

Supplementary Information

Oxidation and temperature dual responsive polymers based on phenylboronic acid and *N*-isopropylacrylamide motifs

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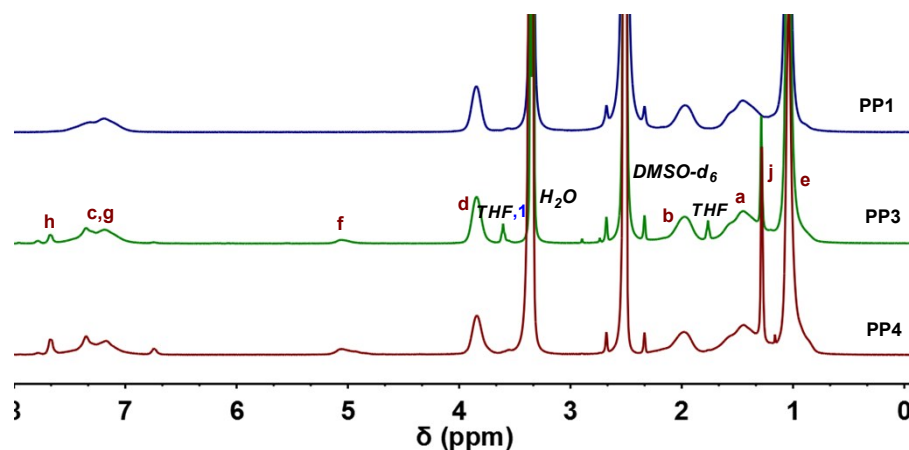


Fig. S1 ¹H NMR spectra of PP1, PP3 and PP4 in DMSO-*d*₆. Molar ratio of M1 to M2 in copolymers PP1 to PP4 is calculated by comparing the integration intensities of peak d (~3.8 ppm) to peak f (~5.0 ppm).

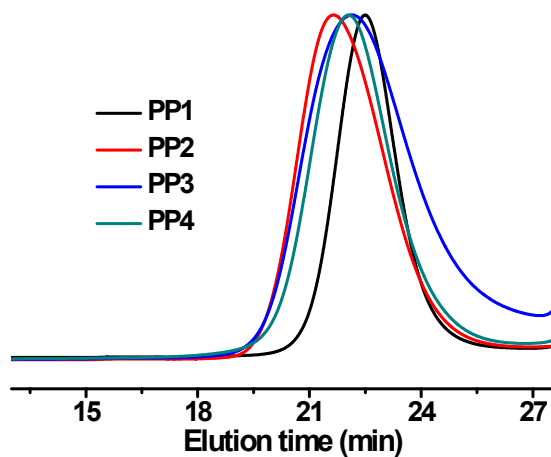


Fig. S2 GPC curves of PP1–PP4 with THF as the eluent.

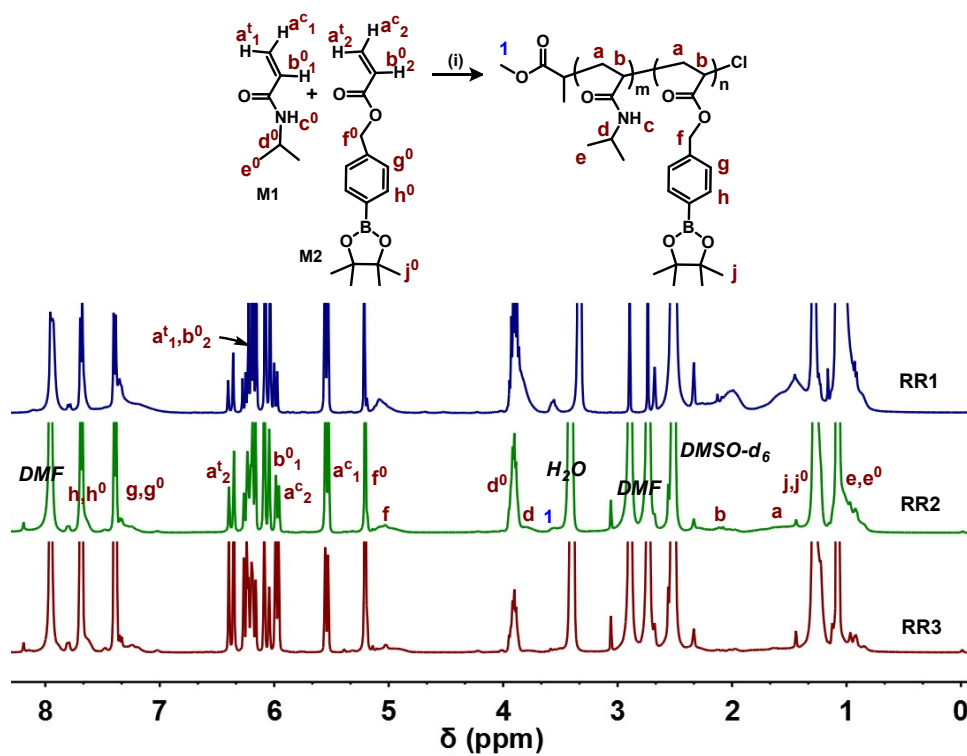


Fig. S3 *In situ* ^1H NMR spectra of polymerization mixture in $\text{DMSO-}d_6$. (i) MCP, CuCl, Me_6TREN , DMF, $60\text{ }^\circ\text{C}$, 24 h.

$$\text{Formula: } \log \frac{c(M_1)}{c(M_1)_0} = \frac{r_1}{1-r_1} \log \frac{c(M_1)_0 c(M_2)}{c(M_2)_0 c(M_1)} - \frac{1-r_1 r_2}{(1-r_1)(1-r_2)} \log \frac{(r_2-1) \frac{c(M_2)}{c(M_1)} - r_1 + 1}{(r_2-1) \frac{c(M_2)_0}{c(M_1)_0} - r_1 + 1}$$

Table S1. Estimation of the Reactivity Ratios of Monomers ^a

Run	M1/M2 in feed ratio	Conversion(%) ^b	
		M1	M2
RR1	90/10	39.0	43.0
RR2	70/30	14.3	18.5
RR3	50/50	15.0	14.0

^a Reactions were performed in DMF at 60 °C, $[M]_0 = 40$ wt %, $[M]:[MCP]:[CuCl]:[Me_6TREN] = 100:0.5:1:1$. ^b Their conversion was calculated by the formula: $\alpha_{M1} = (I_{d+d0} - I_{a^c1})/I_{d+d0} \times 100\%$, $\alpha_{M2} = (I_{f+f0} - 2I_{a^c2})/I_{f+f0} \times 100\%$, respectively.

