Supporting information

Self-assembled Micelles of PEG-Poly(Disulfide Carbamate Amine) Copolymers for Intracellular Dual-Responsive Drug Delivery

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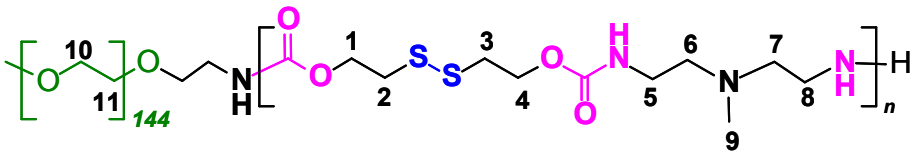
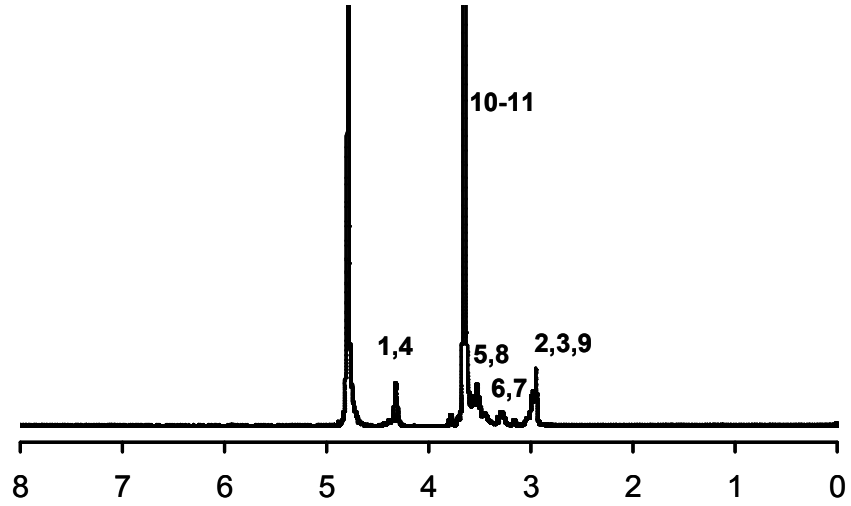
1. ^{1}H NMR spectra of PEG-SSPUA copolymers

a) PEG-SSMDE

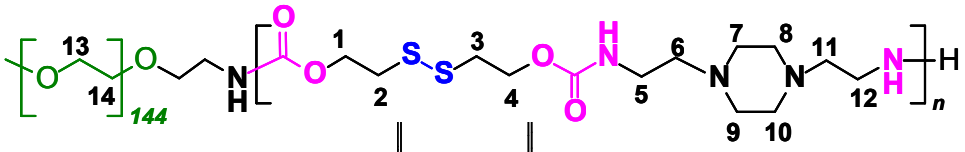
^{1}H NMR (D_2O) δ (ppm)= 4.33 ($SSCH_2C\mathbf{H}_2$); 3.65 ($C\mathbf{H}_2C\mathbf{H}_2O$); 3.55 ($OCONHC\mathbf{H}_2$); 3.38 ($C\mathbf{H}_2N(CH_3)C\mathbf{H}_2$); 3.00 ($CH_2N(C\mathbf{H}_3)CH_2$); 2.95 ($SSC\mathbf{H}_2CH_2$).

