Electronic Supplementary Material (ESI) for Polymer Chemistry.

Methods for production of uniform small sized polymersome with rigid membrane

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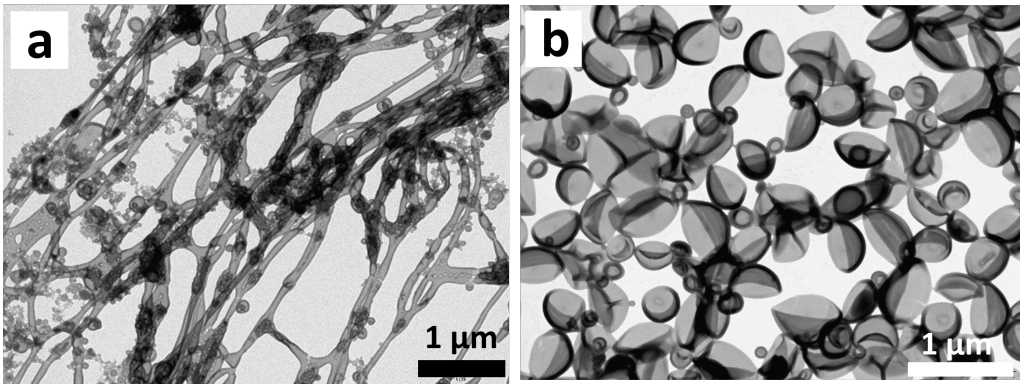


Fig. S1. TEM images of PEG_{45}-*b*-PS_{206} aggregates with a water content at 18% (a) and 20 % (b).

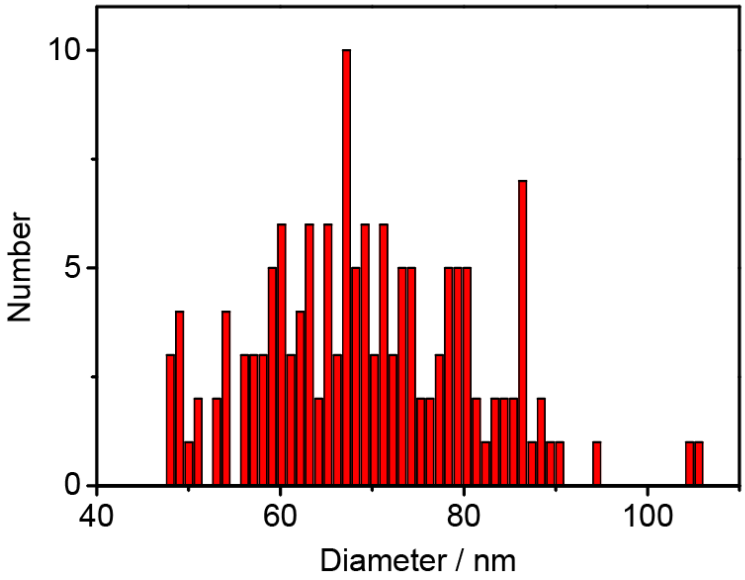


Fig. S2. Size distribution from the TEM image (Figure 1a) counted by ImageJ. The selected number of particles is 100.

