Electronic Supplementary Material (ESI) for Polymer Chemistry.

Room Temperature Synthesis of Poly(poly(ethylene glycol) methyl ether methacrylate)-based Diblock Copolymer Nano-objects via Photoinitiated Polymerization-Induced Self-Assembly (Photo-PISA)

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ADDITIONAL RESULTS

Bioconjugation with Proteins. In this paper, 4-cyano-4-(dodecylsulfanylthiocarbonyl) sulfanylpentanoic acid was used as the RAFT agent. As a result, a certain amount of carboxyl groups were introduced to the surface of vesicles prepared by photo-PISA, which can be used for bioconjugation.

An aliquot of $PPEGMA_{14}$-$PHPMA_{400}$ prepared at 15% w/w was washed twice with 500 μL of MES buffer (pH 5.5, 100 mM), and the sample was redispersed in 400 μL of MES buffer. A solution of EDC and NHS in MES buffer (100 μL, containing 8 mg of EDC and 22 mg of NHS) was added with gentle vortexing for 30 min, then the sample was sedimented by centrifugation and washed twice with 500 μL PBS buffer, and finally dispersed in 500μL PBS buffer. Then a fluorescein-labeled BSA solution (100 μL, 2 mg/mL)[1] was added to the centrifuge tube, and incubated with gentle vortexing for 3 h. The sample was washed three times with PBS buffer.

As a control experiment, we also carried out the bioconjugation protocol as described above without EDC activation.