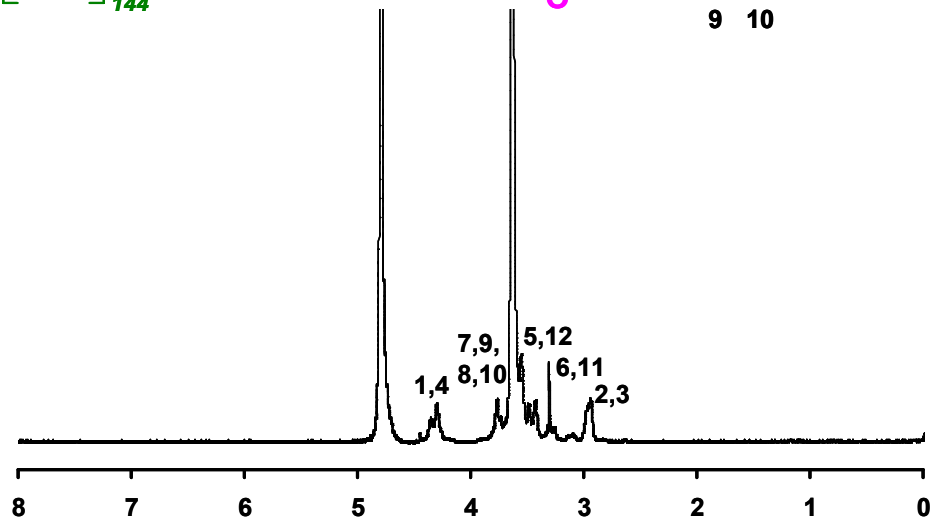




b) PEG-SSPDA

^{1}H NMR (D_2O) δ (ppm)= 4.32 ($SSCH_2C\mathbf{H}_2$); 3.76 ($NC\mathbf{H}_2C\mathbf{H}_2N$); 3.65 ($C\mathbf{H}_2C\mathbf{H}_2O$); 3.57 ($OCONHC\mathbf{H}_2$); 3.45 ($OCONHCH_2C\mathbf{H}_2$); 2.97 ($SSC\mathbf{H}_2CH_2$).





c) PEG-SSBAP

^{1}H NMR (D_2O, ppm): δ 4.30 ($SSCH_2C\mathbf{H}_2$), 3.65 ($C\mathbf{H}_2C\mathbf{H}_2O$); 3.4-4.0 ($NC\mathbf{H}_2C\mathbf{H}_2N$), 3.31 ($OCONHC\mathbf{H}_2$), 3.21 ($OCONHCH_2C\mathbf{H}_2$), 2.95 ($SSC\mathbf{H}_2CH_2$,), 1.95 ($CH_2C\mathbf{H}_2CH_2$).

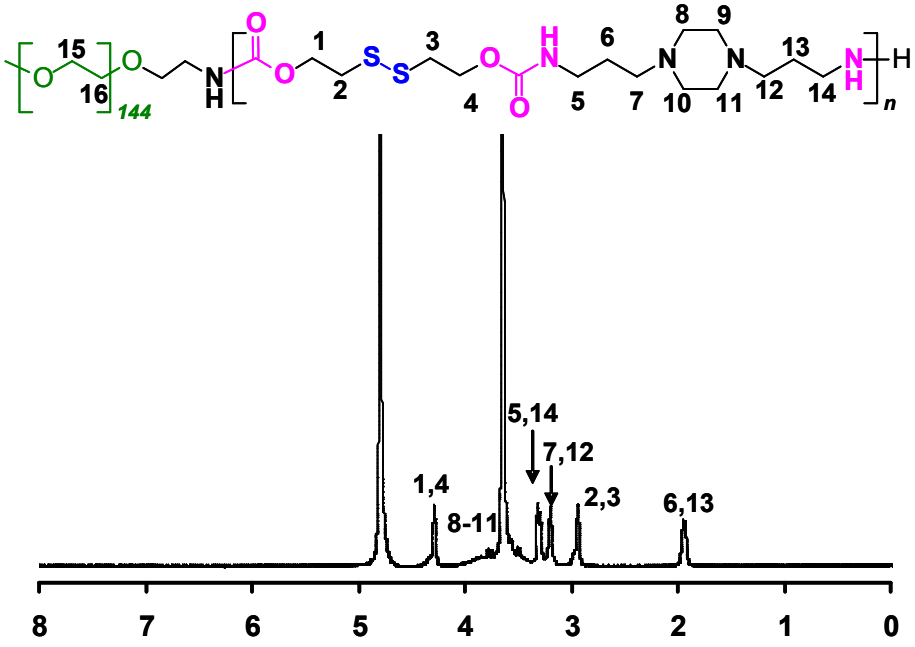


Figure S1. ^{1}H NMR spectra analysis of PEG-SSPCA copolymers. a) PEG-SSMDE; b) PEG-SSPDA; c) PEG-SSBAP.