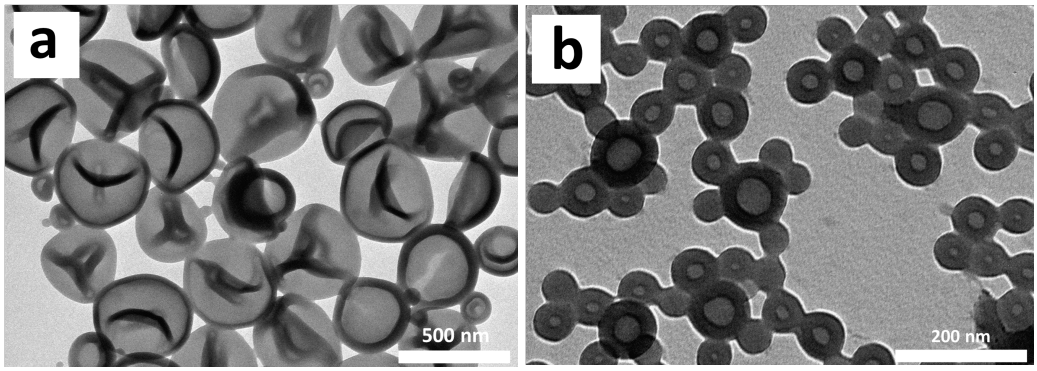


Fig. S3. TEM images of PEG_{45}-b-PS_{206} polymersomes in pure water before (a) and after (b) extrusion by addition of 66.7 % organic solvent.

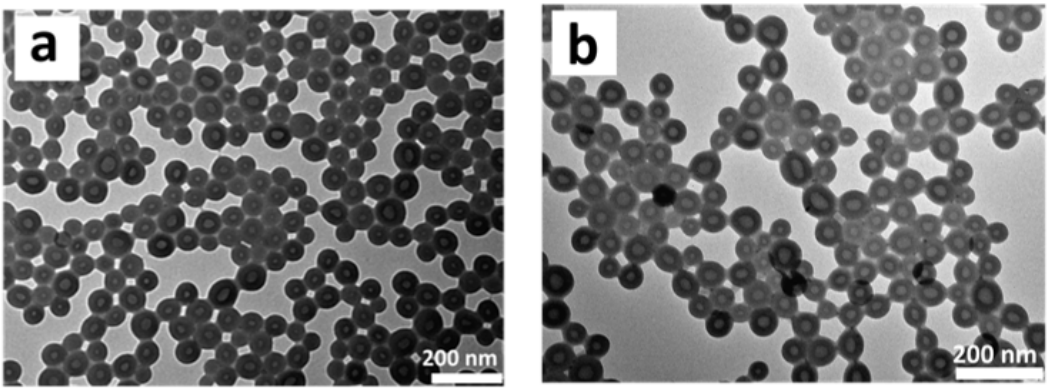


Fig. S4. TEM images of SSP encapsulated with Nile red (a) and Fluorescein sodium salt (b).

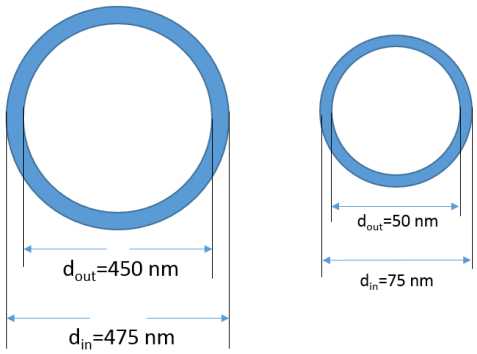
Calculation of the polymersome volume change after resizing:

Since the thickness of the membrane (large and small sized polymersome) is measured the same and the weight of the PEG-PS copolymer used are not lost, the volume of the membrane should be constant. The calculation is presented in the Figure below. As expected, if the volume of the membrane of both large and SSP is constant (*e.i.* the number of SSP is 45.43 times more than large sized polymersomes), the total volume of the lumen of SSP is 531.44/45.43=11.7 times less than the large sized polymersomes. Thus theoretically, the encapsulation efficiency should decrease about 11.7 times after extrusion, but our experiments showed the number only decreased about 4.6 times. The reason might be that more dye absorbed on the PEG corona and SSP contains higher surface energy and larger surface area than the large sized polymersome.

Single polymersome

Volume of membrane = $4/3*\pi*(d_{out}/2)^3-4/3*\pi*(d_{in}/2)^3$

Volume of lumen = $4/3*\pi*(d_{in}/2)^3$



$$\frac{\text{Volume of membrane of large sized polymersomes}}{\text{Volume of membrane of small sized polymersomes}} = 45.43$$

$$\frac{\text{Volume of lumen of large sized polymersomes}}{\text{Volume of lumen of small sized polymersomes}} = 531.44$$