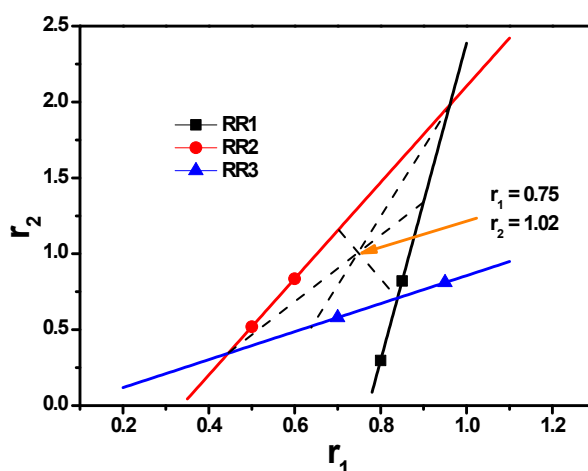
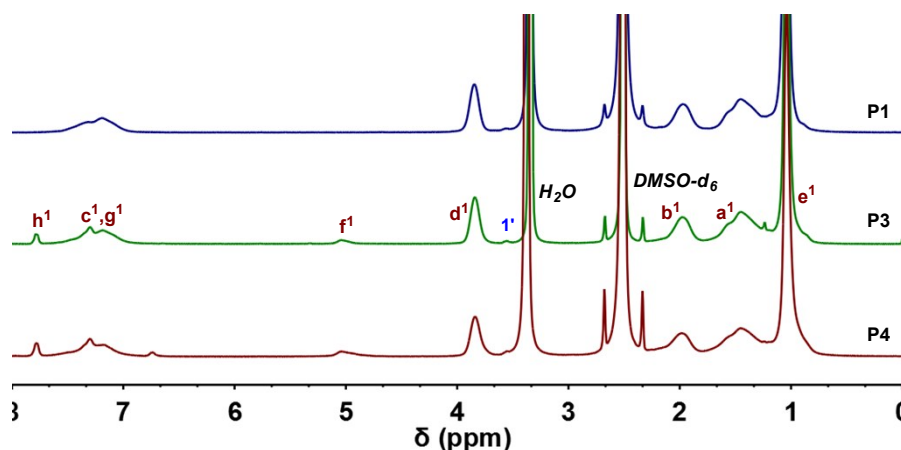
**Fig. S4** Monomer reactivity ratios estimated by Mayo-Lewis method.

Fig. S5 ¹H NMR spectra of **P1**, **P3** and **P4** (without pinacol ester) in DMSO-*d*₆. Molar ratio of **M1** to **M2** in copolymers **P1** to **P4** is calculated by comparing the integration intensities of peak **d**¹ (~3.8 ppm) to peak **f**¹ (~5.0 ppm). Their DP was calculated by the formula: $DP = (6I_{d^1} + 3I_{f^1})/(2I_{1'})$, where I_{d^1} , I_{f^1} and $I_{1'}$ denote the integration intensity of peak **d**¹ (~3.8 ppm), peak **f**¹ (~5.0 ppm) and peak **1**['] (~3.6 ppm), respectively.

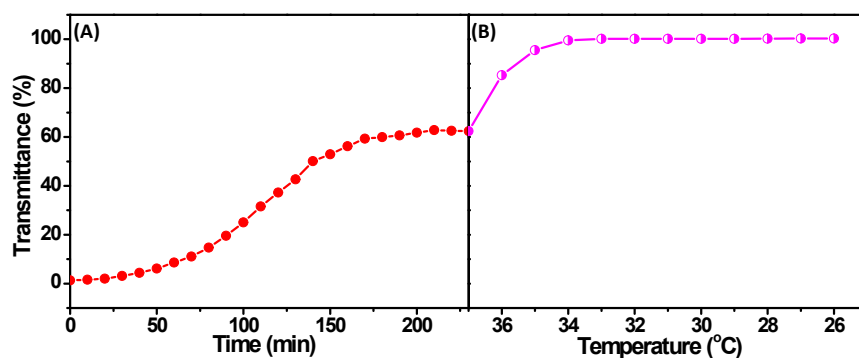


Fig. S6 (A) Plots of transmittance vs oxidation time of copolymer **P2** (1.0 mg/mL) in 50 mM PB solution (pH 7.4) with H_2O_2 (10 mM) at 37 °C. (B) Plots of transmittance vs temperature for the completely decomposed **P2** in the same buffer solution.

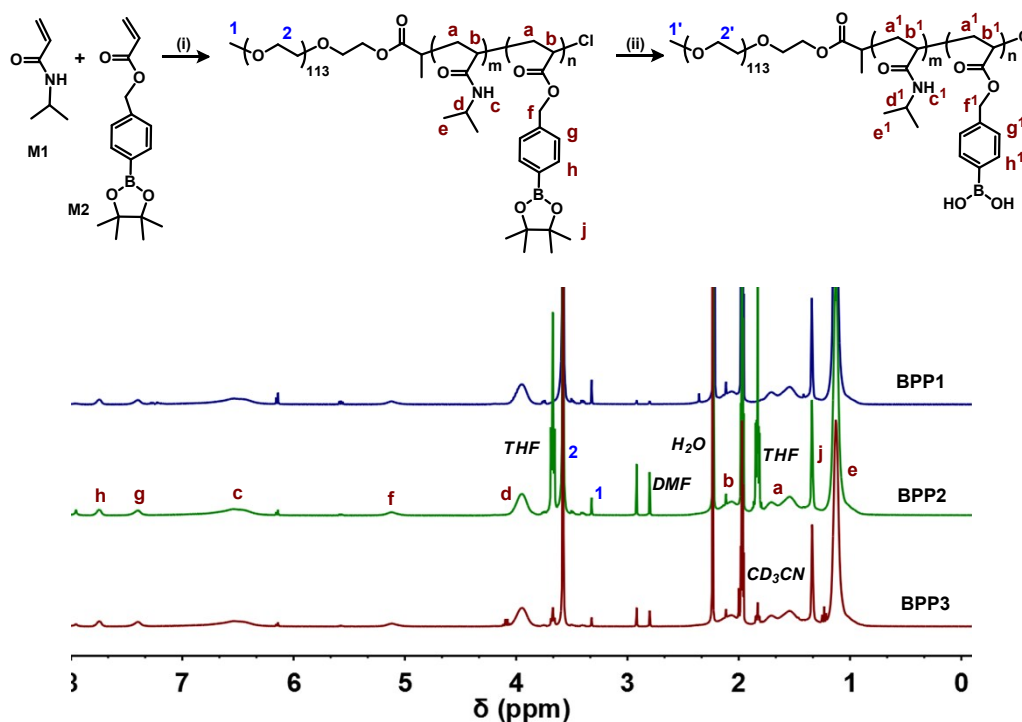


Fig. S7 ^1H NMR spectra of **BPP1–BPP3** (with pinacol ester) in CD_3CN . Molar ratio of **M1** to **M2** in copolymers **BPP1** to **BPP4** is calculated by comparing the integration intensities of peak d (~3.9 ppm) to peak f (~5.1 ppm).