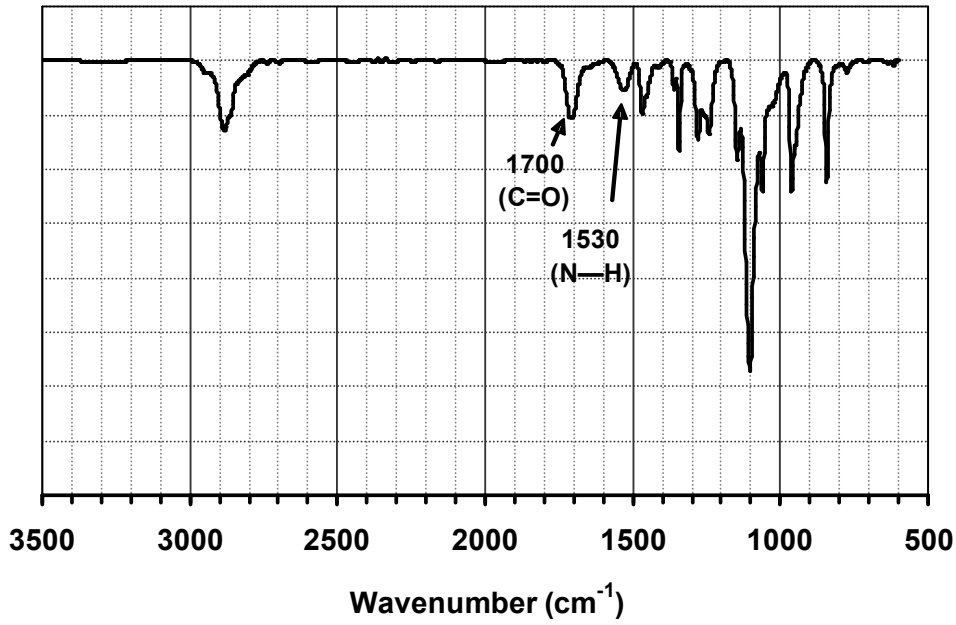


Figure S2. FT-IR spectrum of PEG-SSBAP copolymers showing characteristic peak of carbamate linkage.

