

**Electronic Supplementary Information for**

**Evolution of diverse higher-order  
membrane structures of block copolymer  
vesicles**

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## 1. Calculation of solubility parameter values of different self-assembly systems

The solubility parameter values of mixed solvents in different self-assembly systems are calculated by a previously reported method:<sup>1</sup>  $\delta_1$ ,  $\delta_2$  and  $\varphi_1$ ,  $\varphi_2$  represent the solubility parameter values and volume fractions of solvent 1 and solvent 2, respectively, and the solubility parameter values of mixed solvents can be calculated as follows:

$$\delta_{mix} = \delta_1\varphi_1 + \delta_2\varphi_2$$

In this paper,  $\delta$  of methanol, DMF, dioxane and water are 29.7, 24.8, 20.5 and 47.9.

The solubility parameter values of different self-assembly systems are listed in Table S2.

Table S1 Self-Cross-Linkable PEO-*b*-PTMSPMA Diblock Copolymers Synthesized by ATRP

Polymer	Composition <sup>a</sup>	$M_n^a$	$D^b$
1	PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>59</sub>	16600	1.28
2	PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>83</sub>	22600	1.31
3	PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>110</sub>	29300	1.33
4	PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>180</sub>	46600	1.10
5	PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>207</sub>	53300	1.30

<sup>a</sup> Number of the repeat unit of TMSPMA and number-averaged molecular weights of PEO<sub>45</sub>-*b*-PTMSPMA<sub>x</sub> block copolymers were obtained from <sup>1</sup>H NMR spectra in CDCl<sub>3</sub>. <sup>b</sup> Obtained from THF SEC.

Table S2 Solubility parameter values ( $\delta$ ) of different self-assembly systems

Polymer	Solvent	$C_{ini}$ (mg/mL)	$C_w$ (wt)	Volume Ratio	$\delta$	Morphology of Vesicles
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>59</sub>	methanol/water	1.0	55.0%	0.51:0.49	38.7	single-compartment <sup>2</sup>
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>83</sub>	methanol/water	5.0	67.0%	0.38:0.62	40.9	tubule-like
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>180</sub>	methanol/water	1.0	27.0%	0.77:0.23	33.8	genus
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>180</sub>	methanol/water	1.0	34.0%	0.71:0.29	35.0	genus-multi-compartment
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>180</sub>	methanol/water	1.0	39.0%	0.66:0.34	35.8	multi-compartment <sup>3</sup>
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>207</sub>	methanol/water	5.0	31.0%	0.74:0.26	34.5	onion-like
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>207</sub>	methanol/water	5.0	42.0%	0.64:0.36	36.3	HHH-like
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>110</sub>	methanol/water	20	50.0%	0.56:0.44	37.7	Janus
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>59</sub>	DMF/water	2.0	35.0%	0.66:0.34	32.5	multi-compartment
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>59</sub>	DMF/water	20	51.4%	0.5:0.5	36.3	sunflower-like <sup>4</sup>
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>59</sub>	methanol/DMF/water	20	51.5%	0.02:0.98:1	36.4	multi-petal-sunflower-like
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>59</sub>	methanol/DMF/water	20	51.8%	0.1:0.9:1	36.5	multi-petal-sunflower-like
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>59</sub>	methanol/DMF/water	20	52.3%	0.2:0.8:1	36.8	multi-petal-sunflower-like
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>59</sub>	methanol/DMF/water	20	53.5%	0.5:0.5:1	37.6	bag-like
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>59</sub>	methanol/DMF/water	20	54.9%	0.8:0.2:1	38.3	single-compartment
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>59</sub>	dioxane/DMF/water	2.0	49.0%	1:0:1	34.2	giant single-compartment
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>59</sub>	dioxane/DMF/water	20	48.8%	0.1:1:1	35.4	HHH-like
PEO <sub>45</sub> - <i>b</i> -PTMSPMA <sub>59</sub>	dioxane/DMF/water	20	50.2%	0.5:0.5:1	35.3	sunflower-like

