Supporting information for

Disulfide Crosslinked PEGylated Starch Micelles as Efficient Intracellular Drug Delivery Platforms

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FT-IR characterization

FT-IR spectra were recorded on a Bio-Rad Win-IR instrument using the potassium bromide (KBr) method. The typical absorptions at 1108 cm^{-1} ($\upsilon_{C\text{-}O\text{-}C}$) assigned to the ether bond of PEG successfully confirmed the chemical structure of starch-*g*-PEG copolymers (shown in Fig. S1).

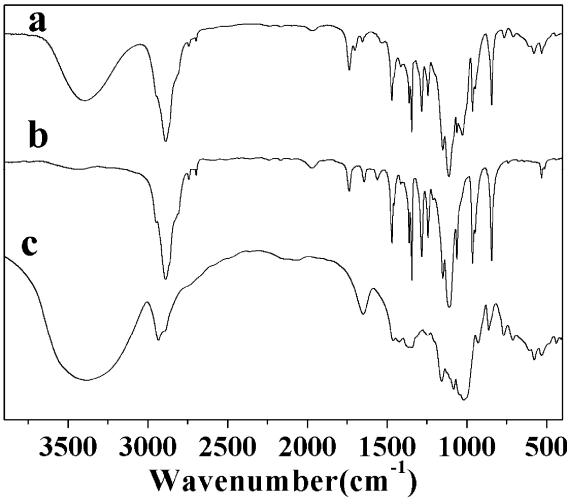

Fig. S1 FT-IR spectra of starch-*g*-PEG_{5K}-2 copolymers (a), PEG_{5K} -COOH (b) and starch (c).

Gel permeation chromatography (GPC) measurements

To further confirm the graft structure of starch-g-PEG copolymers GPC measurements were employed by using a series of linear Tskgel Super columns (AW3000 and AW5000) and Waters 515 HPLC pump with an OPTILAB DSP Interferometric Refractometer (Wyatt Technology) as the detector. The eluent was DMF containing 0.01M LiBr at a flow rate of 1.0 mL min^{-1} at 50 ◦C.

Monodisperse polystyrene standards purchased from Waters Co. were used to generate the calibration curve. Only the GPC results of the copolymers have been given in Fig. S2 due to the solubility of starch is not so good that starch only can be dissolved in DMSO to some extent by heating or ultrasonic treatment. The unimodal curves of GPC with relatively narrow PDI of around 1.16-1.20 indicated that the conjugations were completed successfully and there no a polymer blend composed of starch and PEG.

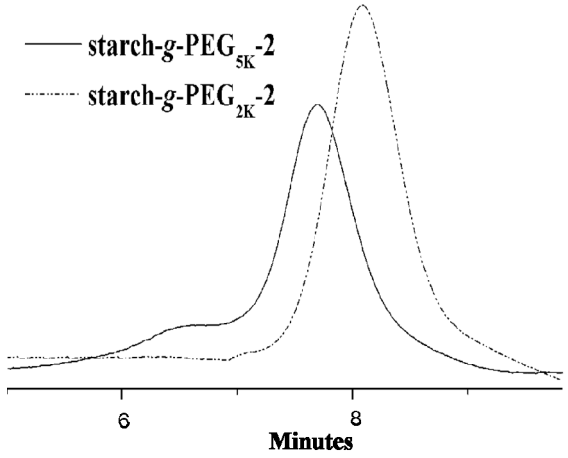

Fig. S2 Typical GPC chromatograms of starch-g-PEG_{5K}-2 and starch-g-PEG_{2K}-2.

Critical aggregation concentration (CAC) measurements

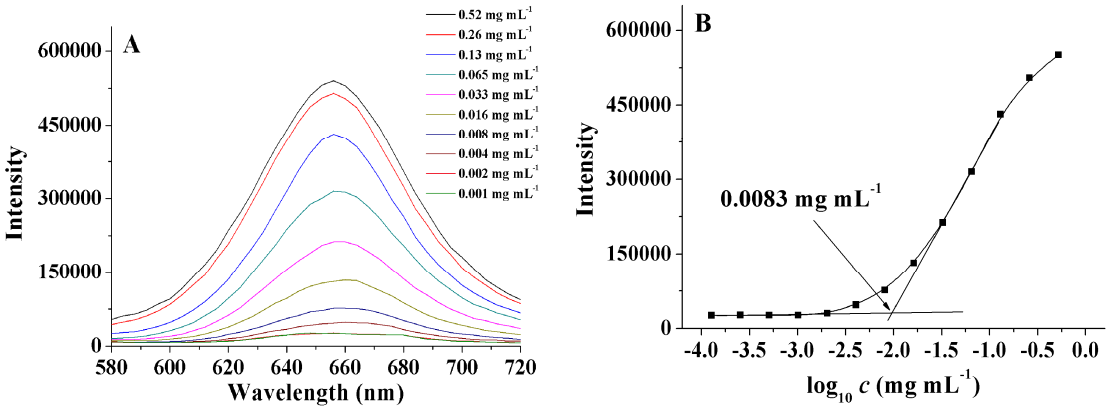

Fig. S3 Fluorescence emission spectra of Nile Red in representative uncrosslinked starch-*g*-PEG_{5K}-2 micelles at varying concentrations (A). Plot of the emission intensity at 656 nm versus the log of concentration (mg mL^{-1}) of uncrosslinked starch-*g*-PEG_{5K}-2 micelles (B)

The self-assembly of starch-*g*-PEG copolymers were also characterized by fluorescence spectra using Nile Red as the fluorescence probe. Fluorescence spectra were obtained at room temperature using a Perkin-Elmer LS50B luminescence spectrometer. The amphiphilic aggregates loaded with Nile Red were selected and diluted for the determination of CAC. Fluorescence measurements

were taken at an excitation wavelength of 550 nm and the emission monitored from 580 to 724 nm. Excitation and emission slit widths were both maintained at 5.0 nm and spectra were accumulated with a scan speed of 200 nm/min. The critical micelle concentration (CMC) could be calculated by tracking the fluorescence intensity of Nile Red as a function of the sample concentration. As shown in Fig. S3 A, at the concentration below CMC, Nile Red exhibits extremely low fluorescence intensity indicating that the Nile Red was in water and few micelles were present. With increasing concentration of copolymers, the fluorescence intensity increased dramatically, demonstrating that Nile Red was encapsulated in the interior of the micelles. Thus, the CMC value could be calculated as the intersection of the tangents to the horizontal line of intensity ratio with relatively constant values and the diagonal line with rapidly increased intensity ratio (shown in Fig. S3 B).