Electronic Supplementary Material (ESI) for Soft Matter

Supporting information for [Kinetics of Multicompartment Micelles Formation by Self-assembly of ABC Miktoarm Star Terpolymer in Dilute Solution]

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The free energy of prolate vesicle (with the area ***S***) with ringlike AC strip structure equals:

$$F = (E_{\text{curvature}} + E_{\text{sst}}) / S \tag{1}$$

where $E_{\text{curvature}}$ and E_{sst} are the vesicle curvature energy and the free energy of phase separation in A and C two components in vesicle wall, respectively. Here, we neglect the thickness of vesicle wall. The curvature free energy is expressed as follows:

$$E_{\text{curvature}} = \oiint \frac{1}{2} k_c (C_1 + C_2 - C_0)^2 dS \tag{2}$$

where k_c is elastic moduli, C_1 and C_2 are the two principal curvatures of the specified surface, and C_0 is the spontaneous curvature which equals zero.

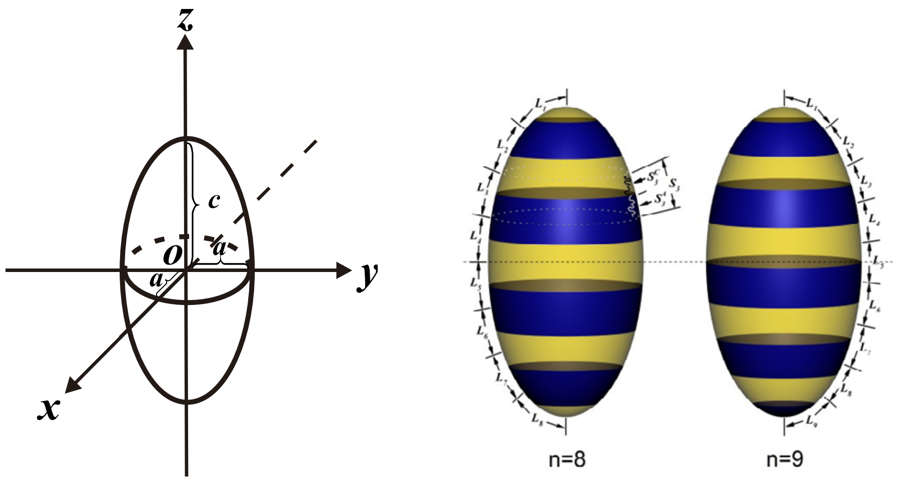


Figure S1

Figure S1 is the scheme of prolate ellipsoid. The minor and major axis are ***a*** and ***c***, respectively. The vesicle area S equals $S = 2\pi a^2 (1 + c \sin^{-1} e / (ae))$ where $e = \sqrt{1 - a^2 / c^2}$. The coordinates Y=(x, y, z) of oblate ellipsoid vesicle is expressed with polar coordinates:

$$Y = (a\sin\theta\cos\phi, a\sin\theta\sin\phi, c\cos\theta) \quad (0 \le \theta \le \pi, 0 \le \phi \le 2\pi) \tag{3}$$

The two principal curvatures C_1 and C_2 equal:

$$C_1 = \frac{ac}{(a^2\cos^2\theta + c^2\sin^2\theta)^{3/2}}, \quad C_2 = \frac{c}{a(a^2\cos^2\theta + c^2\sin^2\theta)^{1/2}} \tag{4}$$

The unit area dS equals:

$$dS = 2\pi(a\sin\theta)(\sqrt{a^2\cos^2\theta + c^2\sin^2\theta})d\theta \tag{5}$$

According to Eq.2, Eq.4, Eq.5 and defining the ratio of minor axis to major axis as $m = a/c$, the final expression of curvature energy is

$$E_{curvature} = \int_0^{\pi} k_c \pi m^{-1}(m^4 Q^{-3} + 2m^2 Q^{-2} + Q^{-1})\sin\theta\sqrt{Q}d\theta \tag{6}$$