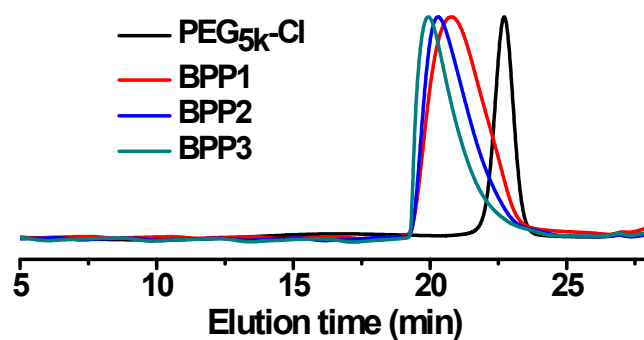


Fig. S8 GPC curves of BPP1–BPP3 (with pinacol ester) and mPEG₁₁₃-Cl.

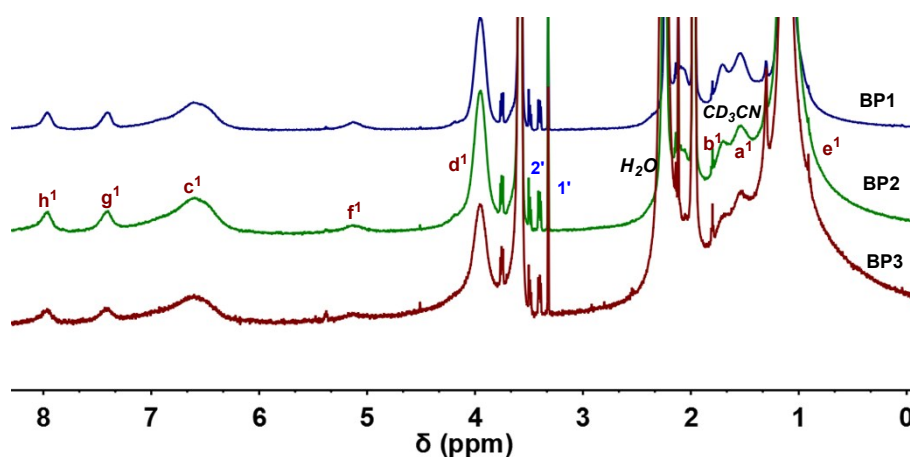


Fig. S9 ¹H NMR spectra of BP1–BP3 (without pinacol ester) in CD₃CN. Molar ratio of M1 to M2 in copolymers BP1 to BP4 is calculated by comparing the integration intensities of peak d¹ (~3.9 ppm) to peak f¹ (~5.1 ppm). Their DP was calculated by the formula: $DP = (6I_{d^1} + 3I_{f^1}) / (2I_{1'})$, where I_{d^1} , I_{f^1} and $I_{1'}$ denote the integration intensity of peak d¹ (~3.9 ppm), peak f¹ (~5.1 ppm) and peak 1' (~3.3 ppm), respectively.

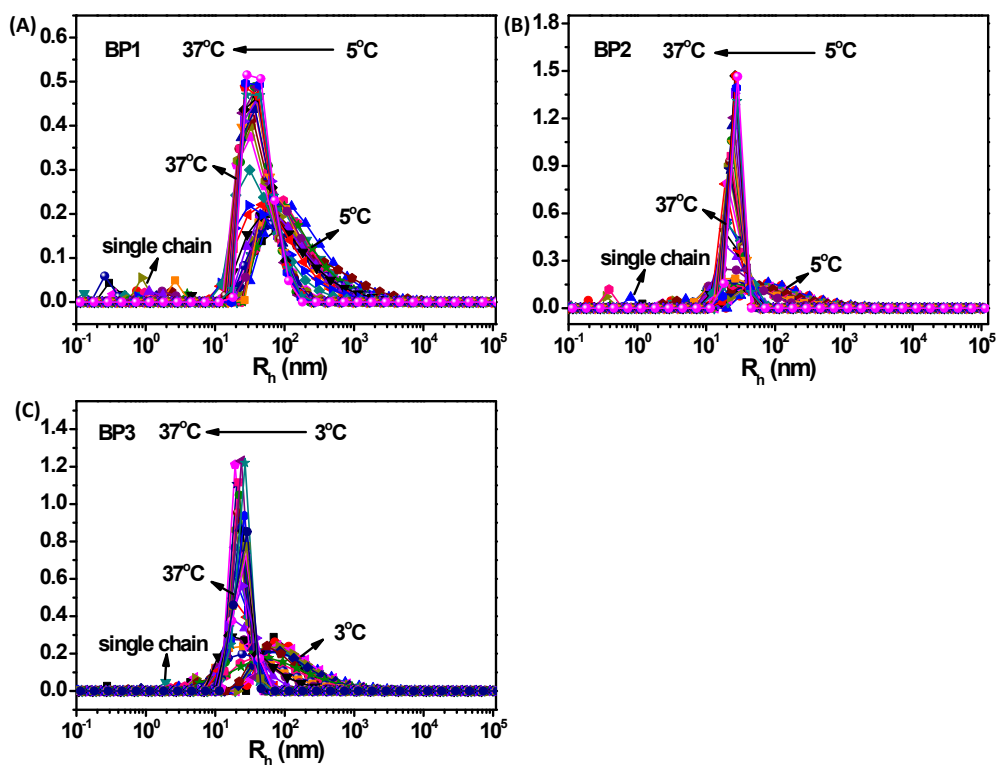


Fig. S10 CONTIN analyses of **BP1–BP3** nanoparticles (0.1 mg/mL) in 50 mM PB solution (pH 7.4) at various temperatures with the slow heating procedure. Detection angle: 90°.