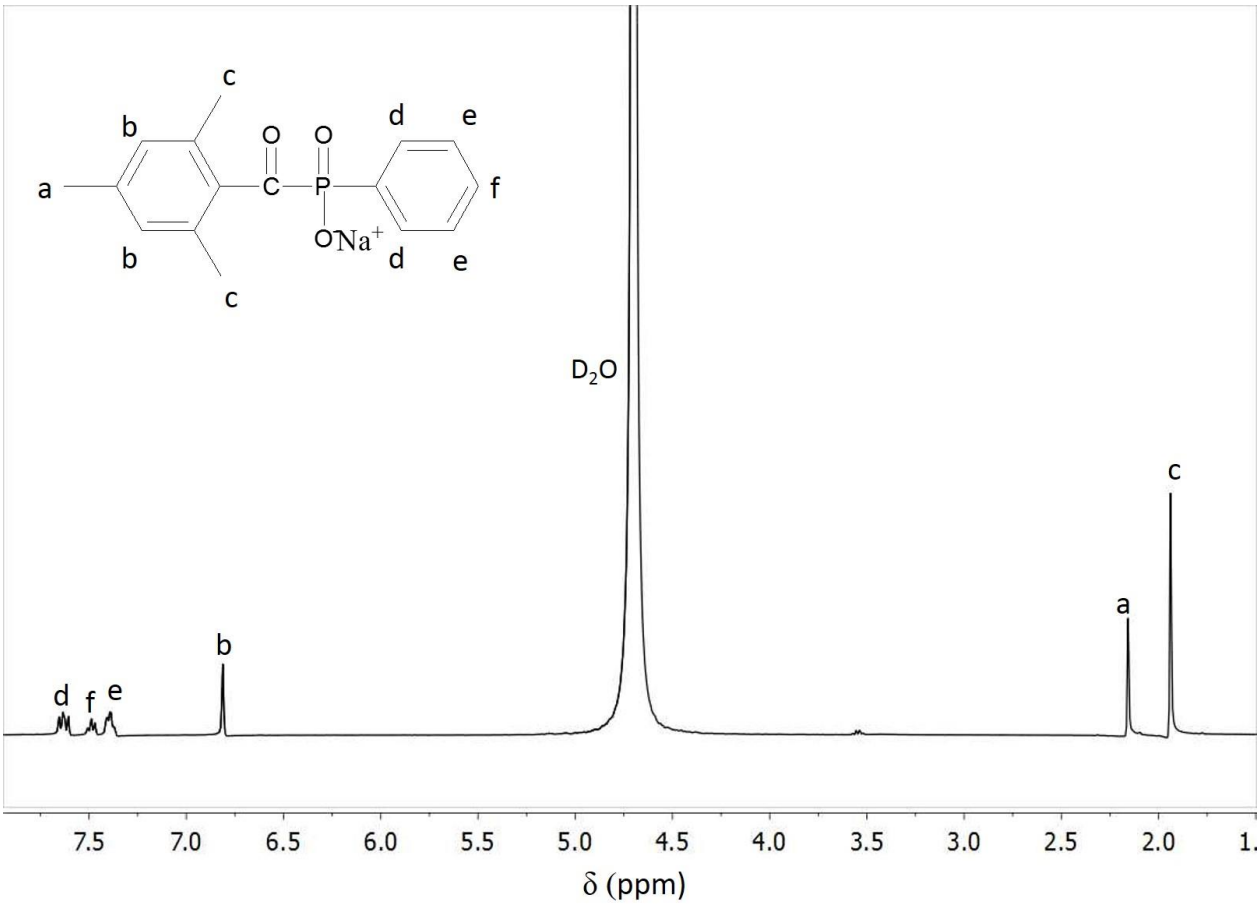

Figure S1. ^{1}H NMR spectrum of sodium phenyl-2, 4, 6-trimethylbenzoylphosphinate (SPTP) in D_2O at 25 ^{o}C.

