Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information

Controlling the self-assembly pathways of amphiphilic block copolymers into vesicles

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The three components of the radius of gyration R_{gx}^2, R_{gy}^2, R_{gz}^2 are also calculated. The difference between R_{gx}^2, R_{gy}^2, R_{gz}^2 becomes more obvious, which indicates the polymer chain takes an anisotropic configuration. Likewise, an asphericity parameter[1], A_s is used, which ranges from zero in the case of perfectly spherical structures to a value of 1 for rodlike species.

$$A_s = < \frac{(R_{gx}^2 - R_{gy}^2) + (R_{gx}^2 - R_{gz}^2) + (R_{gy}^2 - R_{gz}^2)}{2(R_{gx}^2 + R_{gy}^2 + R_{gz}^2)^2} >$$

Thus, the smaller value of the A_s indicates the more spherical shape of the aggregates. For relatively long hydrophobic block length, larger value of hydrophobic-solvent repulsion interaction or high copolymer concentration, with the transition from mechanism Ⅰ to mechanism Ⅱ, we can see the value of A_s decrease gradually.

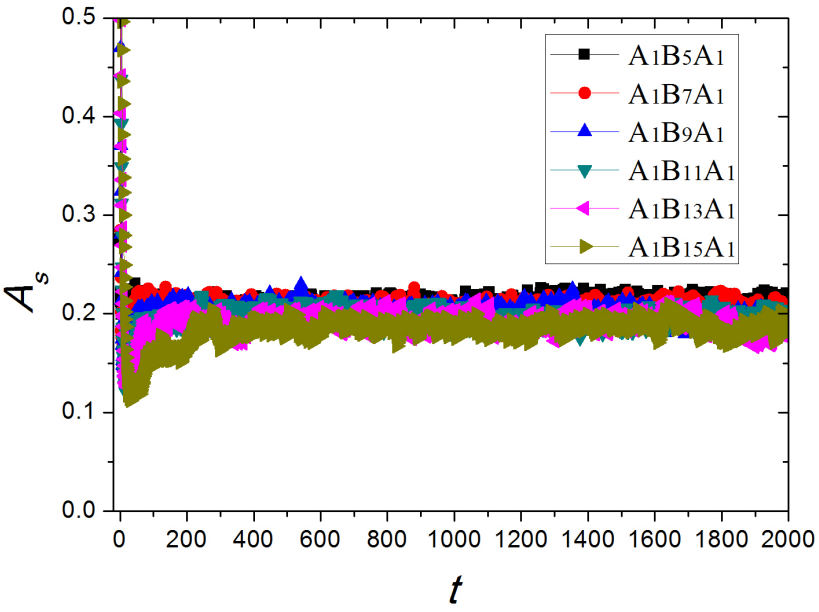

Fig. S1 The variation in A_s of the system of the six different block copolymers with time with a_{BS} = 75.

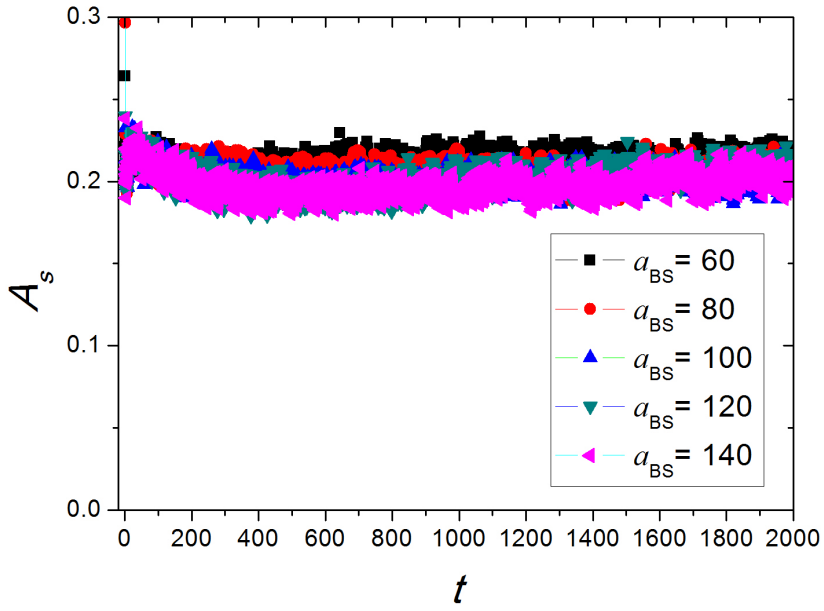

Fig. S2 The variation in A_s of the $A_1B_5A_1$ block copolymer with time with five different a_{BS}.