3. GPC of PEG-SSPCA copolymers

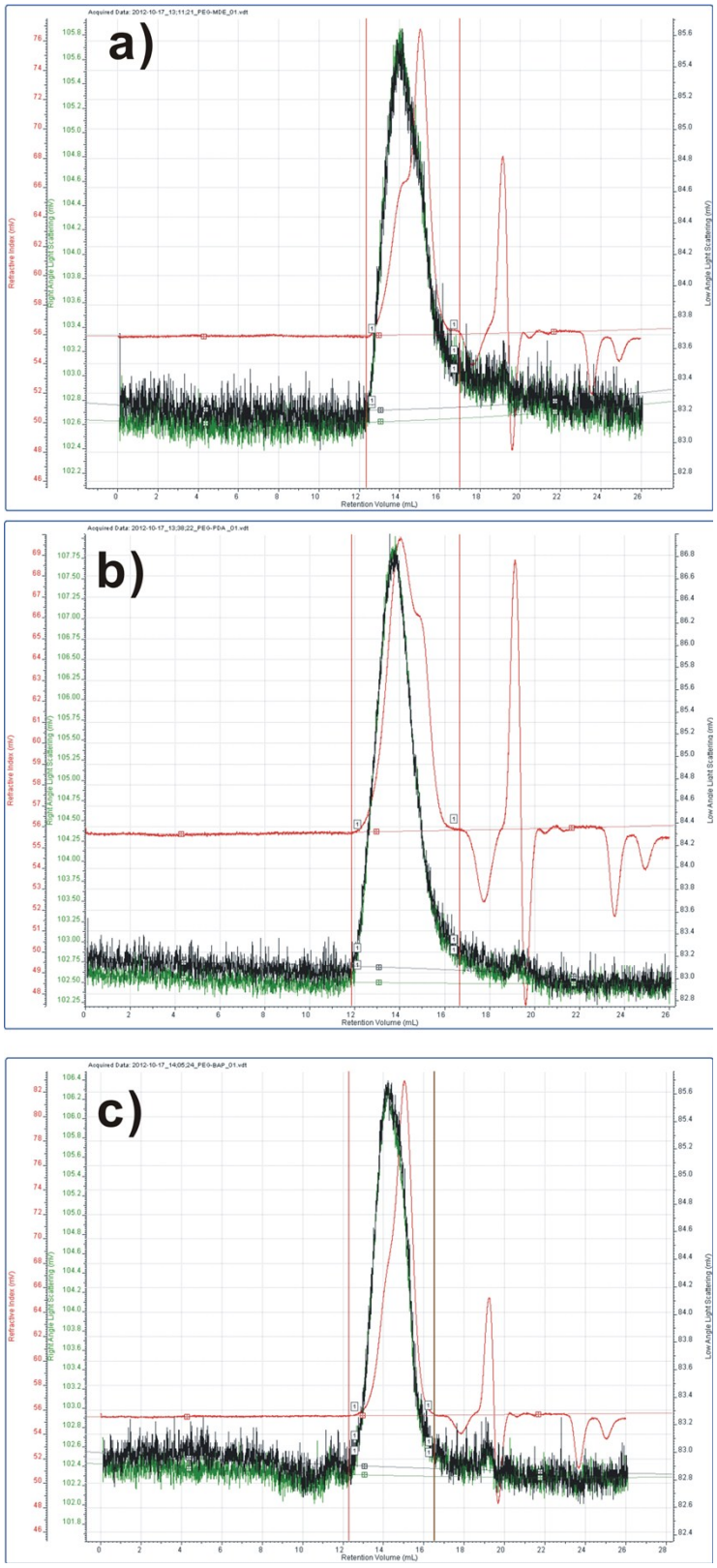


Figure S3. GPC curve of PEG-SSPCA copolymers. a) PEG-SSMDE; b) PEG-SSPDA; c) PEG-SSBAP.

