† Supplementary information, Experimental details:

Materials. Waxy maize starch with macromolecular weight (Mw) of 180 000 was obtained according to a previously published method. [1] Palmitoyl chloride (PA), Acetic anhydride (AC), *N,N*-dimethylaminopyridine (DMAP) and Rhodamine B were obtained from Alfa. All the other chemicals were used as received.

Synthesis of Starch Palmitate (S-PA). The S-PA was prepared according to the following process. Typically, four grams of waxy maize starch dispersed in 40 mL of *N,N*-dimethylformamide (DMF) was reacted with 4 g of PA in the presence of 10 mL of pyridine for 3h at 105 ^{o}C. The S-PA was precipitated, washed with ethanol three times, and dried at 50 ^{o}C.

Synthesis of Acetylated Starch Palmitate (S-PA-AC). Two grams of the S-PA dispersed in 30 mL of N,N-dimethylformamide (DMF) was reacted with 6 mL of acetic anhydride in the presence of 5 mL of pyridine and 0.05 g of DMAP for 3 h at 50 ^{o}C. The S-PA-AC was precipitated, washed with water three times, and dried at 50 ^{o}C.

^{1}H NMR (DMSO-d_6): δ=5.5- 3.9 (AGU H), 2.1-1.9(AC H). 0.88, 1.25, 1.77 , 2.19 (PA H)

Preparation of Starch ester Vesicles. The vesicles were prepared by a nanoprecipitation process. Typically, 100mg of starch ester was dissolved in 20 mL of tetrahydrofuran. Distilled water (25 mL) was then added dropwise to the polymer solution. The resulting suspensions were stirred at room temperature until the tetrahydrofuran was completely vaporized from the aqueous suspension.

NMR Characterizations. The samples of starch ester dissolved in *d*6-DMSO were recorded using a Bruker AV400 spectrometer (Ettlingen, Germany) operating at 400 MHz for ^{1}H NMR at 25 ^{o}C.

SEM Characterizations. The appearance of vesicles was characterized by scanning electron microscopy (SEM) using a model XL 30 ESEM microscope (Philips). A droplet of suspension was placed on a silica surface. After the water was evaporated at ambient, the system was covered by gold before measurement.

TEM Observation. The appearance of vesicles was characterized by transmission electron microscopic (TEM, Hitachi H-800) observation at an acceleration voltage of 100 kV. A droplet of suspension was placed on a copper grid for 1 min. Then the liquid was blotted off with filter paper, and the grid was air-dried before measurement.

PSA Analysis. The particle size and polydispersity of vesicles in aqueous solution were measured by dynamic light scattering using a 90 Plus particle size analyzer (PSA; Brookhaven) at 25 °C. The suspensions were diluted with distilled water to a concentration of about 0.01%. The mean particle size was approximated as the diameter and the combined polydispersity as the polydispersity index (PDI).

CLSM characterization. The distribution of Rhodamine B in vesicle was observed by laser scanning confocal microscopy (CLSM) using a Leica TCS SP2 CLSM. The samples were excited by using a 554 nm He/Ne laser. A droplet of suspension was placed on a glass surface, and visualized directly.

Controlled Release Experiment. The release behavior of the vesicle was examined by encapsulation and release of the fluorescent dye Rhodamine B (λex 554 nm, λem 575 nm). In this process, vesicles were prepared using 0.0015 wt% aqueous Rhodamine B solutions instead of deionized water. Rhodamine B -loaded vesicles were collected and put in a dialysis bag, then immersed into 100 mL of aqueous media with different pH values (phosphate buffer solution with concentration of 0.2 mol.L^{-1} and pH of 4.5, 7.4 and 9.2, respectively) and stirred at 25 ^{o}C. The release of Rhodamine B from the vesicles was reported as a percentage of the total amount released from the dialysis tubes determined by fluorescence at different periodic intervals. Error bars represented one standard deviation of triplicate independent experiments.