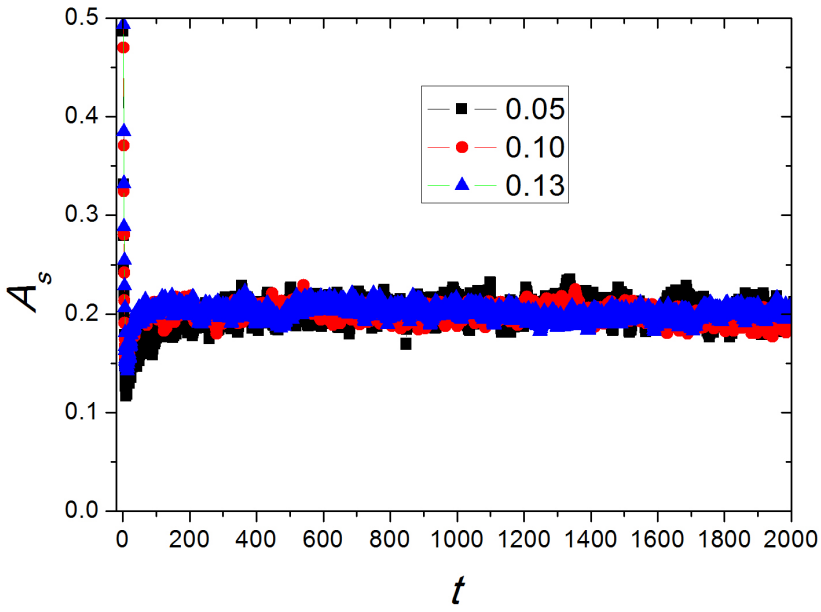

Fig. S3 The variation in A_s of the $A_1B_9A_1$ block copolymer with time at three different concentrations.

The polymer chain numbers of the A-bead inside the one picked vesicle obtained from the $A_1B_{11}A_1$ block copolymer with a_{BS} = 75 can be figured out at different time. The total polymer chain numbers can be calculated by

$$N_{chains} = \frac{L_x \times L_y \times L_z \times \rho \times c}{1+11+1} = [\frac{30^3 \times 3.0 \times 0.1}{13}] = 623$$

We can see that the chain numbers changes with time. The changes maybe fractional in a short time, but these changes can be accumulated in a long time. Thus, the vesicle formation is in a dynamic equilibrium and all the blocks can move around dynamically.

Tab. S1 Unit number of the hydrophilic beads A inside one picked vesicle.

t	**Unit number of the A-beads inside the picked vesicle**	**Varied beads**
1950	45, 54, 96, 133, 133	-
2250	15, 27, 45, 96, 115, 116, 124, 133, 133, 207	out 54 in 15, 27, 115, 116, 124, 207
2550	15, 27, 45, 96, 115, 116, 118, 124, 133, 133, 207	- in 118
3000	15, 25, 27, 45, 62, 96, 115, 116, 124, 126, 133, 133, 207	out 118 in 25, 62, 126
3600	15, 25, 27, 45, 62, 96, 115, 116, 116, 124, 126, 133, 144, 186, 207	out 133 in 116, 144, 186
4200	15, 25, 27, 38, 43, 45, 62, 96, 115, 116, 124,	out 116

	126, 133, 144, 186, 207	in 38, 43
4800	15, 15, 27, 28, 38, 43, 45, 57, 62, 96, 115, 116, 124, 126, 133, 144, 186, 207, 282	out 25 in 15, 28, 57, 282
6000	15, 15, 27, 28, 33, 35, 38, 42, 43, 57, 62, 96, 109, 115, 116, 124, 144, 207, 225, 282, 600	out 45, 126, 133, 186 in 33, 35, 42, 109, 225, 600
7500	15, 15, 27, 28, 28, 35, 38, 42, 43, 50, 57, 109, 115, 124, 144, 207, 225, 282, 519	out 33, 62, 96, 116, 600 in 28, 50, 519
9000	15, 15, 27, 28, 28, 33, 34, 38, 50, 54, 109, 109, 118, 124, 125, 201, 207, 282	out 35, 42, 43, 57, 115, 144, 225, 519 in 33, 34, 54, 109, 118, 125, 201

Reference

1 J. Rudnickt and G. Gaspari, *J. Phys. A: Math. Gen.*, 1986, **19**, L191.