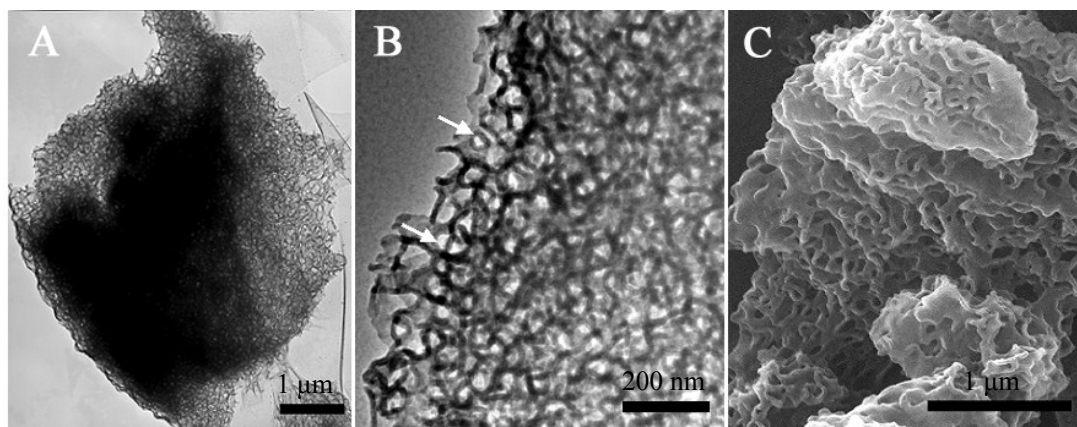


Fig. S1 Electron microscopy images of gels formed by fusion of small vesicles by self-assembly of  $\text{PEO}_{45}\text{-}b\text{-PTMSPMA}_{180}$  copolymer in methanol/water mixture ( $C_{\text{ini}} = 1.0$  mg/mL and  $C_w = 22$  wt%): (A) TEM image of the gel; (B) Magnified TEM image of the edge of the gel; (C) SEM image of the gel.

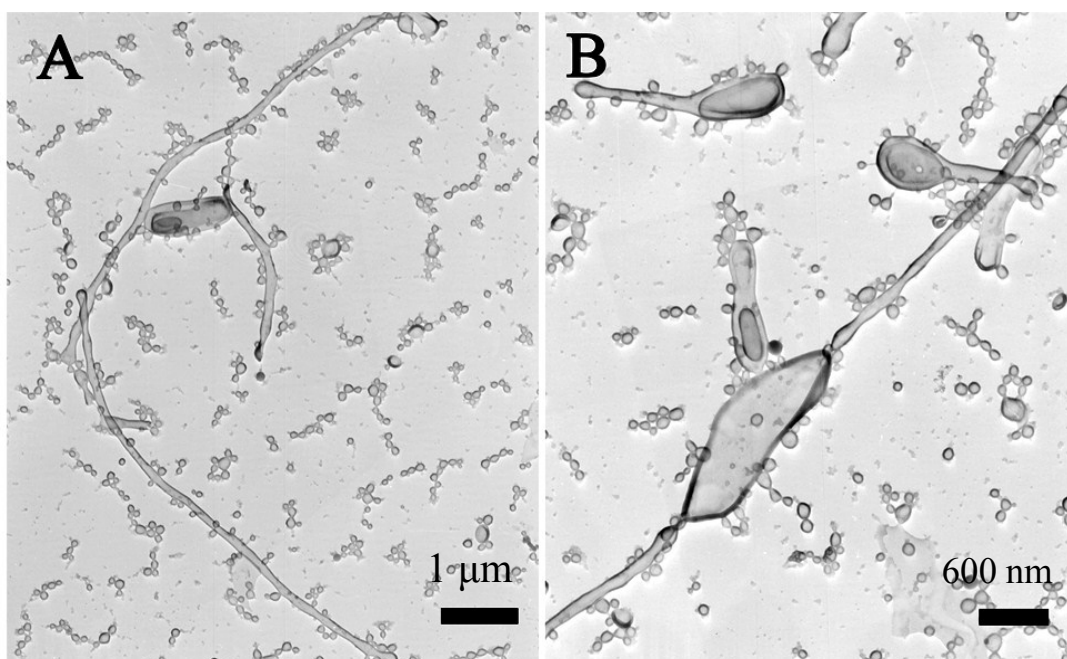


Fig. S2 TEM images of coexisting tubules and single-compartment vesicles self-assembled from  $\text{PEO}_{45}\text{-}b\text{-PTMSPMA}_{83}$  ( $C_{\text{ini}} = 5.0$  mg/mL and  $C_w = 67$  wt%).

