Supporting Information to

An Easy Way to Sugar-containing Polymer Vesicles or Glycosomes

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Materials. 1,3-Butadiene (Sigma-Aldrich) was first distilled from dibutylmagnesium and then from *n*-butyllithium prior to use. Styrene (Sigma-Aldrich) was distilled from CaH_2 and from dibutylmagnesium. Tetrahydrofuran (THF) (BASF AG, Ludwigshafen) was fractionated and distilled twice from Na/K alloy. *sec*-Butyllithium (*s*BuLi) (1 M solution in hexane, Sigma-Aldrich) was used as received.

2,3,4,6-Tetra-O-acetyl-β-D-1-thioglucopyranose (**2**) (97%, Sigma-Aldrich; see chemical structure and ^{1}H NMR spectrum in Figure SI-1) and azoisobutyronitrile (AIBN) (98%, Fluka) were used as received. Chloroform (99%, Roth) and THF (99.5%, Fluka) were distilled from CaH_2, and methanol (99.9%, Merck) was distilled from magnesium turnings. 0.5 M solution of sodium methoxide in methanol was prepared by adding 0.115 g sodium (lump in kerosene, 99%, Sigma-Aldrich) into 10 mL of dry methanol. Amberlite 200C ion exchange resin (Fluka) was washed with 0.5 N NaOH, water, 0.5 N HCl, and water before use.

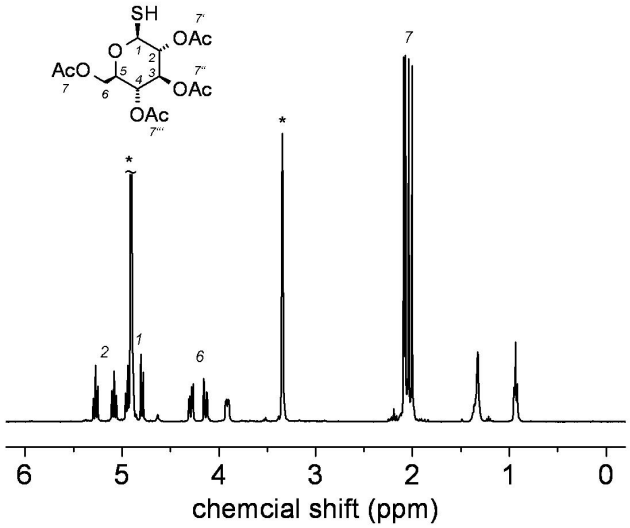

Figure SI-1. Chemical structure and ^{1}H NMR spectrum (400.1 MHz, CD_3OD) of **2**.

Anionic polymerization. 1,3-Butadiene was condensed into a reactor containing a mixture of THF and *s*BuLi, and the solution was stirred overnight at –78 °C. After withdrawal of an aliquot from the reactor, styrene was condensed into the reactor and polymerized for 1 hour at the same temperature. The reaction was quenched with degassed methanol. The 1,2-polybutadiene-*block*-polystyrene (**1**) was precipitated into methanol, filtered, and dried under vacuum at +40°C.

Photoaddition. A solution of 100 mg of **1**, 450 mg of **2**, and 11 mg of AIBN in 6 mL of dry THF was degassed by three freeze-pump-thaw cycles and then put under an argon atmosphere. After stirring for 5 h under irradiation with a mercury lamp, most solvent was removed and the crude product was isolated by precipitation into MeOH and filtration. Product **3a** was purified by dissolving in THF and precipitating into MeOH twice.