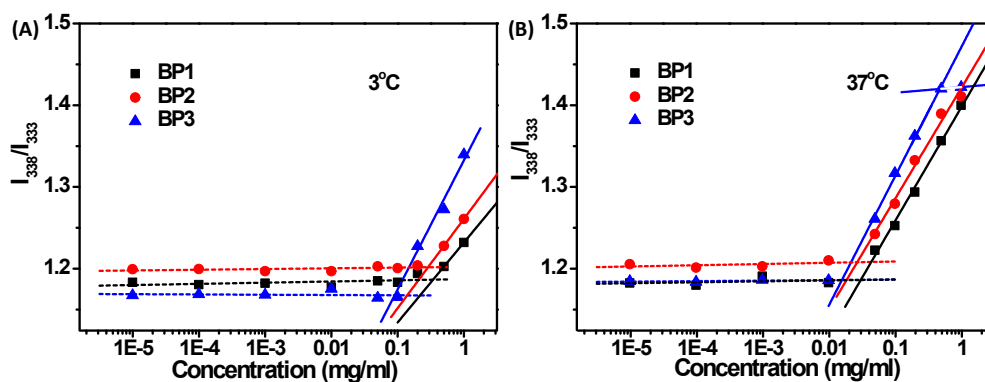


Fig. S11 Relationship between I_{338}/I_{333} ratio of pyrene and the concentration of **BP** copolymers at (A) 3 °C and (B) 37 °C. Pyrene was dissolved (or dispersed) in **BP1–BP3** aqueous solution with the concentration of 1.0×10^{-6} mM.

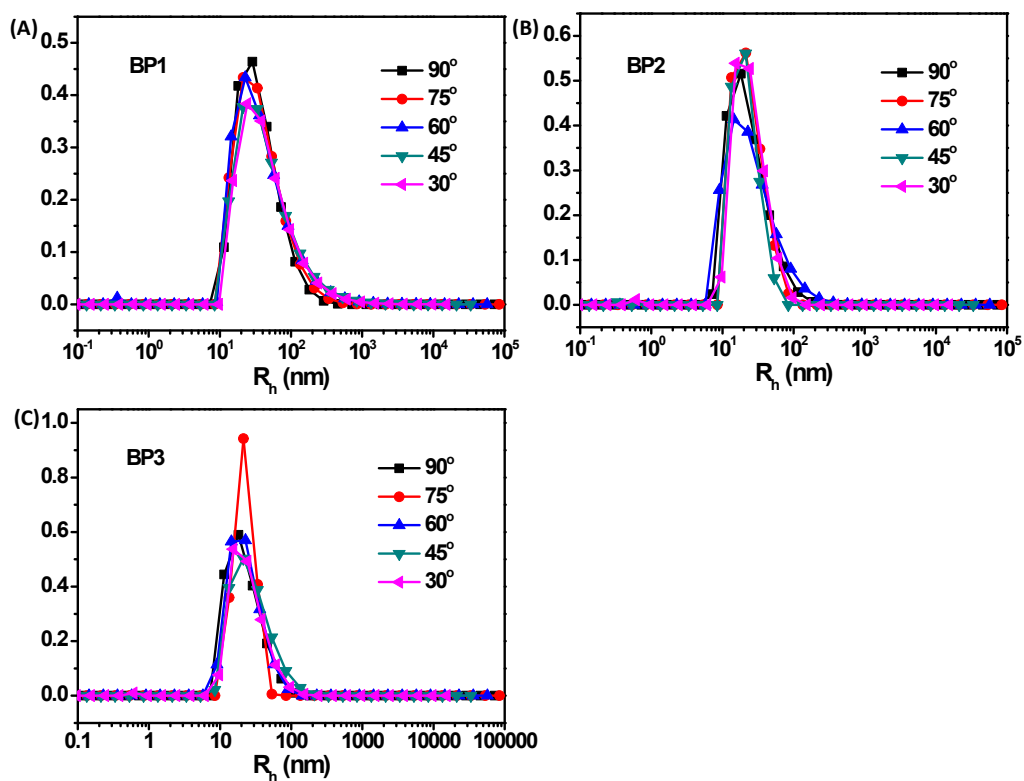


Fig. S12 Size distribution of BP1–BP3 nanoparticles (0.1 mg/mL) in 50 mM PB solution (pH 7.4) at 37 °C. The nanoparticles were prepared by the fast heating process.

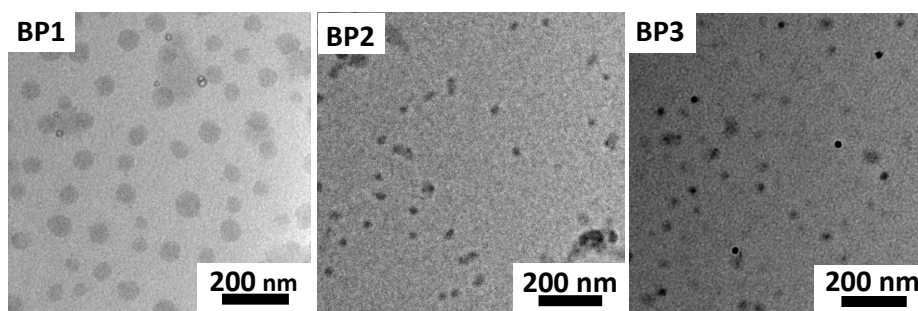


Fig. S13 TEM photographs of BP1–BP3 nanoparticles (0.1 mg/mL) formed in 50 mM PB solution (pH 7.4) at 37 °C.