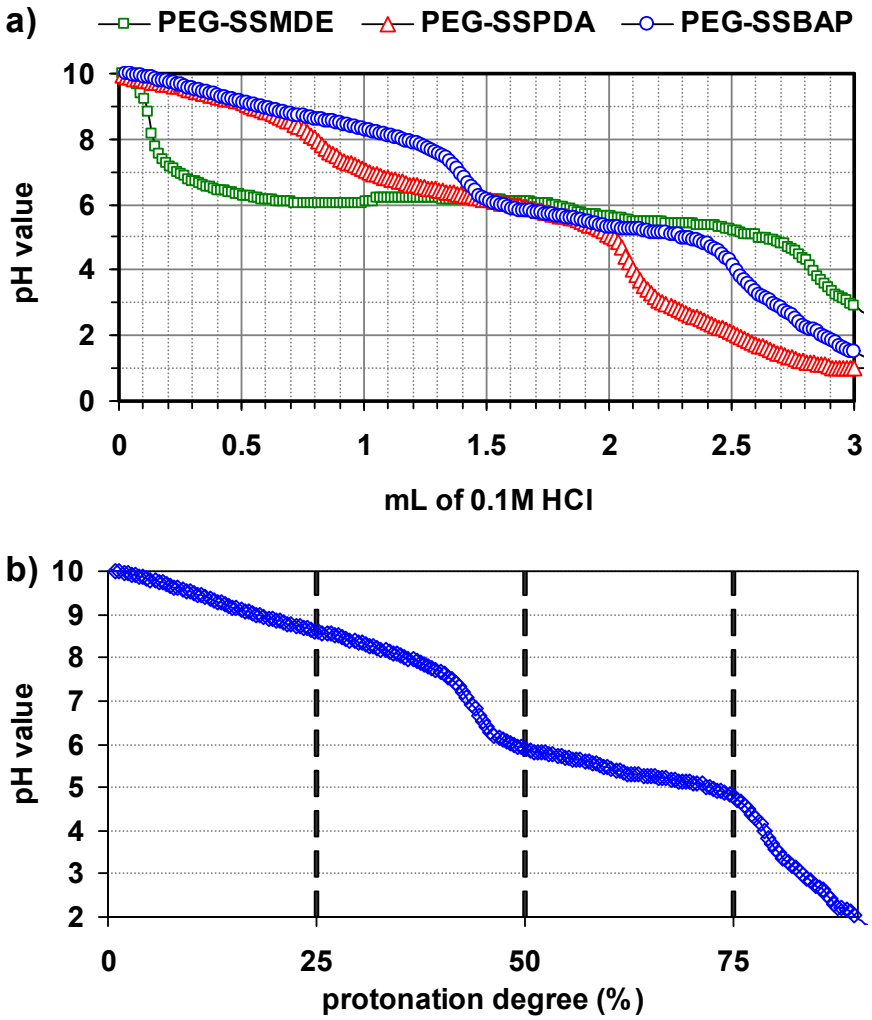


Figure S4. a) Acid-base titration curve of PEG-PCA copolymers; b) Acid-base titration of PEG-SSBAP copolymer gives pH value as the function of apparent protonation degree of tertiary amines in PEG-SSBAP copolymer.

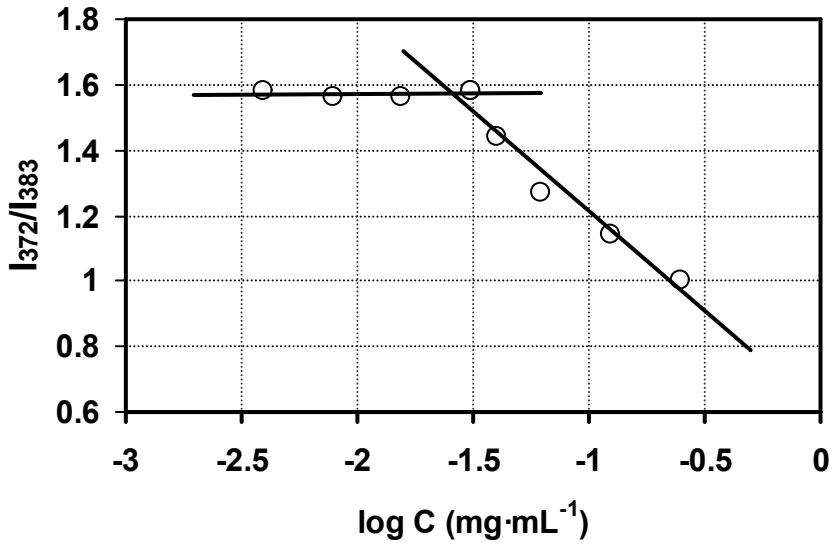


Figure S5. The ratio of fluorescence intensity at 372 and 383 nm (from pyrene excitation spectra) as a function of the concentrations of PEG-SSBAP.