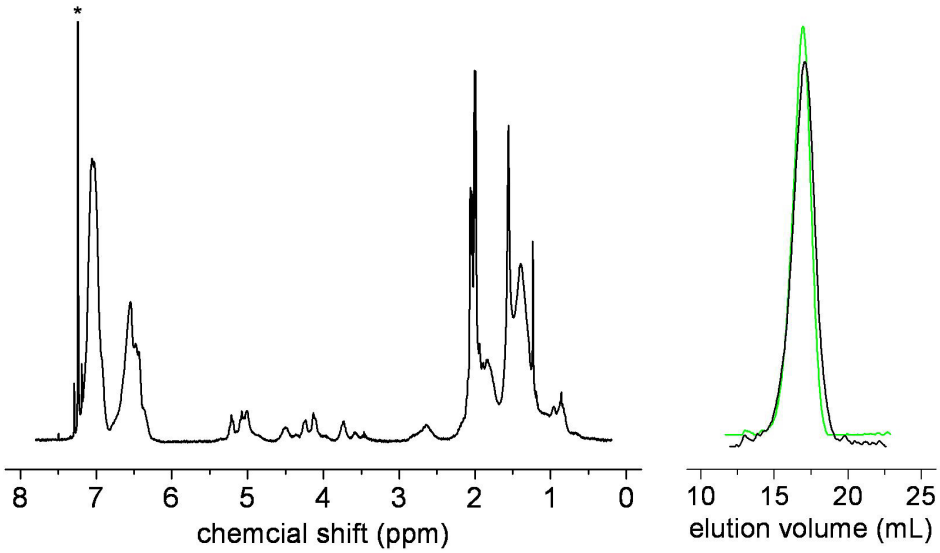

Figure SI-2. Left: ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of **3a**. Right: SEC chromatograms ($CHCl_3$, detector: RI) of **3a** (black) and the precursor polymer **1** (green).

Deacetylation. A solution of 100 mg of **3a** in 9 mL chloroform and 1 mL of 0.5 M sodium methoxide in methanol was stirred for 1 h at room temperature. After neutralization with Amberlite 200C ion exchange resin, filtration, and evaporation of solvent, product **3b** was suspended in water and freeze-dried.

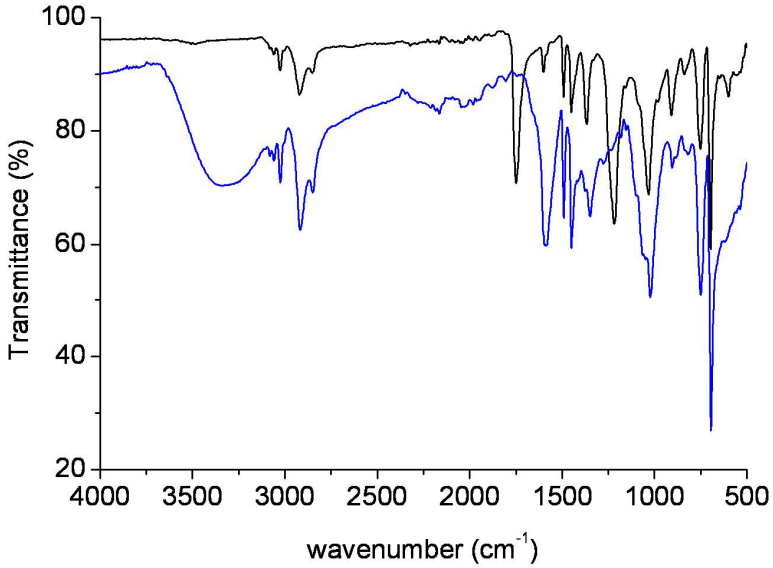

Figure SI-3. FT-IR spectra of **3a** (black) and **3b** (blue) (solid samples).

Sample preparation for structural analysis. 1 mL of a 0.3 wt % solution of the glucose-grafted 1,2-polybutadiene-*block*-polystyrene (**3b**) in THF (+ 20 µL of water) was stirred at room temperature for 24 h. Deionized water was added slowly to the solution until the water content reached 50 wt %. The solution was then stirred in the open vial to remove the THF until constant weight. This stock solution was then diluted with water by a factor of 100. For Dynamic Light Scattering (DLS) measurements, the sample was passed through a 5 µm filter (Schleicher-Schüll). For visualization of aggregates with Transmission Electron Microscopy (TEM), a drop of the solution was deposited onto a copper grid coated with a thin film of Formvar and a film of carbon. After 10 minutes, the excess solution was absorbed by a piece of filter paper, and the grid was dried in the air overnight.