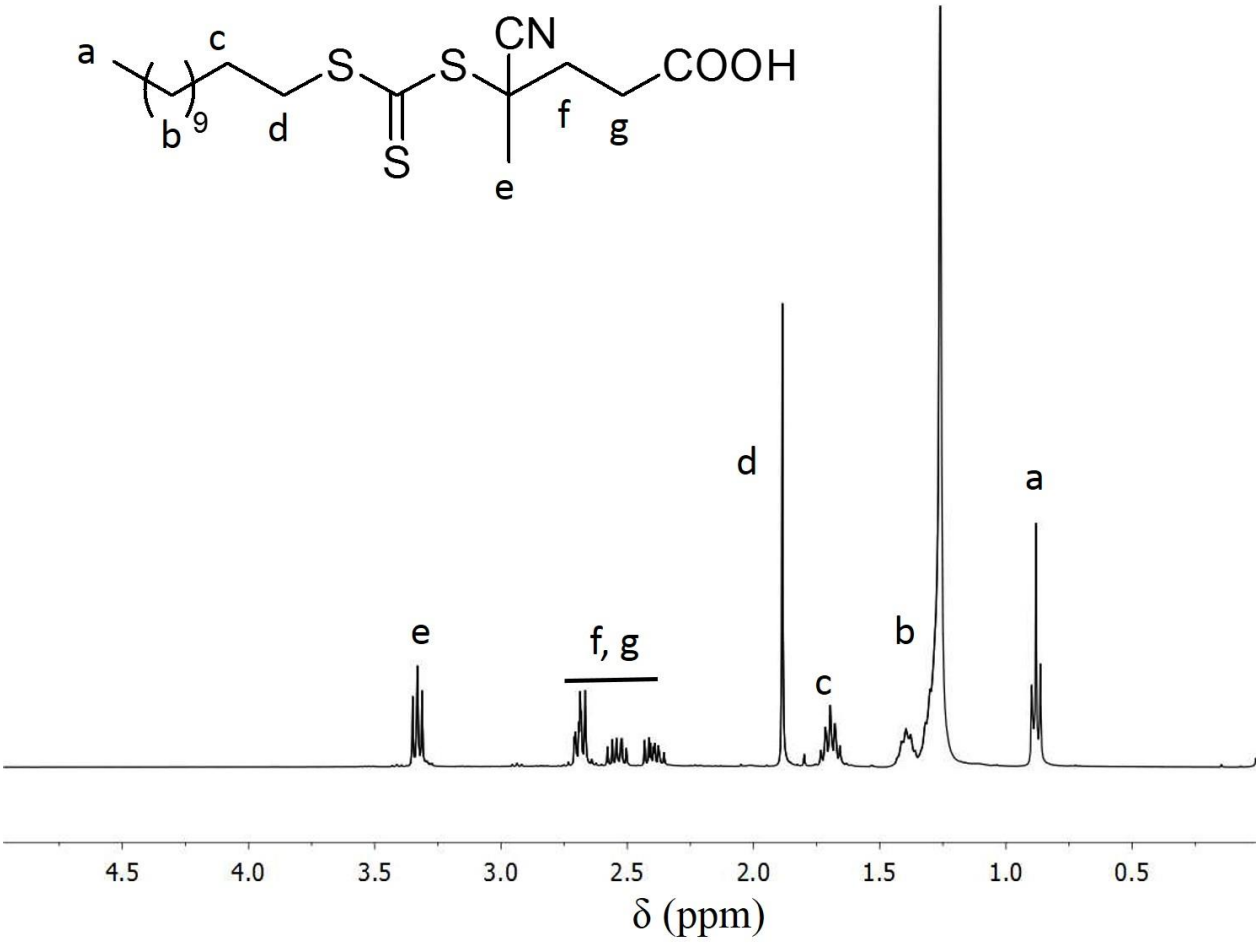

Figure S2. ^{1}H NMR spectrum of 4-cyano-4-(dodecylsulfanylthiocarbonyl) sulfanylpentanoic acid (CDPA) in $CDCl_3$ at 25 ^{o}C.