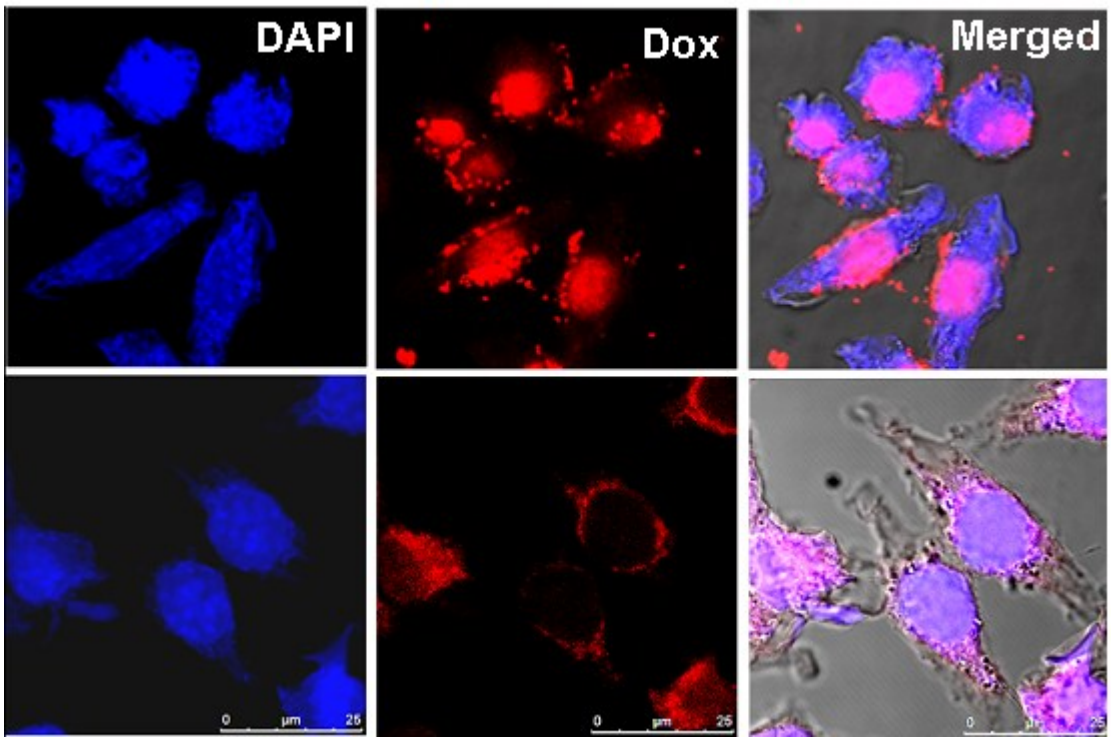


Figure S6. CLSM observation of intracellular distribution of Dox 1 h after incubating free Dox (up) or Dox-loaded PEG-SSBAP micelles (down) with SKOV-3 cells.