Analytical methods and instrumentation. C/H/N/S-specific Elemental Analysis was done with a Vario EL Elemental Analyzer. ^{1}H NMR spectra were recorded at room temperature with a Bruker DPX-400 spectrometer operating at 400.1 MHz. Fourier-transform infrared (FT-IR) spectroscopy was done at room temperature with a BioRad 6000 FT-IR spectrometer equipped with a Single Reflection Diamond ATR. Size exclusion chromatography (SEC) with simultaneous UV and RI detection was performed in chloroform at 25 °C using a column set of two 300 x 8 mm MZ-SD*plus* (spherical polystyrene particles with an average diameter of 5 µm) columns with pore sizes of 10^3 and 10^6 Å. Calibration was done with commercial polystyrene standards. Dynamic Light Scattering (DLS) measurements were carried out on a home-built goniometer with a fixed scattering angle of 90° at 25 °C. The instrument was connected via a single mode fiber to a single photon detector (ALV/SO-SIPD), the output of which was fed to a multiple-tau digital correlator (ALV 5000). The light source (Polytec, 34 mW) was a HeNe laser operating at a wavelength of λ = 633 nm. From the measured time-correlation functions, intensity-weighted particle size distributions were calculated according to H. Schnablegger and O. Glatter, *Appl. Opt.* **1991**, *30*, 4889-4896. Transmission Electron Microscopy (TEM) was performed on Zeiss EM 912 Omega microscope at an acceleration voltage of 120 kV.

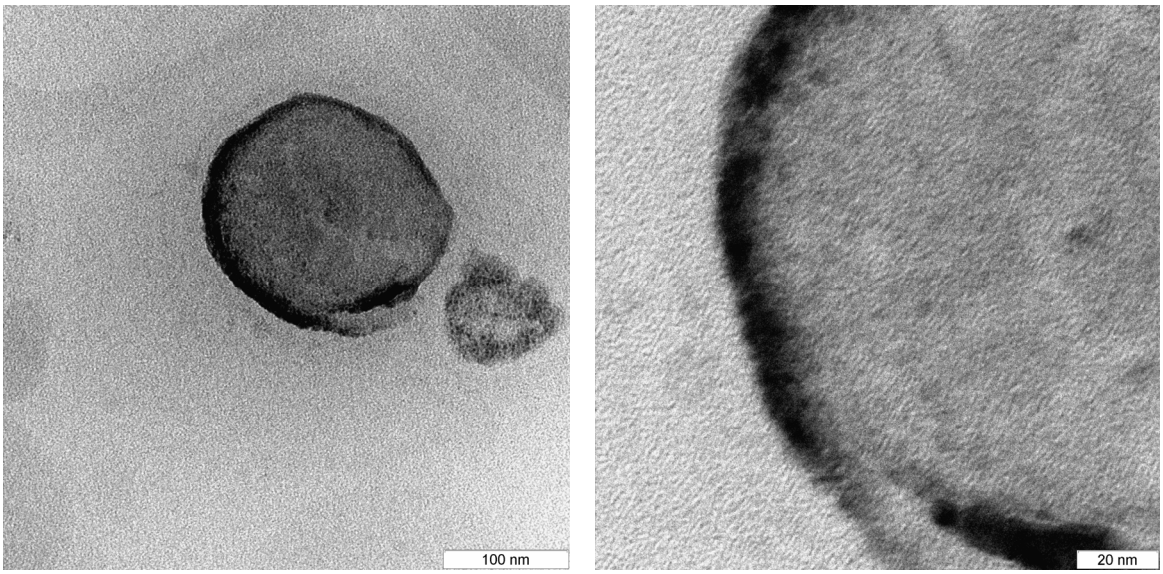

Figure SI-4. TEM images of a collapsed vesicle of **3b** in THF. Specimen was prepared by placing a drop of a 0.1 wt % polymer solution on a deep-frozen grid and allowing the solvent to evaporate in air.

