Supporting Information

pH-Sensitive Vesicles Formed by Amphiphilic Grafted Copolymers with Tunable Membrane Permeability for Drug Loading/Release: A Multiscale Simulation Study

Zhonglin Luo[†,‡], Yan Li,[†] Biaobing Wang,[†] and Jianwen Jiang[*,‡]

[†]School of Material Science and Engineering, Jiangsu Collaborative Innovation Center of Photovolatic Science and Engineering, Changzhou University, Changzhou, Jiangsu, 213164, China

[‡]Department of Chemical and Biomolecular Engineering, National University of Singapore, 117576, Singapore

Table S1. Molecular weights and coarse-grained beads.

Component	MW (g/mol)	Volume per repeat unit (Å^3)	Number of repeat units (molecules) per bead	Number of beads
PAE	3822	480.4	1	14
PEG	2100	67.8	6	8
PLA	288 ~ 1152	111.3	4	1 ~ 4
H_2O	18	31.2	16	1
THF	72	140.2	3	1
DOX·HCl	580	723.8	0.66	1

Table S2. Solubility parameters (δ), van de Walls (δ_{vdW}) and electric (δ_{ele}) terms for PEG, PLA, PAE and PAEH blocks.

	δ	δ_{vdW}	δ_{ele}
PEG	20.93	19.48	7.67
PLA	19.73	18.25	7.49
PAE	19.27	18.38	5.81
PAEH	19.73	15.32	12.43

$\delta^2 = \delta_{vdw}^2 + \delta_{ele}^2$

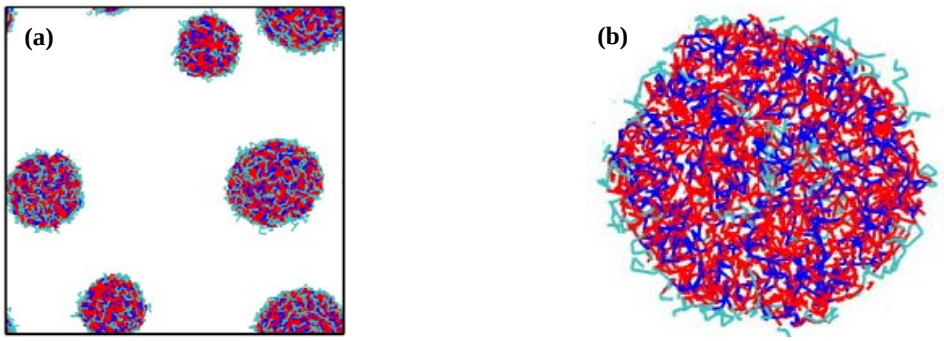

Figure S1. Morphology of 4% PAE_{14}-g-P(EG_8)(LA_3)$_{13}$ in H_2O (a) equilibrium snapshot and (b) section view. PEG, PAE and PLA are in cyan, blue and red, respectively. H_2O is not shown.

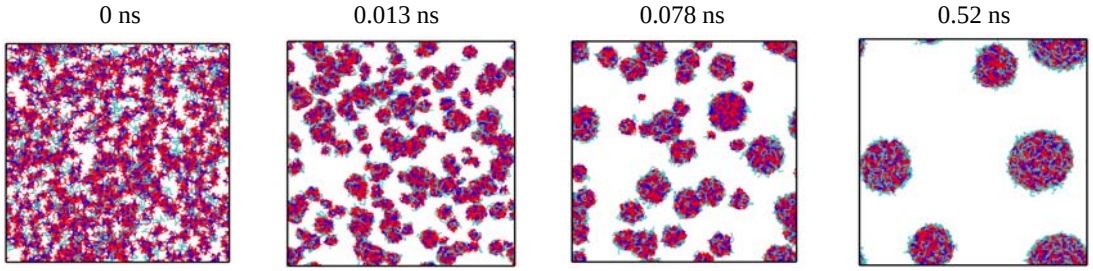

Figure S2. Dynamic assembly of 4% PAE_{14}-g-P(EG_8)(LA_3)$_{13}$ in H_2O. PEG, PAE and PLA are in cyan, blue and red, respectively. H_2O is not shown.