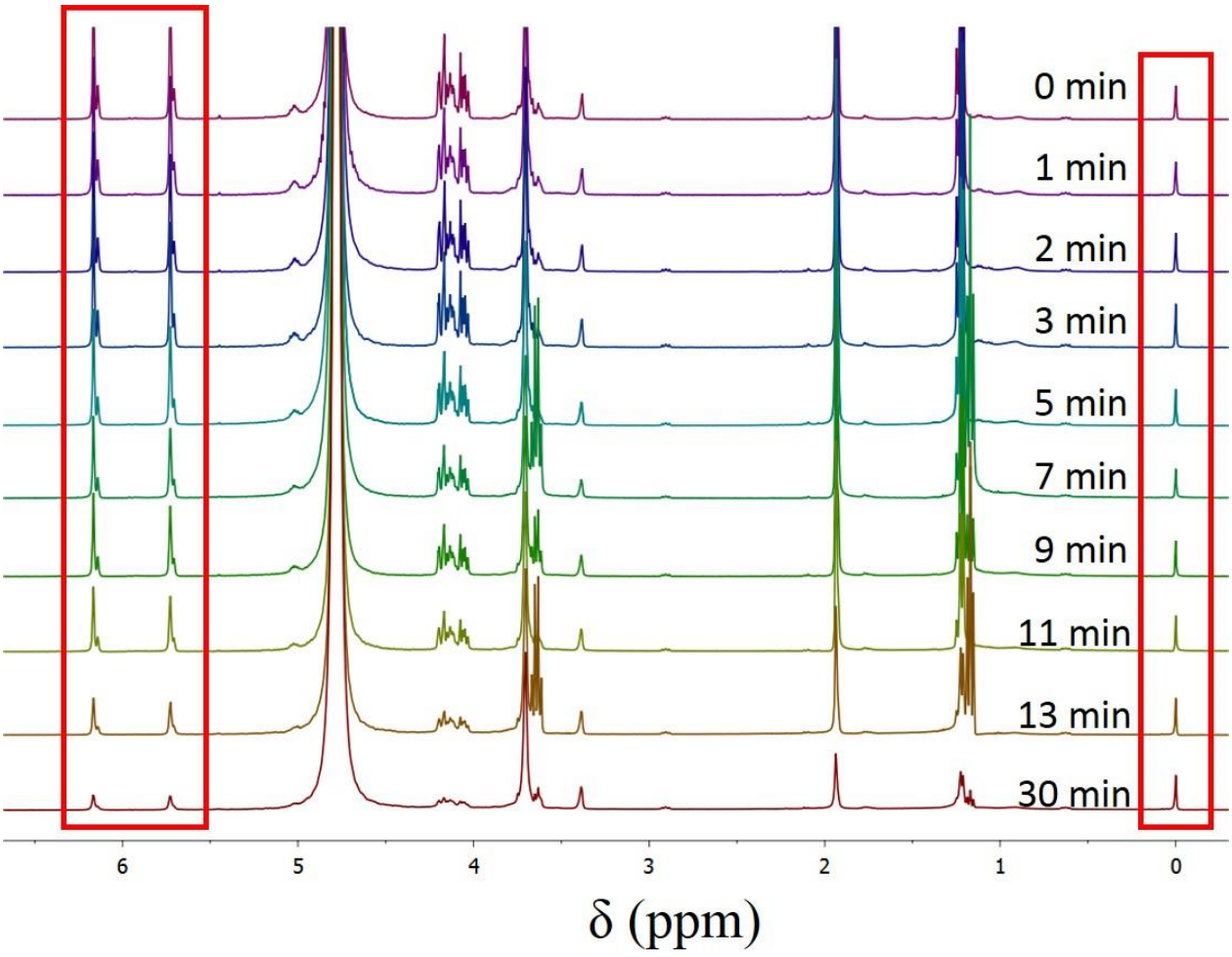

Figure S3. ^{1}H NMR spectra of the dispersions prepared via aqueous photo-PISA of HPMA at predetermined times using a $PPEGMA_{14}$ macro-RAFT agent, and the targeted DP of PHPMA was 200. The ^{1}H NMR spectra were measured in D_2O at 25 ^{o}C.

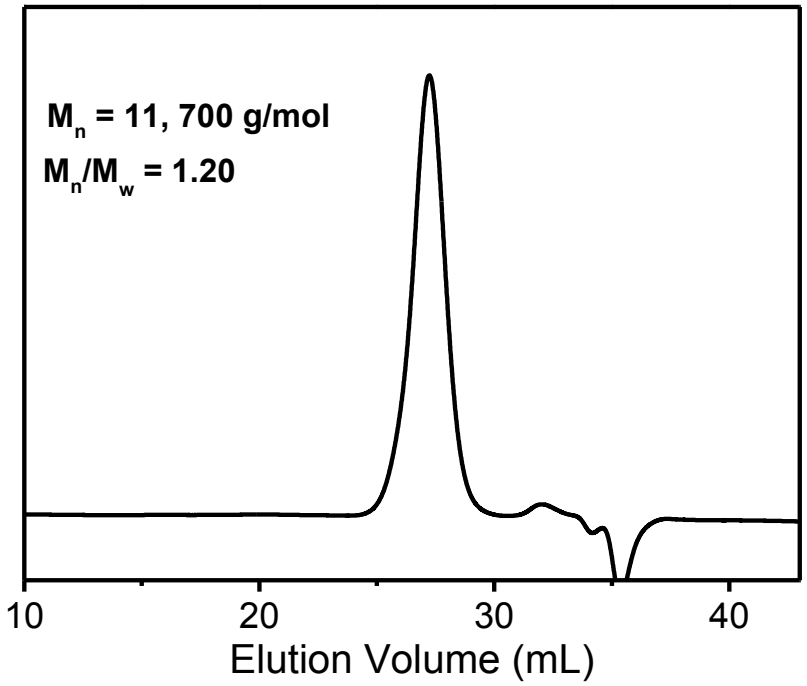

Figure S4. THF gel permeation chromatography (GPC) (vs. poly(methyl methacrylate) standards) obtained for $PPEGMA_{25}$-CDPA.