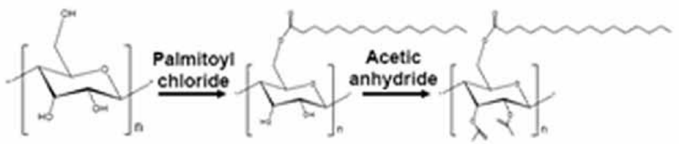

Figure S1. Synthesis of starch mixed esters.

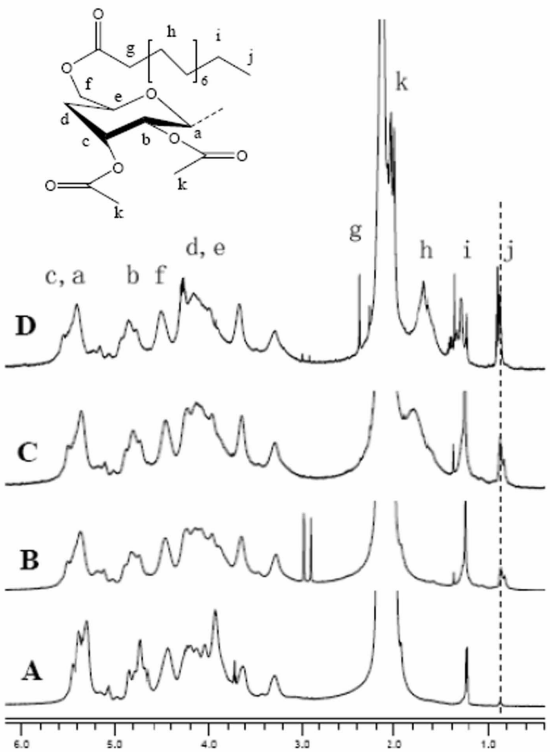

Figure S2. 1H NMR spectrum of S-PA-AC. A) S-PA-AC1, B) S-PA-AC2, C) S-PA-AC3 and D) S-PA-AC4. Inset shows the structure of S-PA-AC and peak assignment.

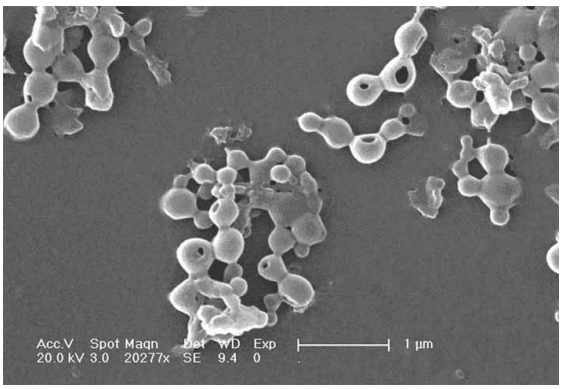

Figure S3. SEM image of starch esters vesicles prepared from S-PA-AC3.

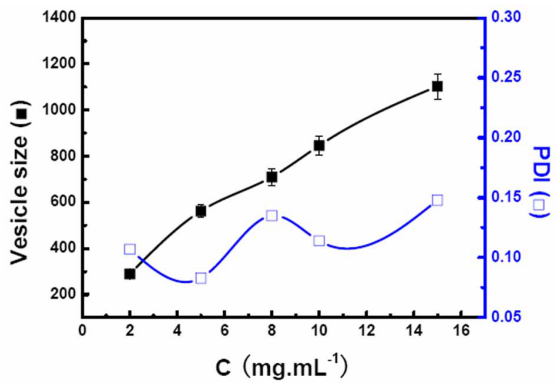

Figure S4. The effect of initial concentration of S-PA-AC3 on the vesicle size and size distribution.

Notes and references

1. Y. H. Chang, J. H. Lin and C. Y. Lii, *Carbohydr. Polym.*, 2004, ***57***, 89.