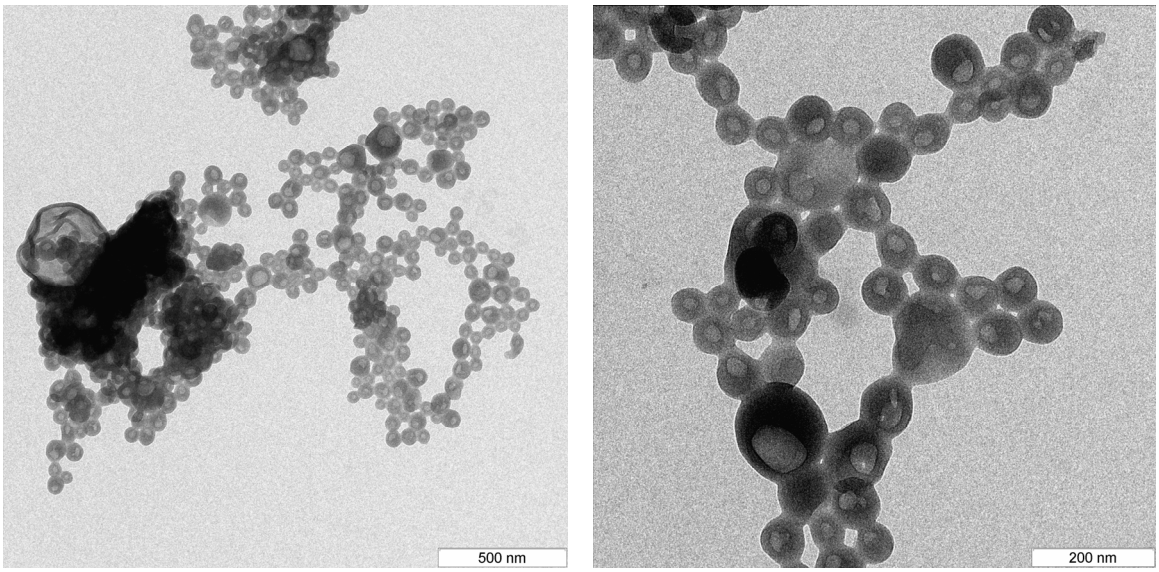

Figure SI-5. TEM images of (collapsed) vesicles of **3b** in water. Specimen was prepared by placing a drop of a 0.003 wt % polymer solution on a grid and allowing the solvent to evaporate in air.

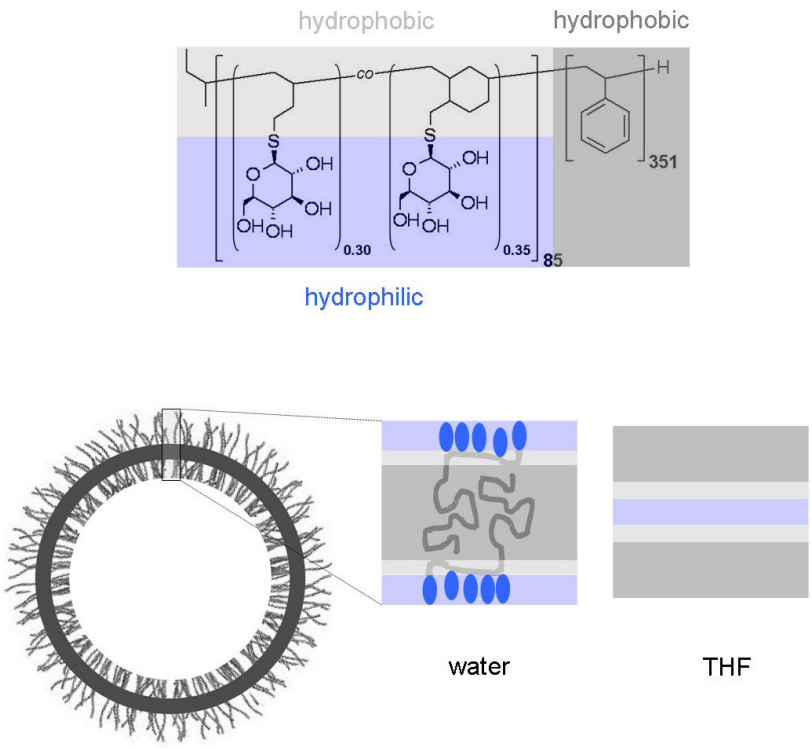

Figure SI-6. Schematic illustration of the structure of the vesicle membrane (working hypothesis).