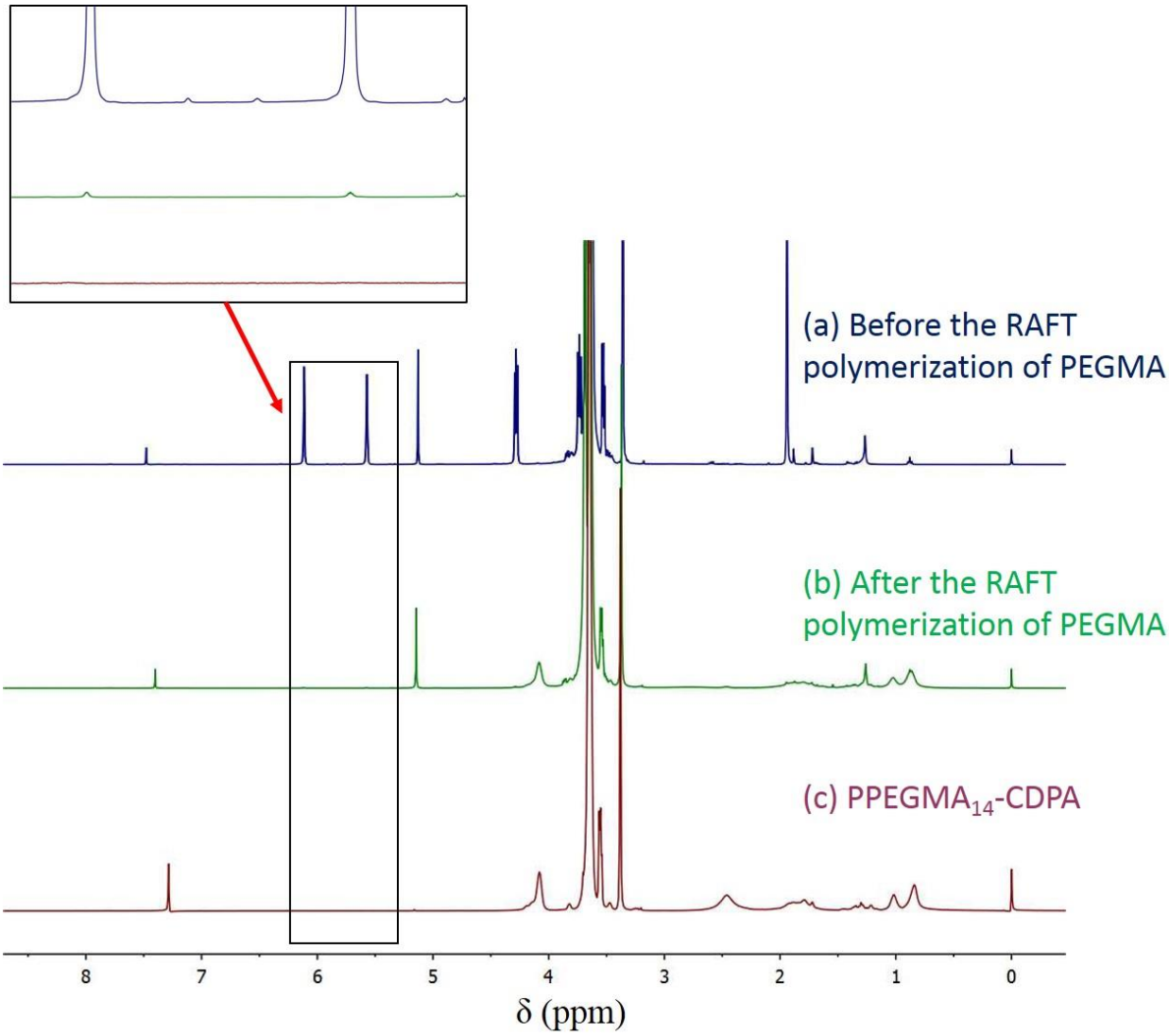

Figure S5. (a) ^{1}H NMR spectrum of the sample obtained before the RAFT solution polymerization of PEGMA; (b) ^{1}H NMR spectrum of the sample obtained after the RAFT solution polymerization; (c) ^{1}H NMR spectrum of PPEGMA$_{14}$-CDPA after several washes with diethyl ether. No vinyl signal was observed from the ^{1}H NMR spectrum of PPEGMA$_{14}$-CDPA, which indicates all the unreacted monomers have been removed.

