Electronic Supplementary Material (ESI) for Chemical Society Reviews

Self-Assembly of Block Copolymers

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Discussion of the Decrease in the Dimension of the PS Region, S_c, and A_c as the Morphology Changes from Spheres to Cylinders and to Lamellae or Vesicles

The discussion starts with A_c. For dry spheres, the values of the A_c can be calculated from the radius of the core (R_{core}), as given in eq. (S1):

$$A_c = 4\pi R_{core}^2 / N_{agg} \qquad \text{(S1)}$$

where N_{agg} is the aggregation number, which is defined as the average total number of polymer chains in an aggregate, and can be calculated from

$$N_{agg} = \frac{4}{3}\pi R_{core}^3 / V_s N_{PS} \qquad \text{(S2)}$$

where V_s is the volume per polystyrene repeat unit (0.167 nm^3), N_{PS} represents the degree of polymerization of PS block. A combination of eqs. (S1) and (S2) yields the relationship between A_c and R_{core} as

$$A_{c,\,spheres} = 3V_s N_{PS} / R_{core} \qquad \text{(S3)}$$

Similar to the derivation of eq. (S3) for spheres, one can also obtain equations for cylinders and lamellae, respectively

$$A_{c,\,cylinders} = 2V_s N_{PS} / R_{core} \qquad \text{(S4)}$$

$$A_{\text{c, lamellae}} = V_{\text{s}} N_{\text{PS}} / R \qquad \text{(S5)}$$

For lamellae, R is half the lamellar thickness. Clearly, for each morphology, the value of A_{c} decreases as the dimension of the PS region (R_{core} or R) increases. However, among these three different structures, the values of A_{c} are different, and characterized by the factors of 3, 2 and 1 in eq. (S3), (S4), and (S5), respectively; a spherical micelle has the largest A_{c} and the lamellae the smallest. Thus, A_{c} usually decreases as the morphology changes from spheres to cylinders and to lamellae (vesicles are formed by the closing of open lamellae).

The discussion of the decreases in the dimension of the PS region and S_{c} as the morphology changes can start with the morphological transition from spheres to cylinders. According to eqs. (S3) and (S4), although the A_{c} of the cylinders is usually smaller than that of the spheres, it cannot be too small. Otherwise, the repulsion among the corona chains would be too strong and the cylinders would be unstable. When spheres with a core radius of R_{core} transform to cylinders, the core radius of the cylinders generally tends to be smaller than R_{core}. Otherwise, the A_{c} of the cylinders would be much smaller than that of the spheres, which makes the cylinders unstable. However, the core radius of the cylinders cannot be reduced infinitely because of the increased total interfacial energy between the core and the nonsolvent, which is induced by increases in the A_{c} and in the total interfacial area as the core size decreases. As a result, the cylinders decrease their core dimensions to some extent, and the degree of stretching of the PS blocks decreases correspondingly. The same principle applies to the morphological transition from cylinders to bilayers. Thus, the PS chains in spherical micelles are usually more stretched than in cylindrical micelles, in which they are more stretched than in lamellae or vesicles.