Electronic Supplementary Information

1. Materials and Instrumentation

Tetrahydrofuran and 1,4-dioxane were purchased from Sigma-Aldrich. The dialysis cell was home made at the Techno Centre of the Radboud University Nijmegen. The dialysis membranes were Spectra/Por Dialysis Membrane 4 (MWCO 12-14,000) from Spectrum Laboratories, Inc. The custom-made dialysis flow cell used for the experiments had the following dimensions:

Depth (pathlenth) 5.1 mm, Width: 6.9 mm, Height 5.75 mm, Surface area separating the two chambers is 5.1 x 6.9 mm^2.

For the birefringence measurements, a 1.5 mW intensity stabilized HeNe laser (632.8 nm) was used from Research Electro-Optics Inc. To increase the sensitivity of the birefringence measurements, a photo-elastic modulator (PEM) at 50 kHz was used. The flow cell with the polymersomes was placed between two crossed-polarizers. The magnetic field was applied using a Varian V-3900 2T electromagnet. The setup was calibrated by measuring the Cotton-Mouton constant of toluene, which is defined by: $C = \Delta n / B^2$. The Cotton Mouton constant of toluene was determined at $(3.13 \pm 0.15) \cdot 10^{-9}\ T^{-2}$, which is in agreement with values stated in literature ($3.27 \cdot 10^{-9}\ T^{-2}$).[1,2]

(Cryo-)SEM was performed on a JEOL 6330 Cryo Field Emission Scanning Electron Microscope at an acceleration voltage of 3 kV in cryo-mode and 10 kV in dry mode. TEM was performed on a JEOL 1010 Transmission Electron Microscope at an accelerating voltage of 60 kV, for which 4 μL of sample was air dried on 200 Mesh carbon coated copper grids. DLS was performed with a Malvern Zetasizer Nano S instrument and its data was analyzed with the corresponding software from Malvern Instruments.

2. Polymersome sample preparation

Polymersomes were self-assembled as follows. First, 10 mg of PEG_{44}-PS_{133} powder was dissolved in a mixture of 600 μL tetrahydrofuran (THF) and 400 μL 1,4-dioxane and the solution was stirred for 30 minutes. Next, 3 mL of water was added at a rate of 1 mL/h (still under rigorous stirring) at which point polymersomes were formed. Polymersome formation was observed by the transition from a clear colourless solution to a cloudy suspension. Afterwards, the organic solvents were removed by dialysis against pure water in a 12-14 kDa cutoff membrane tubing over 48 hours. During this time, the water was replenished 5 times at regular intervals. The resulting sample consisted of spherical polymersomes in pure water. A transition of polymersomes into stomatocytes during this dialysis step was prevented by performing the self-assembly step in an excess of water (75:25 water : organic solvent), rather than the 50:50 ratio that, upon dialysis against water, leads to the formation of stomatocytes.

3. Averages and standard deviation of points C, E and G

During the experiment the polymersome sample was dialyzed against a mixture of 50% water, 40% THF and 10% 1,4-dioxane. For each of the eight points on the birefringence curve (a-h), a new dialysis was performed since the experiment had to be stopped when taking a sample. The sample was quenched by injecting it in an excess of water, preventing further dialysis and expelling the organic solvent rapidly from the membrane, thereby storing the current morphology. Repetition of the dialysis led to the following statistics:

Point on birefringence curve	Time (min)	Standard deviation (min)
C (begin peak)	188	24
E (top peak)	247	25
G (end peak)	303	2

Maximum birefringence (at E)	$2.49 \cdot 10^{-6}$	$0.23 \cdot 10^{-6}$

4. Dynamic Light Scattering

Point on birefringence curve	Hydrodynamic radius (nm)	PDI
A	251.7	0.134
B	242.2	0.102
C	265.4	0.088
D	221.8	0.112
E	233.9	0.102
F	208.9	0.133
G	214.9	0.094
H	217.7	0.120

5. Additional TEM and SEM on points a, b, e-h and cryo-SEM on points c, d.

Dry-TEM, Dry-SEM and additional cryo-SEM were performed on samples taken at points a-h on the birefringence curve. The results are shown below in figure S1. Also with dry-TEM and dry-SEM the transition from polymersomes to flat disks to stomatocytes could be observed. For points c and d only cryo-SEM images were obtained since the TEM and SEM images for these two points showed drying effects. This was probably due to an increased flexibility of the membrane, caused by 3 hours of dialysis, in combination with a large inner volume. Instead some more cryo-SEM images of these two points were taken.