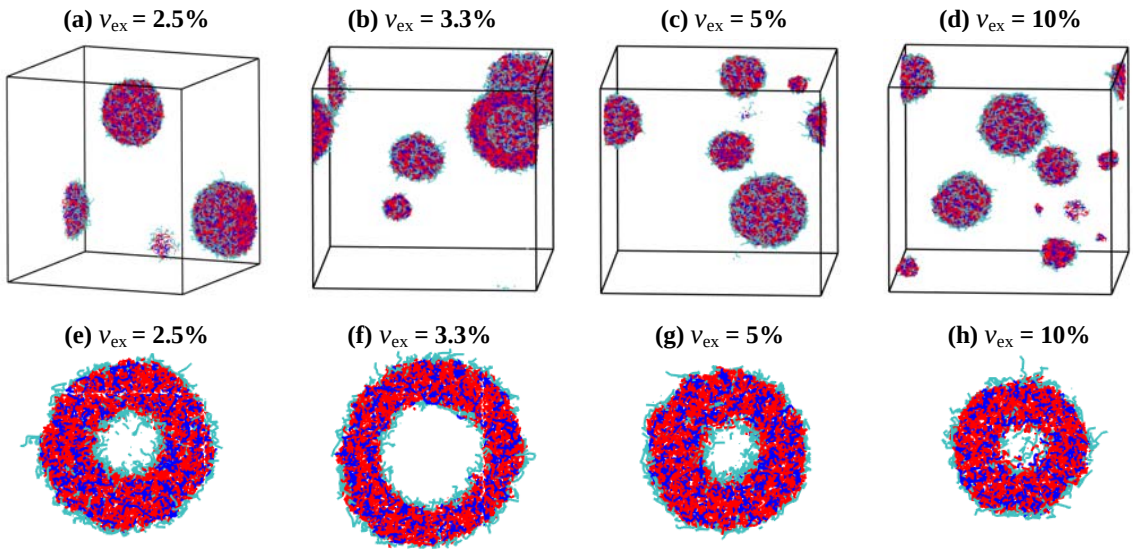

Figure S3. Morphologies of 4% PAE_{14}-g-P(EG_8)(LA_3)$_{13}$ formed after THF/H_2O exchange with t_{eq} = 6.5 ns and various v_{ex}: (a) 2.5% (b) 3.3% (c) 5% and (d) 10%. (e)-(h) are the section views of the largest vesicles in (a–d). PEG, PAE and PLA are in cyan, blue and red, respectively. H_2O is not shown.