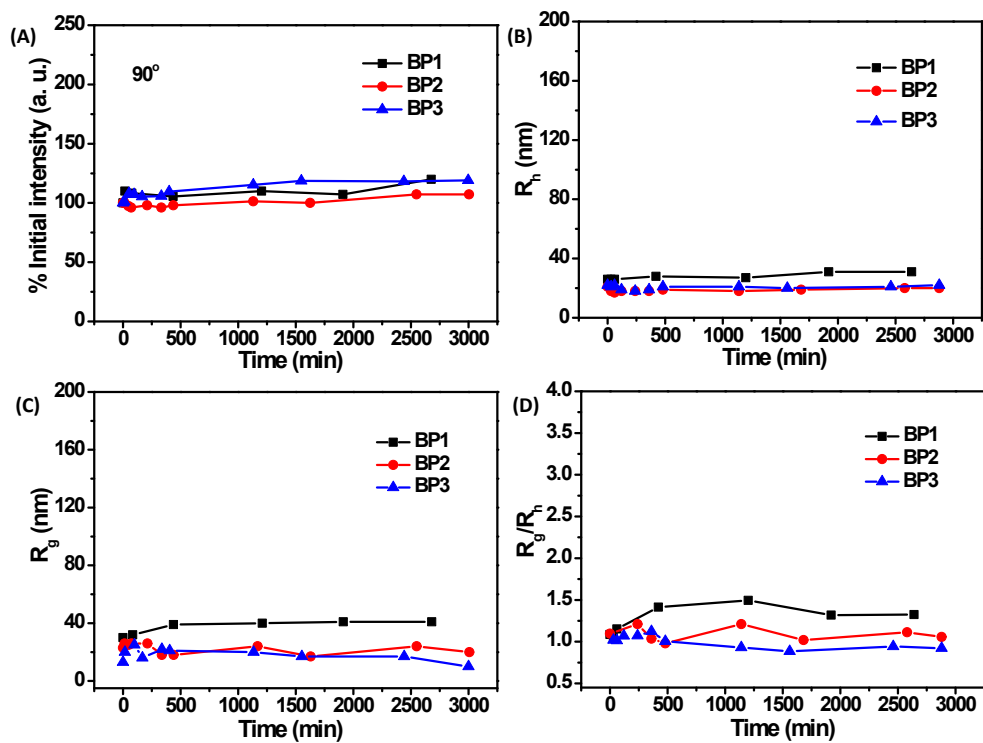


Fig. S14 (A) excess scattered intensity, (B) R_h , (C) R_g , and (D) R_g/R_h of **BP1–BP3** nanoparticles (0.1 mg/mL) in 50 mM PB solution (pH 7.4) incubated for different times at 37 °C, without H₂O₂.

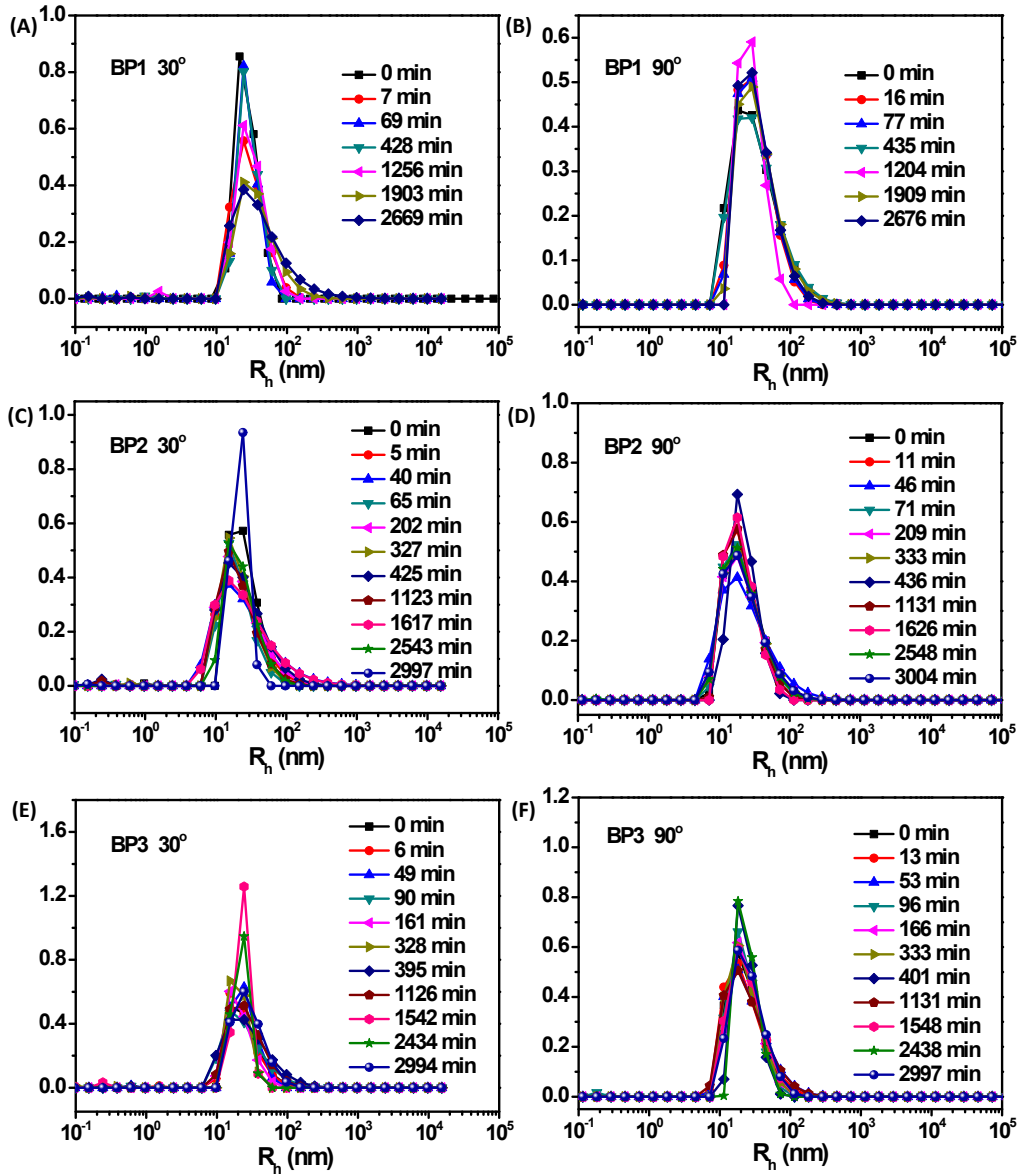


Fig. S15 CONTIN analyses of **BP1–BP3** (0.1 mg/mL) nanoparticles in 50 mM PB solution (pH 7.4) incubated for different times at 37 °C, without H₂O₂. Detection angle: 30° and 90°.