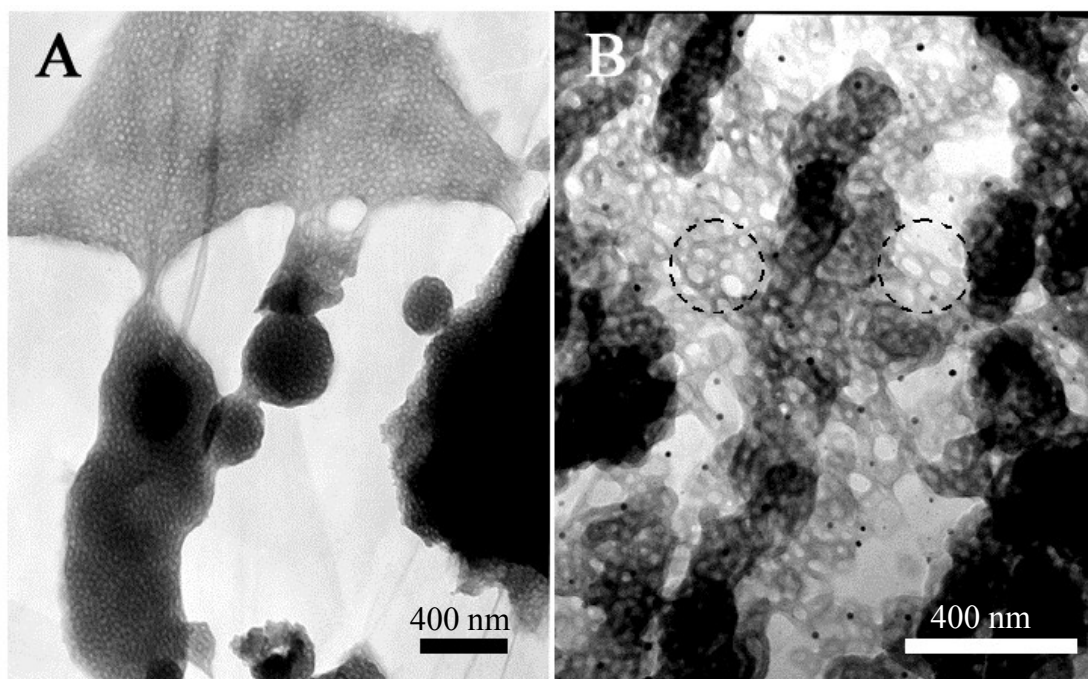


Fig. S3 TEM images of membranes fused by small vesicles based on PEO<sub>45</sub>-*b*-PTMSPMA<sub>59</sub> at  $C_{ini} = 2.0$  mg/mL in DMF and  $C_w = 30$  wt%. The circles highlighted the fusion of small vesicles.

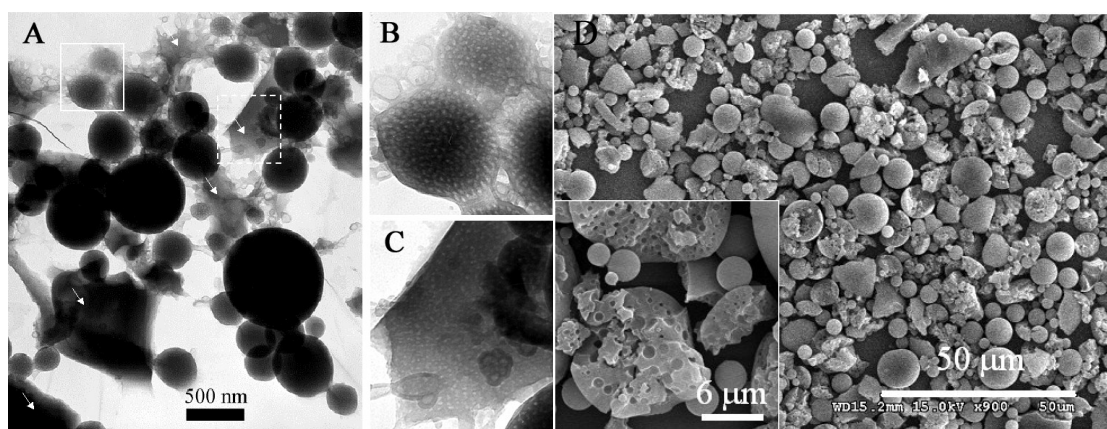


Fig. S4 TEM and SEM images of the gelled multi-compartment vesicles from PEO<sub>45</sub>-*b*-PTMSPMA<sub>180</sub> at  $C_{ini} = 20$  mg/mL in DMF and  $C_w = 51$  wt%. (A) TEM images; (B) and (C) are magnified images from A; (D) SEM images.