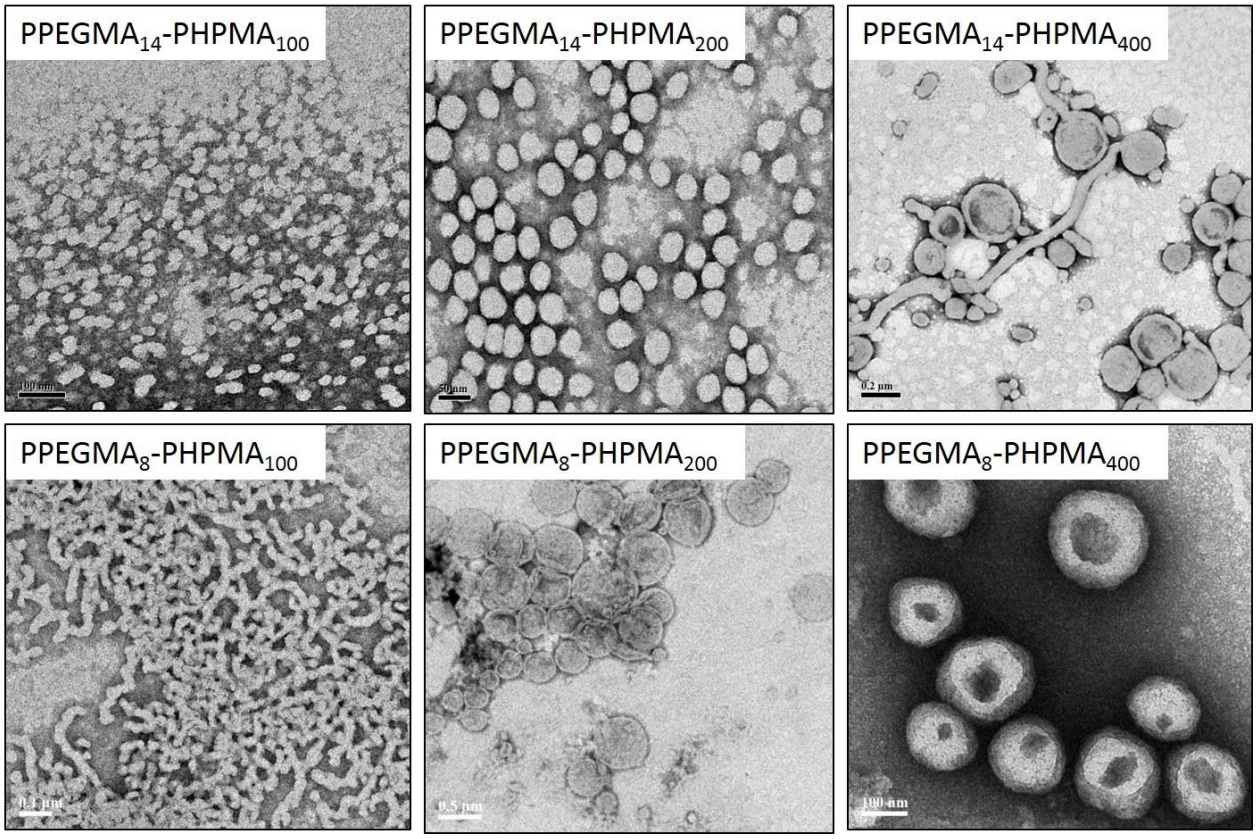

Figure S6. TEM images of $PPEGMA_{14}$-$PHPMA_{\chi}$ and $PPEGMA_{8}$-$PHPMA_{\chi}$ (χ = 100, 200, 400) prepared by photo-PISA of HPMA at 10% w/w concentration.