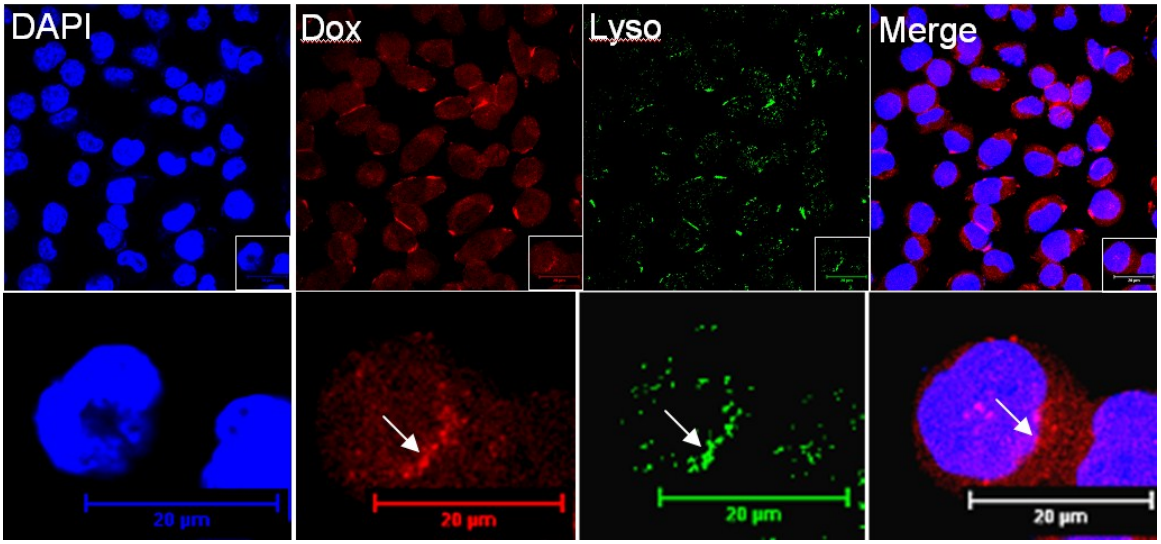


Figure S7. CLSM observation of intracellular location of Dox 4 h after incubating Dox-loaded PEG-SSBAP micelles with MCF-7 cells. This figure indicates Dox-loaded micelles (in red) locate in the lysosomes (in green) stained by LysoTracker green DND26 (Lyso). The cellular nucleus in blue is stained by DAPI. The arrow shows the co-localization of Dox-loaded micelles and lysosome.

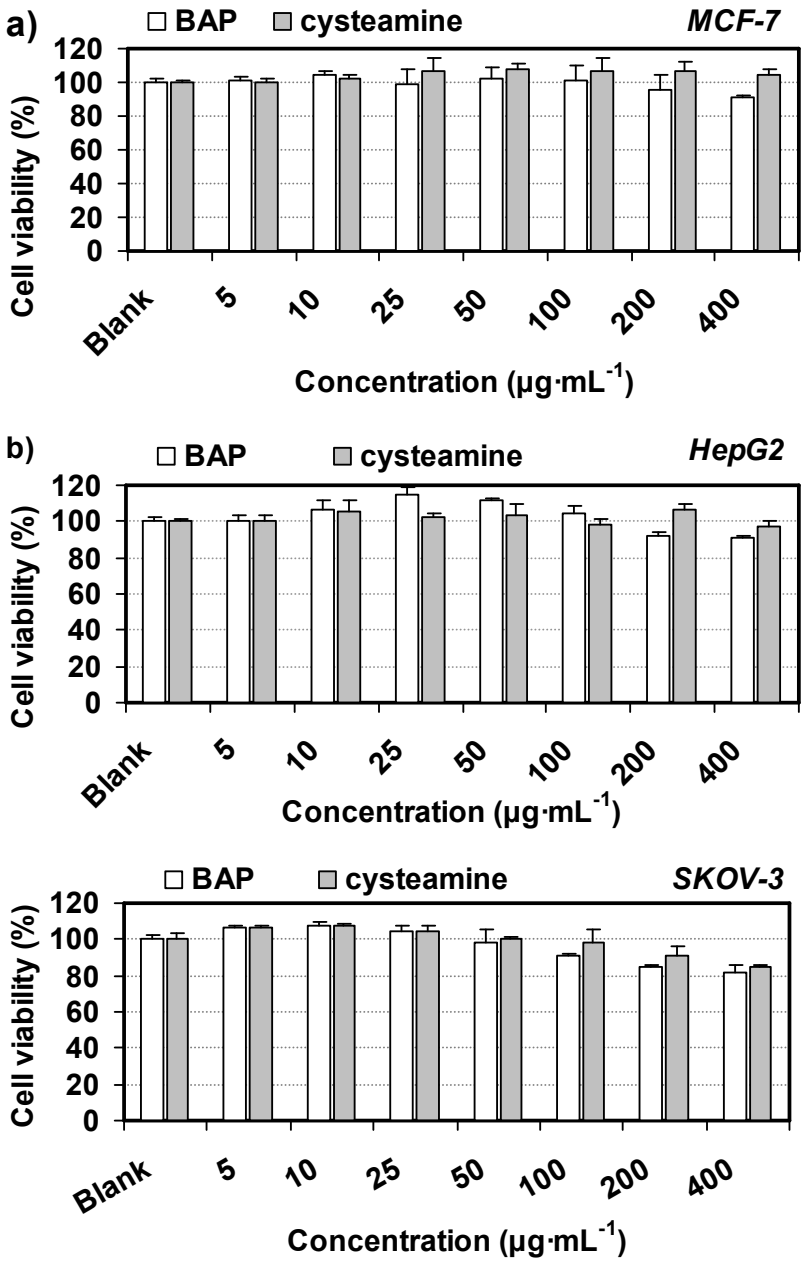


Figure S8. Cytotoxicity of BAP and cysteamine, as degradation products from PEG-SSBAP, at varied concentration from 5 to 400 μg·mL^{-1} against three types of cell lines: a) MCF-7, b) HepG2 and c) SKOV-3 cells. PBS group was used as a blank control and set as 100% cell viability.