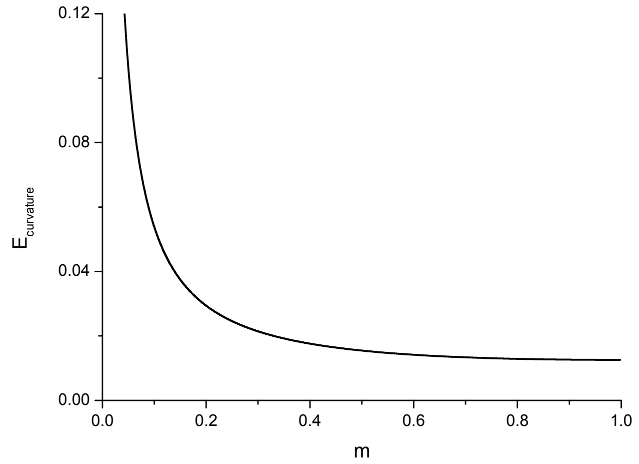
where $Q = m^2\cos^2\theta + \sin^2\theta$.

In Eq.1, the interface energy of A and C strip phase equals $E_{\text{interface}} = \sum_{i=1}^{n} 2\pi R_i \gamma$, where n is the interface number, γ is the tension of phase interface, R_i is the radius of the ith AC interface ring. Obviously, R_i equal $a\sin\theta_i$ according to Eq.3. The stretching length of chain in longitude direction in present model is assumed to be equal i.e., $L_i = L_j \ (i, j \in n)$. Meanwhile, the incompressible condition makes the A and C areas (S_i^A and S_i^C) at every copolymer layer equal $S_i^A = S_i^C (i = 1 \sim n)$. So, the elasticity energy of block polymer chain equals:

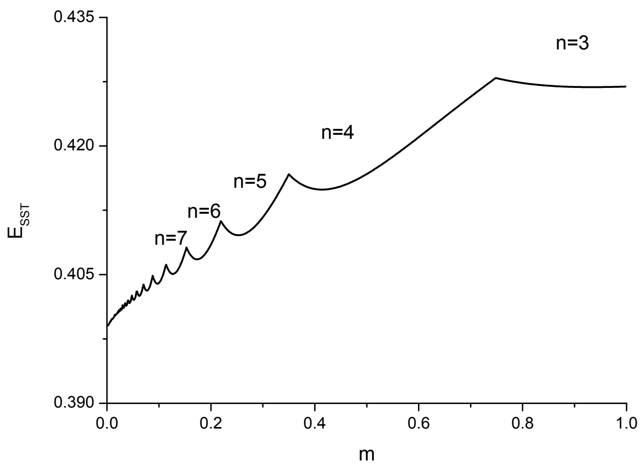
$$\begin{aligned} E_{\text{AC-elasticity}} &= \sum_{i=1}^{n} \iint_{S_i} \frac{1}{2} k_e l_i^2 dS_i \\ &= \sum_{i=1}^{n} \int_{L_i} \frac{1}{2} k_e l_i^2 (2\pi R_i^l) dL_i \end{aligned} \tag{9}$$

where k_e is the elastic module of polymer chain and l_i is the longitude arclength from area unit of S_i to the ith interface. R_i^l is the section radius of area unit of S_i parrallel to the ith AC interface.

In numerical calculation, ***a*** and ***c*** are firstly solved with the area equation of prolate ellipsoid after the area S, axis length ratio m and interface number n are fixed. Further, θ_i is numerically calculated to satisfies $L_i = L_j\ (i, j \in n)$ and $S_i^A = S_i^C (i = 1 \sim n)$. Then, total free energy F is numerically integrated from Eq.1, Eq.5 and Eq.9. Finally, the free energy at differently interface number n are compared to determine the stable structure with the lowest energy at fixed S and m. Figure S2 show the dependences of the curvature energy $E_{\text{curvature}}$ and phase separation energy E_{sst} on m, respectively, at $k_c = 5.0\times10^{-3}$, k_e=1.0, $\gamma = 0.03$ and S=5.



a



b

Figure S2. The dependences of the curvature energy $E_{\text{curvature}}$ and the energy E_{sst} of phase separation on m, respectively. $k_c = 5.0\times10^{-3}$, k_e=1.0, $\gamma = 0.03$. The vesicle area S equals 5.