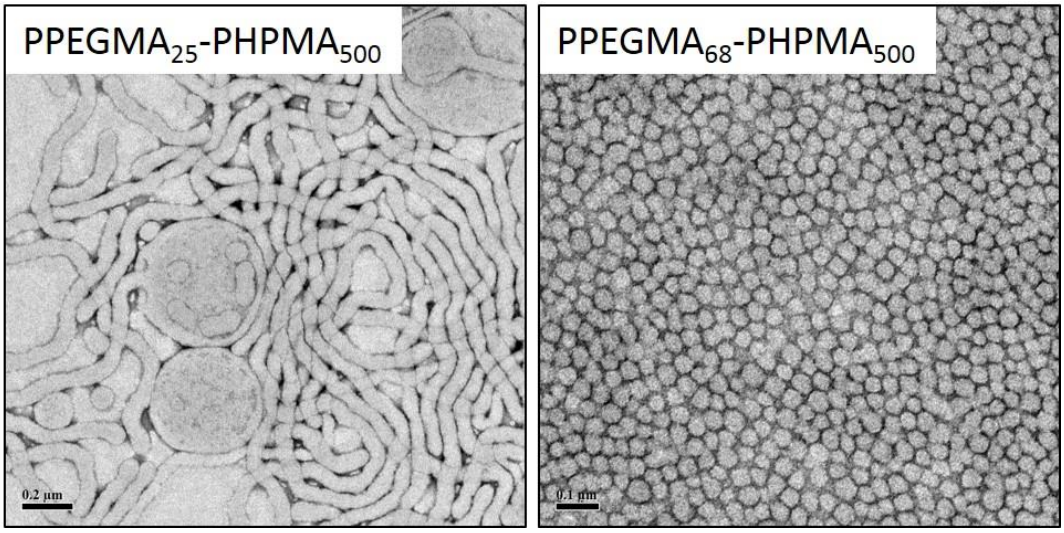

Figure S7. TEM images of $PPEGMA_{25}$-$PHPMA_{500}$ and $PPEGMA_{68}$-$PHPMA_{500}$ nanoparticles prepared by photo-PISA of HPMA at 20% w/w concentration.

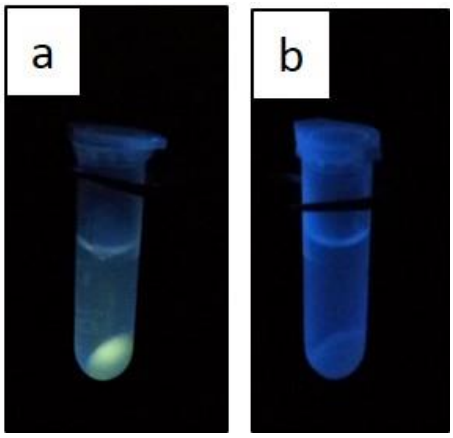

Figure S8. (a) Centrifuge tube containing sedimented $PPEGMA_{14}$-$PHPMA_{400}$ vesicles (prepared at 15% w/w), activated with EDC and NHS, and treated with fluorescein-labeled BSA; (b) Centrifuge tube containing sedimented $PPEGMA_{14}$-$PHPMA_{400}$ vesicles (prepared at 15% w/w), without EDC activation, and treated with fluorescein-labeled BSA. Both centrifuge tubes were exposed to 365 nm light.

REFERENCE

(1) Tan, J.; Sun, H.; Yu, M.; Sumerlin, B. S.; Zhang, L. *ACS Macro Lett.* **2015**, *4* (11), 1249.