Electronic Supplementary Material (ESI) for Soft Matter. This journal is © The Royal Society of Chemistry 2017

Electronic Supplementary Information

Structural Transformation of Vesicles Formed by Polystyrene-b-Poly(acrylic

acid)/Polystyrene-b-Poly(4-Vinyl Pyridine) Mixture: From Symmetric to

Asymmetric Membranes

Zhen Geng^{ab}, Yuanyuan Han*^a and Wei Jiang*^a

^aState Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry,

Chinese Academy of Sciences, Changchun 130022, People's Republic of China

^bUniversity of Chinese Academy of Sciences, Beijing 100049, People's Republic of China



Scheme S1. Schematic illustration of the procedures for 3D confinement strategy.



Figure S1. TEM images of micelles evolve from symmetric vesicles in DMF/THF/water (60/15/25, v/v/v): (a) addition of HCl, and (b) addition of NaOH. Scale bar = 200 nm.



Figure S2. TEM images of bowl-shaped particles deform from symmetric vesicles in water after addition of HCl for 12 hours: (a) unstained particles and (b) particles stained by iodine vapor. Scale bar = 200 nm.

Time (minute) ^a	Average Diameter ^b (nm)		
0	131.1 ± 29.0		
720	132.8 ± 24.7		
725	136.7 ± 28.1		
730	133.3 ± 30.3		
736	124.4 ± 20.6		
740	137.6 ± 24.6		
750	137.9 ± 39.5		

Table S1. The statistical results of outside diameters for aggregates upon different annealing time.

"The curing process upon addition of HCl are kept for 12 hours, therefore, annealing time are recorded from 720 minutes. "Each measurement is operated on all the aggregates in 10 different TEM images and the total number of aggregates is larger than 500.



Figure S3. (a) TEM images of bowl-shaped particles evolve from symmetric vesicles in water after addition of NaOH for 12 hours. Morphological transitions from the bowl-shaped particles to asymmetric vesicles upon addition of NaOH for different solvent annealing time: (b) 5, (c) 10, (d) 15 min. (e) The ζ potential at pH 3.1 and 4.2 for outside corona of polymer particles against the curing and annealing time. The curing process upon addition of HCl are kept for 12 hours, therefore, the annealing time are recorded from 720 minutes. Histograms f-h are statistical percentages of different morphologies existed in different annealing time: (f) 5, (g) 8, (h) 15 min. Scale bar = 200 nm.



Figure S4. TEM images of (a) Asymmetric vesicles, (b) Large spherical micelles (LSMs) transformed from the asymmetric vesicles after dialyzing against water to remove HCl and annealing in chloroform for 24 hours, and (c) Symmetric vesicles swelling from LSMs in DMF/THF/water (60/15/25, v/v/v).

Table S2. ζ potential results and probable corona composition for aggregates.

	Vesicles ^{(PS-b-} P4VP)	Asymmetric Vesicles	LSMs	Symmetric Vesicles	Vesicles ^(PS-b-PAA)
ζ pot. pH 3.1	32.4 ± 5.1	21.8 ± 4.5	19.5 ± 3.4	11.5 ± 2.7	-3.1±1.8
ζ pot. pH 4.2	15.3 ± 2.8	10.5 ± 2.3	8.6 ± 3.1	-5.1 ± 2.6	-8.5 ± 2.7
Corona Composition	P4VP	Mostly P4VP	Mostly P4VP	PAA and P4VP	P4VP