Supplementary Information

Micropipette aspiration of double emulsion-templated polymersomes

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Polymersome preparation.

Double emulsion template method: Water-in-oil double emulsion droplets were produced using glass microcapillary devices.[1, 2] The inner phase consisted of a sucrose solution (290 mOsm), the middle hydrophobic phase consisted of 0.1 wt % polymer in a mixture of toluene and chloroform (2.6:1 v/v), and the outer phase consisted of PBS (290 mOsm). A polyethylene oxide-polybutadiene diblock copolymer, PEO_{30}-b-PBD_{46} (M_W= 3800 g mol^{-1}, PolymerSource, Dorval, Canada)[3], was used. When incorporating a dye into the membrane (Fig. 1), the near infrared chromophore, porphyrin {a meso-to-meso ethyne bridged (porphinato)zinc(II) dimer (PZn_2)}, which was synthesized in the Therien laboratory following methodology previously described,[3] was used. The PZn_2 chromophore was dissolved in the toluene: chloroform (2.6:1 v/v) mixture and added to the diblock copolymer, PEO_{30}-b-PBD_{46}, at a 4 M: 1 M ratio (polymer: fluorophore) to make up the middle phase. Polymersomes prepared for aspiration studies did not have any fluorophore in the membrane. After formation, ~0.5 mL of double emulsion drops were collected in ~2.5 mL of PBS inside 20 mL glass vials. The vials, containing PEO_{30}-b-PBD_{46} double emulsions, were left loosely capped overnight, put on a rocker for the following day, and left loosely capped and stationary for the subsequent 30 days.

Film hydration method: PEO_{30}-b-PBD_{46} was dissolved in methylene chloride (3.8 mg mL^{-1}). The resulting solution was uniformly coated on the rough side of a Teflon strip and the solvent was evaporated for > 24 h. The film was hydrated in 2 mL of sucrose solution (290 mOsm). After hydration of the polymer film, the system was heated at 60°C for > 24 h and vortexed, resulting in spontaneous budding of giant polymersomes off the Teflon into the surrounding aqueous solution.

Micropipette Aspiration.

Mircopipette aspiration of polymersomes followed similar procedures to those described by Evans et al.[4] Briefly, polymersomes were picked up by the micropipettes, suction pressure was applied via a syringe connected to a manometer, and pressure was increased stepwise in 5 cm H_2O increments. The membrane was allowed 10 s after each pressure change to equilibrate. The resulting membrane extensions and membrane diameter were analyzed with ImageJ software[5] and used to calculated the area expansion modulus (K_a) of the different polymersomes. Samples of vesicles formed from double emulsions were analyzed through aspiration on days 3, 7, 15, and 35 after production. The area expansion modulus (K_a) of the polymersomes was calculated at each time point.

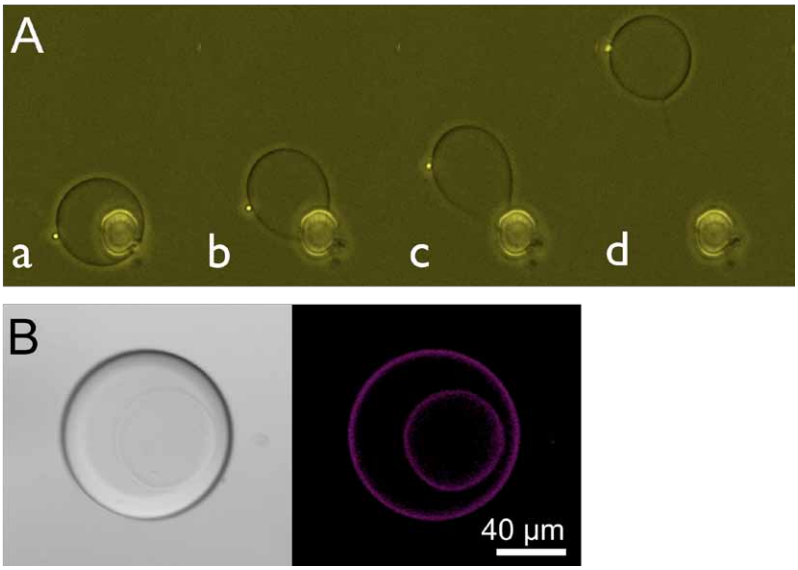

Figure S1. Vesicle formation from W/O/W double emulsions. (A) Excess polymer is concentrated as the membrane bilayer forms and the oil phase undergoes a wetting transition[6] during evaporation from the double emulsion. Ultimately, the polymersome is released from the excess polymer. Panels are taken at 5 min intervals 1 day post production. (B) Several polymersomes were also found to contain smaller interior vesicles, which are likely to be the result of invagination of excess polymer into an internal membrane. (Left) DIC image (Right) PZn_2 fluorescence from polymersome membrane

References

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