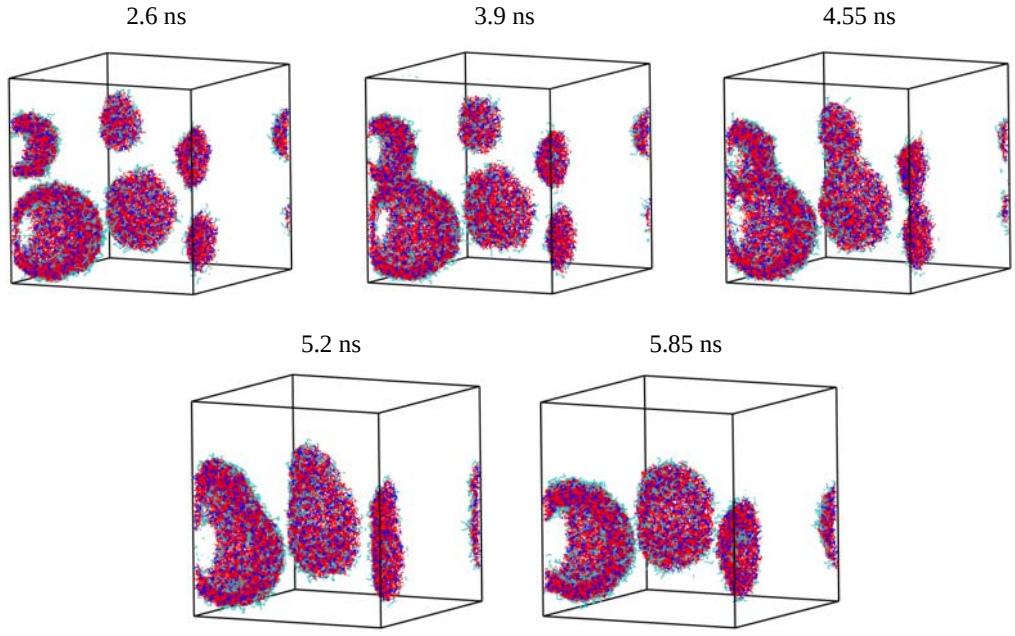

Figure S4. Dynamic fusion of 4% PAE_{14}-g-P(EG_8)(LA_3)$_{13}$ after multi-stage THF/H_2O exchange, first with v_{ex} = 2.5% and t_{eq} = 6.5 ns until 10% THF left, then with v_{ex} = 0.05% until 5% THF left, finally with v_{ex} = 0.025% until ϕ_{THF} = 4.325% (ϕ_{H_2O} = 95.675%). PEG, PAE and PLA are in cyan, blue and red, respectively. H_2O and THF are not shown.

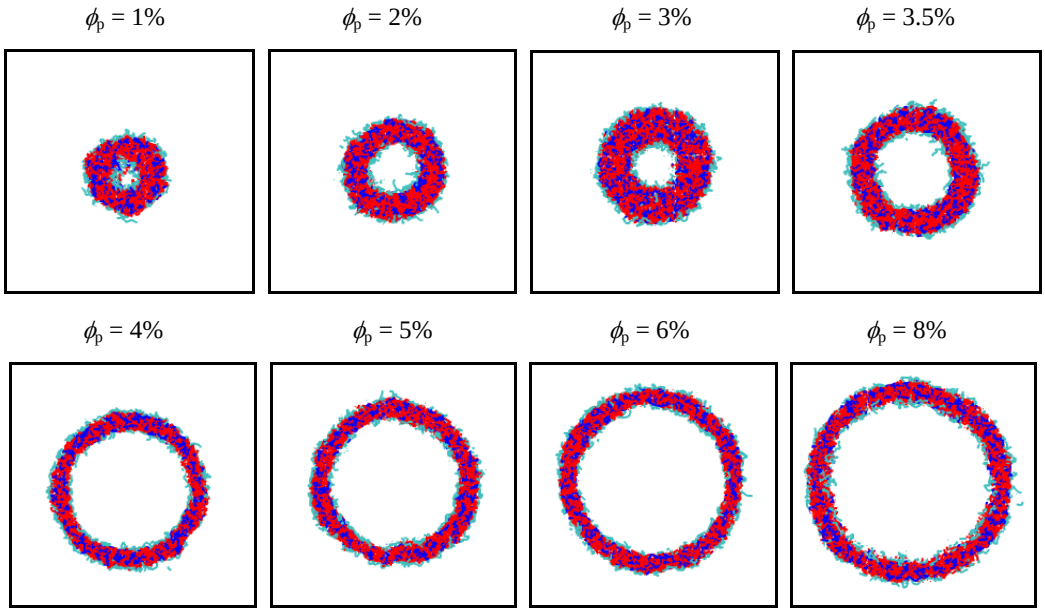

Figure S5. Typical vesicles formed by PAE_{14}-g-$P(EG_8)(LA_3)_{13}$ at various ϕ_p. PEG, PAE and PLA are in cyan, blue and red, respectively. H_2O is not shown.

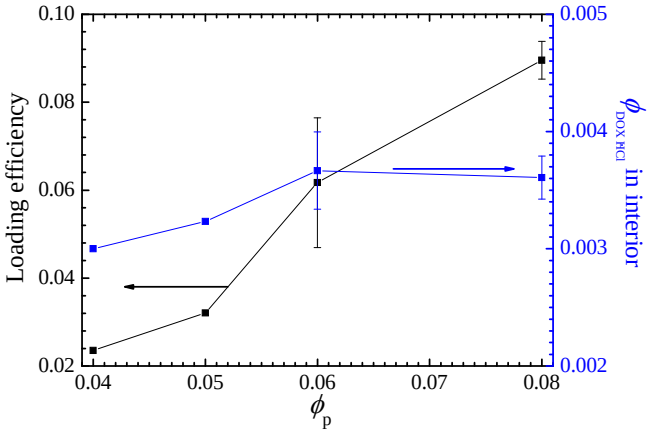

Figure S6. Loading efficiency and volume fraction of DOX·HCl in vesicle interior versus ϕ_p.