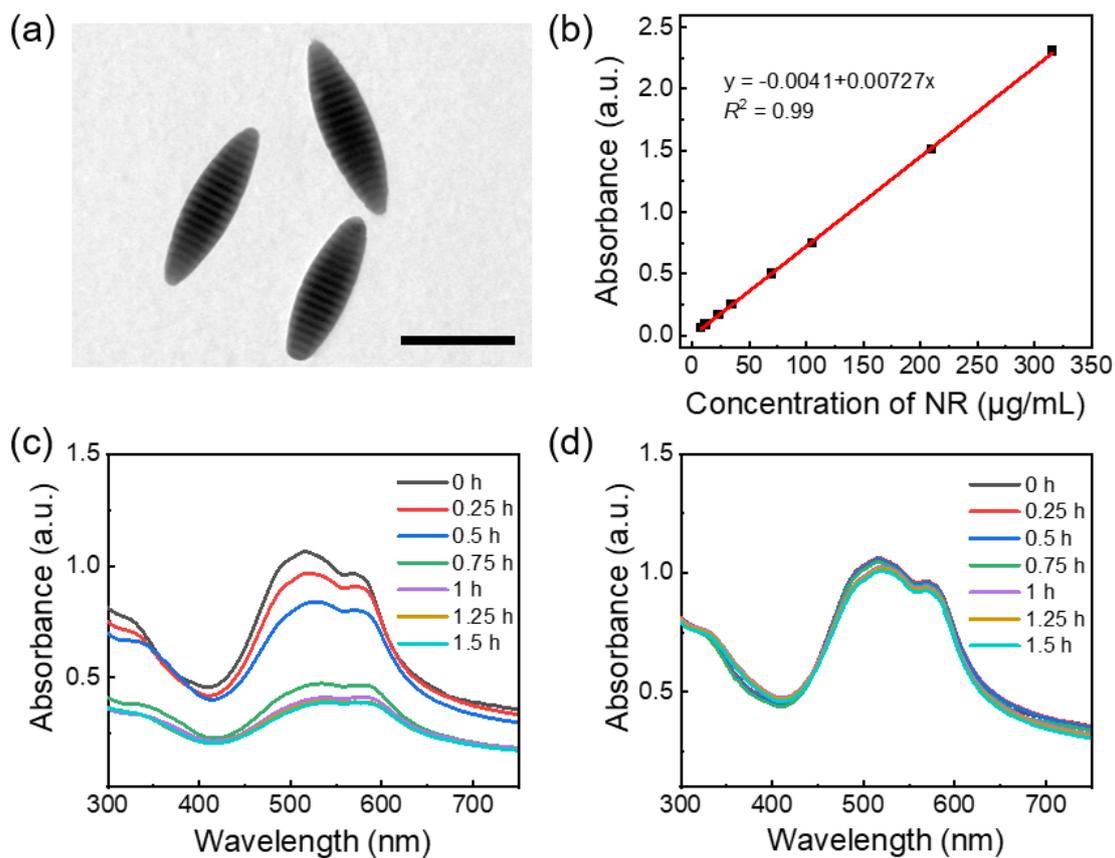


Fig S11. (a) TEM image of the NR-loaded BCPs, (b) calibration curve of maximum absorption intensity (at 530 nm) against the different concentrations of NR in BCP solution, absorption spectra of of NR-loaded BCP particles (c) under UV and (d) without light irradiation. Scale bar: 1.0 μm . The P2VP domains are stained by I_2 vapor for TEM observation.

4. References

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