Supporting Information

Shape-Anisotropic Diblock Copolymer Particles from Evaporative Emulsions: Experiment and Theory

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Figure S1. PS_{16k}-b-PDMS_{17k} dBCP particles stabilized by (a) SDS and (b) PVA. Use of SDS as the sole surfactant results in spherical particles with PS as the outermost layer, because the SDS surfactants at the particle surface prefer interacting with PS block over the PDMS block. By contrast, when the particles are produced by PVA surfactant solution, the PDMS block constitutes the droplet surface, because the PDMS domain has a stronger interaction with the PVA surfactants at the particle surface.

Figure S2. (a) TEM image of 3 μm-sized oblate PS_{31k}-b-PDMS_{17k} particle; (b) Voronoi diagram constructed from the locations of the PDMS domain centers in the oblate particles. White polygons indicate PDMS cylinders with six nearest neighbors, yellow polygons have five nearest neighbors, and red polygons have four nearest neighbors.
Figure S3. (a) Optical microscopy image of as prepared emulsions (evaporation time = 0 h); (b) Cryo-EM image of PS-b-PDMS particles acquired at evaporation times of 1 h. The initial chloroform emulsion droplets had spherical shape, with no observable microphase separated dBCP domain.
Details for the free energy calculation

Previous model to describe prolate particles from lamella-forming dBCPs was developed with three contributions: 1) entropic penalty associated with dBCP chain stretching, 2) interfacial energy between two blocks, and 3) surface energy between the surrounding medium and the dBCP particle. In this model, the stretching energy was calculated using the exact volume of prolate with the major axis of $L$ and the minor axis of $S$. The interfacial energy was calculated by summing all the interfacial areas between the stacked lamellae. And, the surface energy was calculated by multiplying the surface area of prolate particle by surface tension.

![Schematic illustration of the oblate particle](image)

**Figure S4.** Schematic illustration of the oblate particle with a width of $W$ and a height of $H$, respectively, consisting of $n$-layered (from the center to the periphery) dBCP cylinders.

To apply the same concept for the oblate particles from cylinder-forming dBCPs, we constructed the free energy model of the oblate particle with a width of $W$ and a height of $H$, consisting of $n$-layered (from the center to the periphery) dBCP cylinders (Figure S4) as followings:

$$
\frac{F_{ob}}{k_b T} = \frac{6A}{\pi b^2} \sqrt{\frac{N}{6}} + \frac{\pi^3 (1 - \sqrt{f})^2 W^4 H}{96(1-f)^2N^2b^5(2n-1)^2} 
$$

$$
+ \frac{\pi[(1-f)\gamma_{PS} + f\gamma_{PDM5}]}{2(1+\Sigma)^a} W^2 \left[ 1 + \frac{H^2}{2W^2\sqrt{1-H^2/W^2}} \ln \frac{1 + \sqrt{1-H^2/W^2}}{1 - \sqrt{1-H^2/W^2}} \right] 
$$

(S1)

The first and second terms in the right hand side (RHS) of Equation S1 present the interfacial energy between the two blocks and the chain stretching energy of the dBCPs, respectively, assuming that the oblate particle consists of closed-packed cylinder pillars. The last term is the surface energy between the dBCPs and surrounding medium. Total interfacial
area $A$ is calculated numerically based on given geometry of oblate particle. The AR values were plotted as a function of $W$ (orange line in Figure S6) by using this model. The deformation of the particle shape from sphere to oblate was restricted, increasing AR value only up to 2.2 even for very large particle size ($i.e.$, $W = 6.0 \mu m$).

To develop more realistic model, we add the bending energy term into the previous model. When the cylinders and lamellae of dBCPs are stacked within the oblate and prolate particle respectively, they are bent along with the particle surface. As a result, the dBCP chains cost high entropic penalty for bending either cylinders or lamellae compared to the unbent bulk cylinders and lamellae. It is assumed that the outmost layer contributes the most of total bending energy because the bending energy is rapidly reduced (scales with $C^2$) as the curvature is decreased for inner layers. Therefore, we approximate the total bending energy by considering the outmost layer as depicted in Figure S5.

![Figure S5](image)

**Figure S5.** Schematic illustration showing the total volume of curved polymer layers ($V_c$) and radius of curved cylinder or lamellae ($r$) with the curvature $C$ for the (a) oblate particle and (b) prolate particle.

The stretching energy and interfacial energy between two blocks of bent (curved) polymer layers ($C$ and $V_c$ as curvature and volume, respectively) were calculated separately by
using strong segregation theory (SST). The bending energy was calculated by subtracting free energy of bulk periodic BCP layer with $L_0$ as a periodicity from total free energy (stretching energy and interfacial energy) of bent layer. With the approximation of small curvature, the bending energy can be calculated explicitly by multiplying elastic modulus of bulk dBCPs (cylinders for oblate particles and lamellae for prolate particles) by square of curvature of curved layers ($C^2$), as shown in the equations S2 and S3.

\[
\frac{F_{bending, ob}}{k_BT} = \frac{\pi^2 (1 - \sqrt{f})^2 L_0^4 C^2 V_c}{512(1 - f)^2 N^2 b^5} \tag{S2}
\]

\[
\frac{F_{bending, pr}}{k_BT} = \frac{\pi^2 L_0^4 C^2 V_c}{1024 N^2 b^5} \tag{S3}
\]

Our new model that includes entropic penalty associated with bending of the dBCP chains correctly described the significant increase of AR as a function of the size of oblate particle (black line in Figure S6). For the reference, the AR calculation based on the model without considering the bending term is plotted as the orange line.

**Figure S6.** Theoretically calculated AR as a function of the width ($W$) of oblate PS$_{31k}$-$b$-PDMS$_{17k}$ particles based on the previous free energy model (orange) and our new theoretical model (black) that additionally considers the contribution of the entropic penalty associated with the bending of the dBCP chains. $\alpha = 0.9$ and $\beta = 0.85$ were used in this plot.
Figure S7. Plots of experimentally measured (●) and theoretically calculated (—) height ($H$) as a function of the width ($W$) for representative populations of oblate PS$_{31k}$-b-PDMS$_{17k}$ particles.
Figure S8. Schematic illustration showing release of bending energy of (a, b) curved cylinders and (c, d) curved lamellae by reducing the curvature ($C$) and volume ($V_c$) of curved layers. The amount of reduced bending energy is much larger for the oblate particles, leading to the almost linear increase of AR as the particle size increased.
Figure S9. Plots of calculated bending energy/surface energy per chain as a function of AR for the (a) oblate particle and (b) prolate particle; (c) Total free energy per chain as a function of AR for the oblate (red) and prolate (green) particles with $N = 527$ and diameter of spherical emulsion = 1000 nm.

Figure S10. Plots of calculated bending energy/surface energy per chain as a function of AR for the (a) oblate particle and (b) prolate particle; (c) Total free energy per chain as a function of AR for the oblate (red) and prolate (green) particles with $N = 527$ and diameter of spherical emulsion = 3000 nm.
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