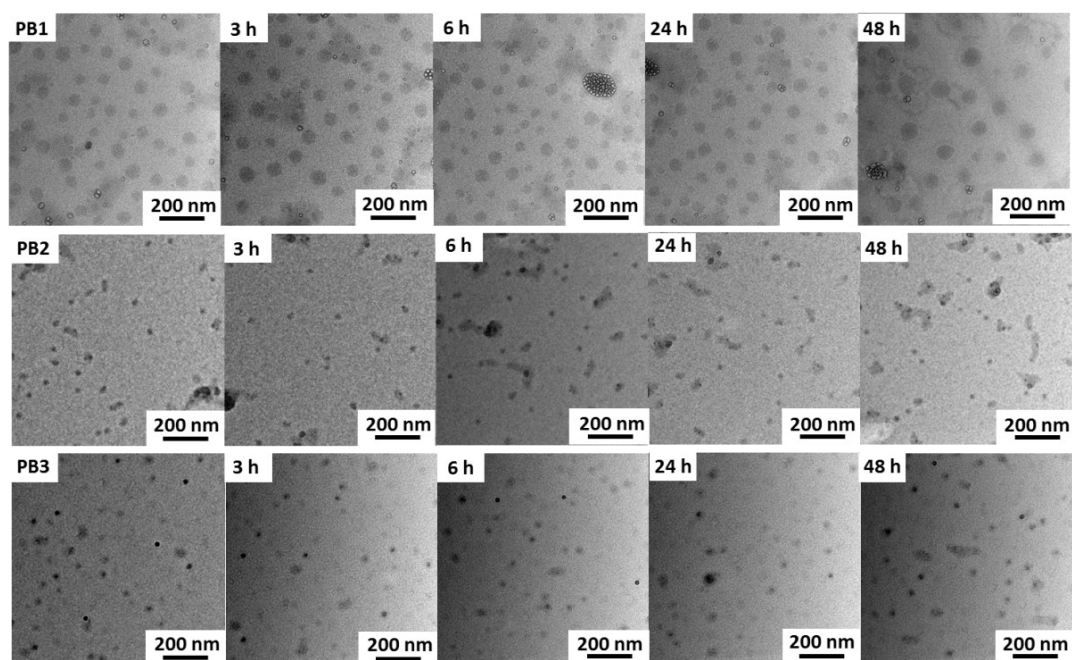


Fig. S16. TEM photographs of **BP1–BP3** nanoparticles (0.1 mg/mL) formed in 50 mM PB solution (pH 7.4) and incubated for various times at 37 °C, without H₂O₂.

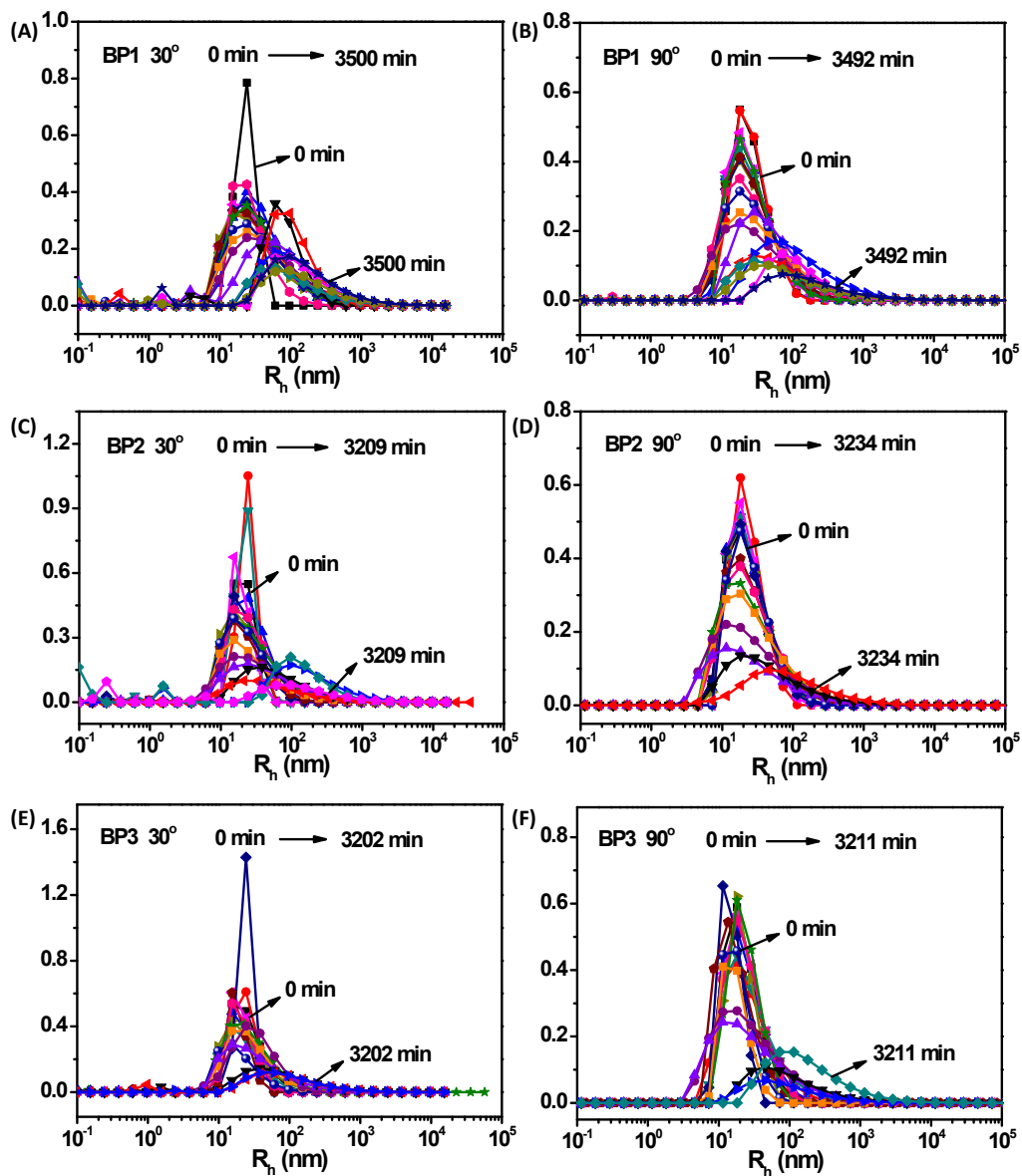


Fig. S17 CONTIN analyses of **BP1–BP3** (0.1 mg/mL) nanoparticles in 50 mM PB solution (pH 7.4) incubated for different times at 37 °C, with 0.5 mM H₂O₂ at 37 °C. Detection angle: 30° and 90°.