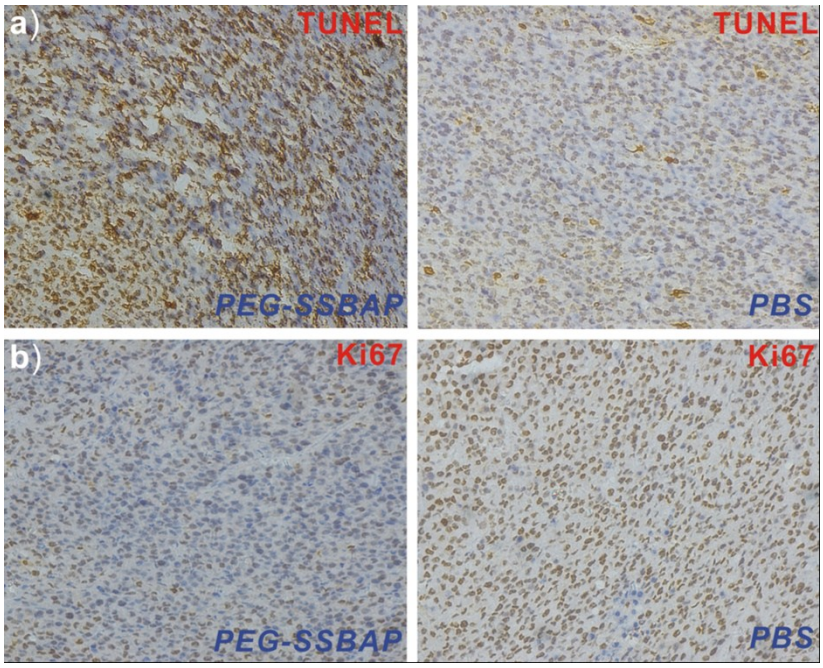


Figure S9. TUNEL (a) and Ki67 (b) staining of tumor section of the mice 28 day after chemotherapy using Dox-loaded PEG-SSBAP micelles. PBS group was used as a positive control.

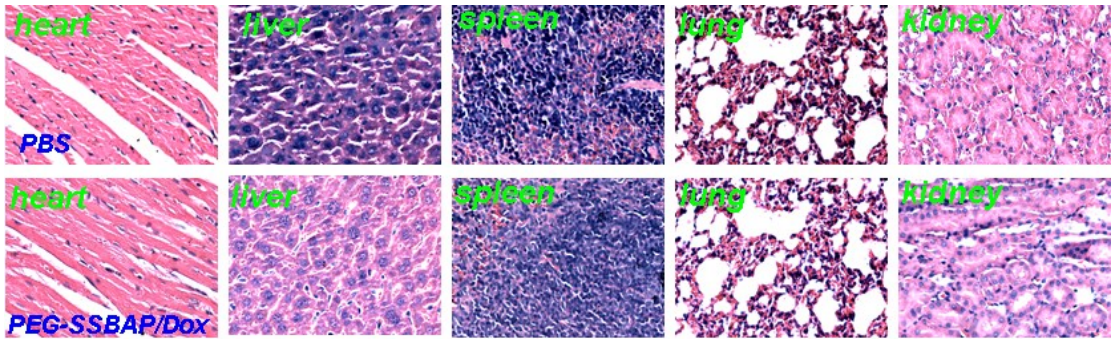


Figure S10. H&E staining of other organ section of the mice 28 day after chemotherapy using Dox-loaded PEG-SSBAP micelles. PBS group was used as a control.