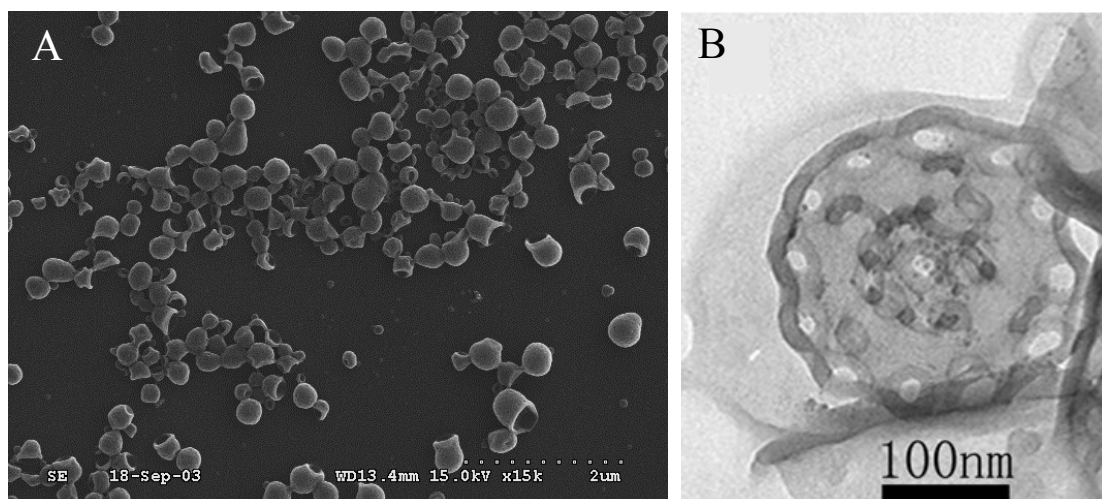


Fig. S5 SEM images (A) and higher magnification TEM images (B) of bag-like vesicles self-assembled from PEO<sub>45</sub>-*b*-PTMSPMA<sub>59</sub> diblock copolymer when the volume ratio of methanol: DMF: water is 0.5: 0.5: 1. The initial copolymer concentration in methanol/DMF is 20.0 mg/mL.

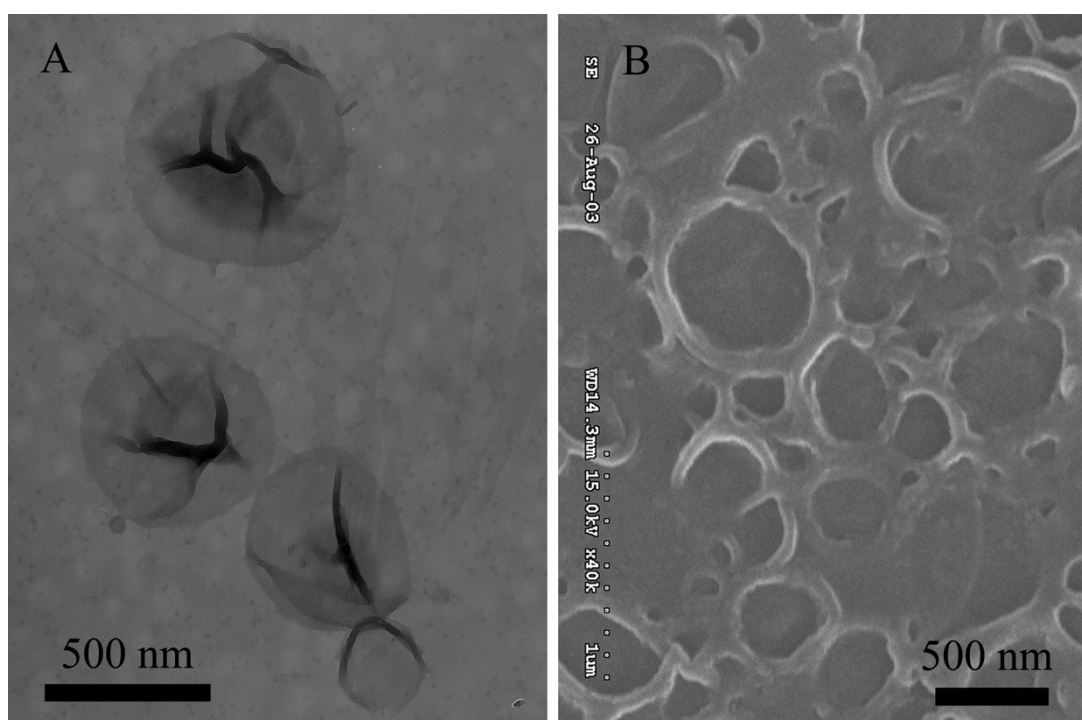


Fig. S6 TEM (A) and SEM (B) images of vesicles self-assembled from PEO<sub>45</sub>-*b*-PTMSPMA<sub>59</sub> copolymer when the volume ratio of dioxane/water is 1:1. The initial copolymer concentration is 2.0 mg/mL.

## References

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