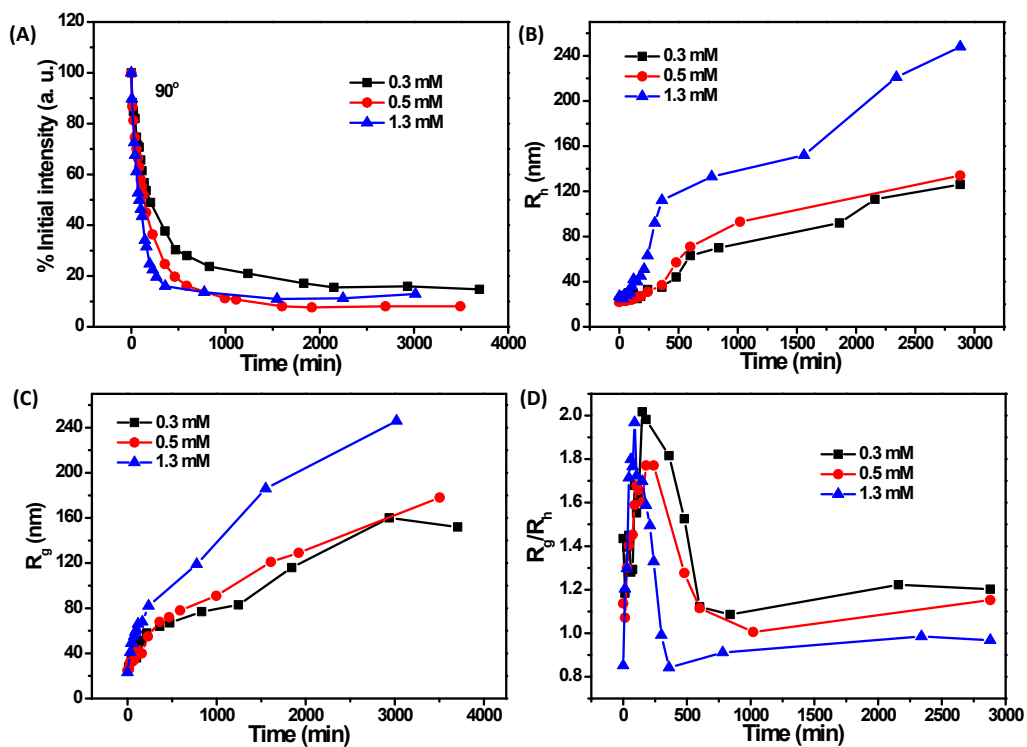


Fig. S18 (A) excess scattered intensity, (B) R_h , (C) R_g , and (D) R_g/R_h of **BPI** nanoparticles (0.1 mg/mL) in PB solution (50 mM, pH 7.4) incubated for different times at 37 °C, with different concentrations of H₂O₂, 37 °C.

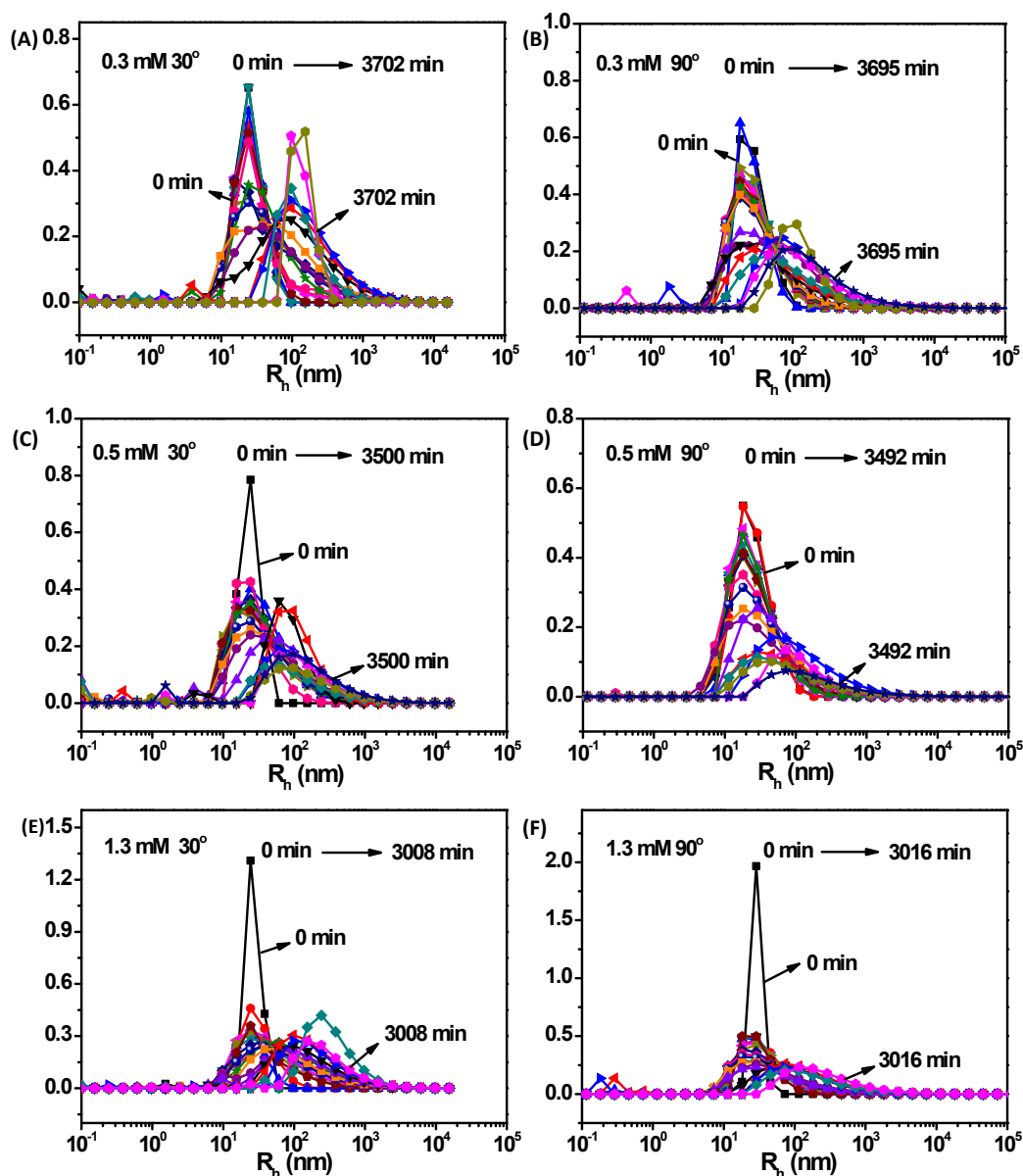


Fig. S19 CONTIN analyses of of **BPI** nanoparticles (0.1 mg/mL) in PB solution (50 mM, pH 7.4) incubated for different times at 37 °C, with different concentrations of H₂O₂, 37 °C. Detection angle: 30° and 90°.