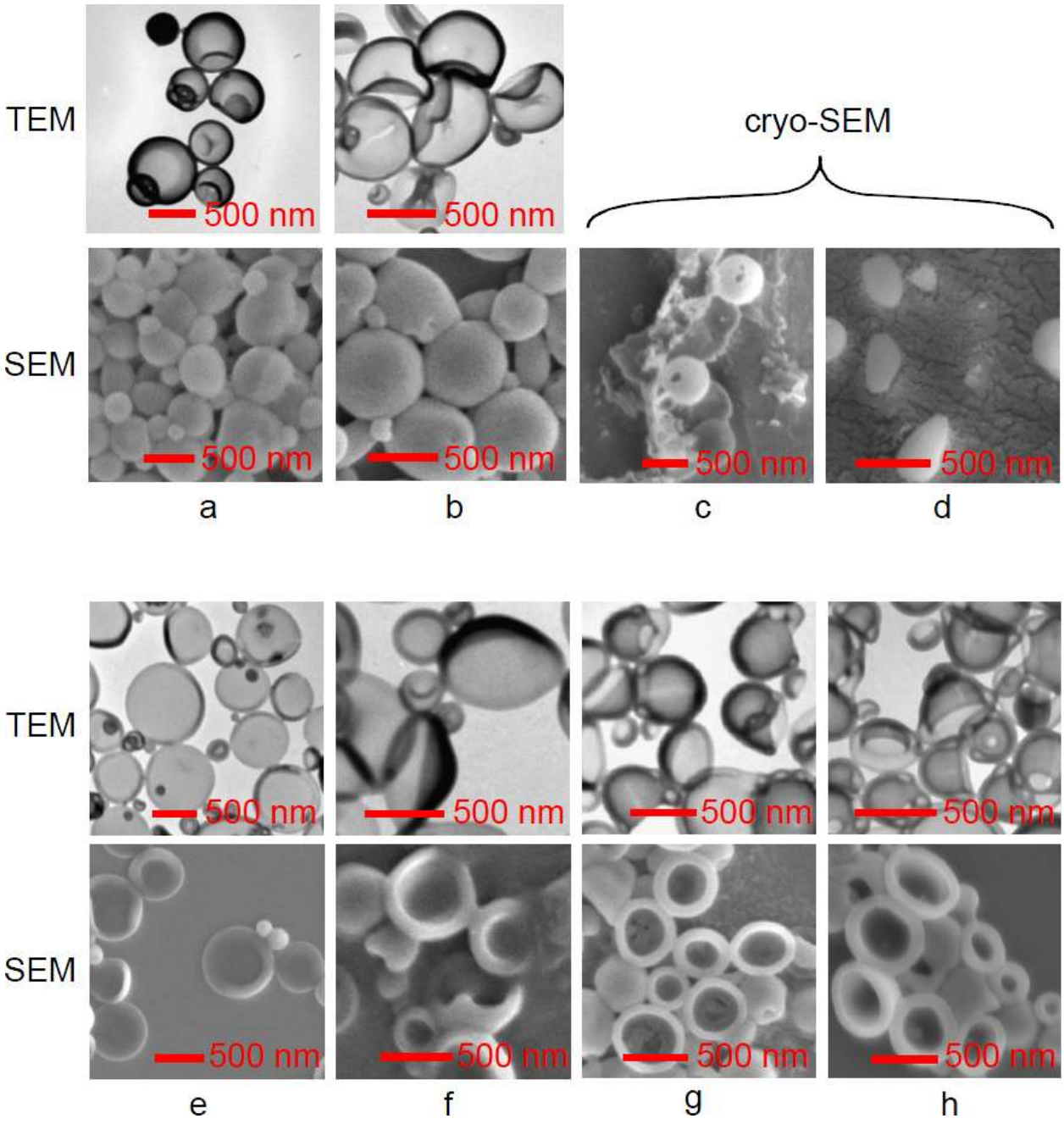

Fig. S1. Additional dry-TEM, dry-SEM or cryo-SEM images of points a-h. These images correspond with the cryo-SEM images shown in figure 2 of the article.

1. M.R. Battaglia and G. L. D. Ritchie, *J. Chem. Soc., Faraday Trans. 2*, 1977, **73**, 209
2. S. Sprunt, G. Nounesis, J. D. Litster, B. Ratna and R. Shashidhar, *Phys. Rev. E*, 1993, **48**, 328