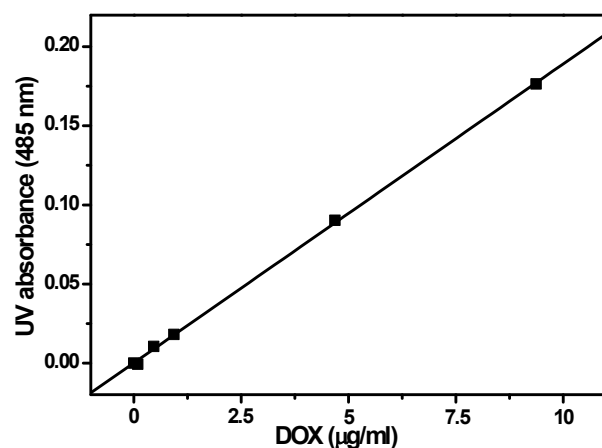


Fig. S20 The calibration curve of DOX in 10 mM PB solution (pH 7.4).

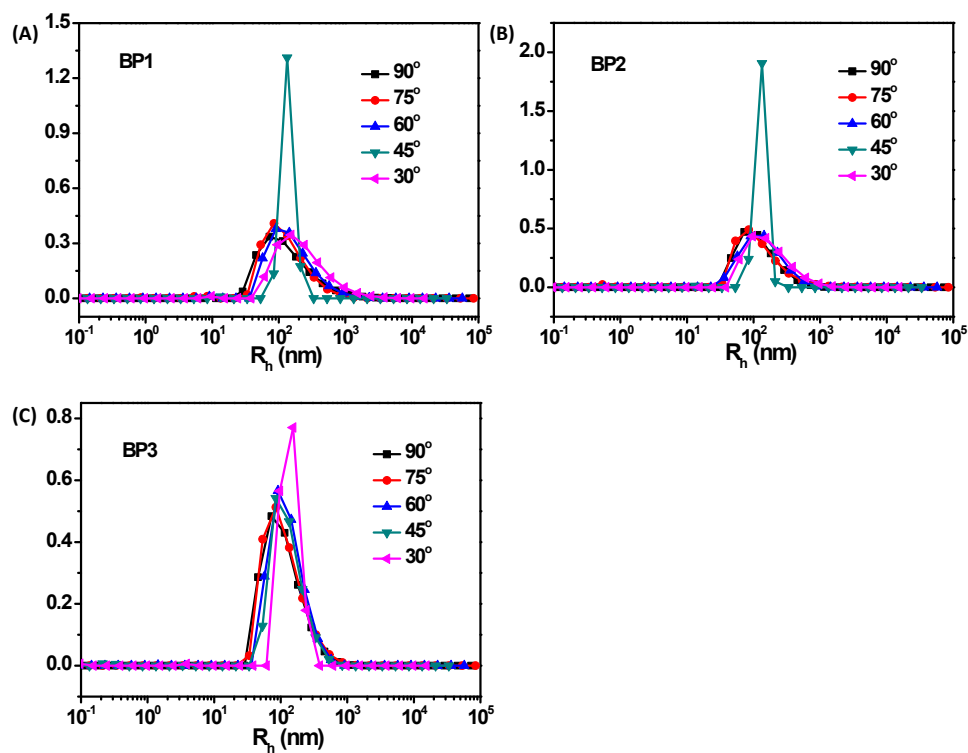


Fig. S21 Size distribution of the DOX-loaded **BP1–BP3** nanoparticles (0.1 mg/mL) in 10 mM PB solution (pH 7.4) at 37 °C.

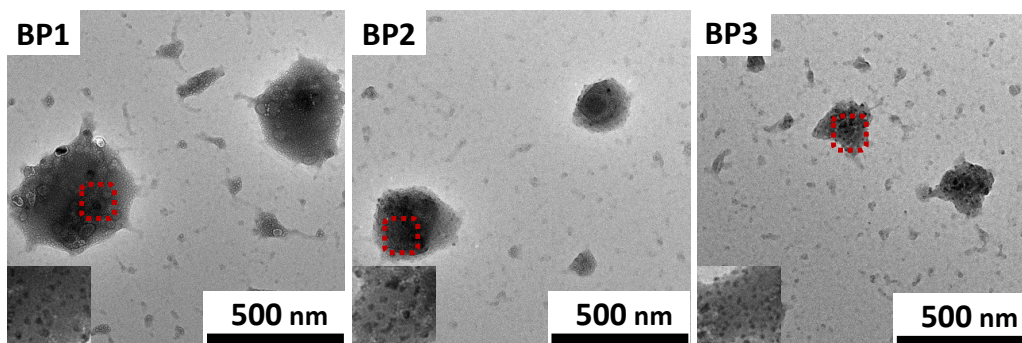


Fig. S22 TEM photographs of the DOX-loaded **BP1–BP3** nanoparticles (0.1 mg/mL) formed in 50 mM PB solution (pH 7.4) at 37 °C.

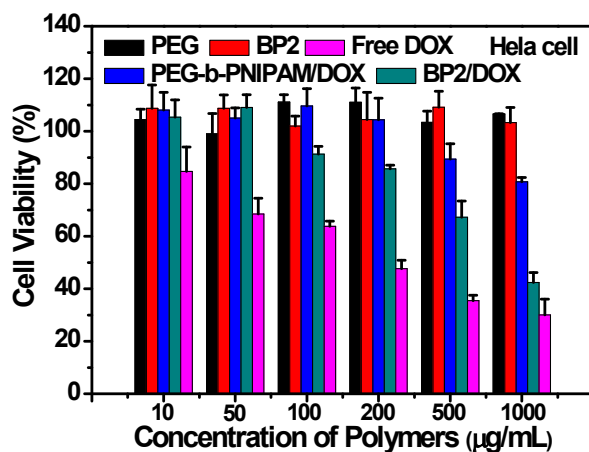


Fig. S23 Cell viability of HeLa cells measured by CCK-8 assay at 37 °C. The DOX-loading contents of the drug-loaded **BP2** and PEG-*b*-PNIPAM nanoparticles were 3.0 wt% and 3.3 wt%, respectively. The concentrations of DOX are 0.3, 1.5, 3.0, 6.0, 15 and 30 µg/mL, respectively.