A Simple Scaling for the Core−Shell Nanostructure Formed by Self-Assembly of Block Copolymers in a Selective Solvent

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Introduction

Polymeric core−shell nanostructure can be formed through the self-assembly of diblock or triblock copolymers in a selective solvent in which only one block is soluble.[1−5] For example, poly(ethylene oxide)-*b*-poly-(propylene oxide) (PEO-*b*-PPO) was one of the mostly studied block copolymers because at temperatures higher than ∼20 °C the PPO block become insoluble in water.[2−4] The self-assembly of the insoluble PPO blocks could result in a core−shell nanostructure with the PPO blocks as the core and the soluble PEO blocks as the shell. Such core−shell nanostructures have been experimentally confirmed by both dynamic laser light scattering[6] and small-angle neutron scattering[7] and attracted much attention both in theory and in practice.[8] Pioneered by de Gennes,[9] different theories have been proposed to describe the formation of copolymeric micelles and to predict the size and the association number in terms of the lengths of both the blocks and the polymer chain.[10,11] Thermodynamically, Noolandi et al.[11] calculated the core/water interfacial energy and the conformational distortion energy of the soluble blocks, which involves many parameters.

Recently, we proposed and proved a simple structural model for the stabilization of colloidal particles;[12] namely, for each given stable dispersion, the surface area occupied per stabilizer, which could be surfactant or ionic group or polymer chains, approaches a constant, independent of the particle size. Encouraged by the success of this structural model in the study of polymeric dispersion, we thought that for the core−shell nanostructure made of block copolymers, the surface area (*s*) occupied by each soluble block in the shell, which is also acted as a stabilizer, should also be a constant. For the polymeric micelle made of triblock copolymer PEO-*b*-PPO-*b*-PEO (E$_m$P$_n$E$_m$), where *m* and *n* are the numbers of the repeating EO and PO units, respectively, the radius of the core (*R$_c$*) was inversely proportional to *m* for a constant *n*,[13] indicating a possible simple scaling for such a core−shell nanostructure. Enlightened by the similarity between the core−shell nanostructure and the adsorption of polymer chains on a nanoparticle, we proposed a simple scaling for the core−shell nanostructure as follows.

Basic Principle

Let us follow Noolandi's notation;[11] namely, the core has a radius of *R$_c$*, the shell has a thickness of δ, and

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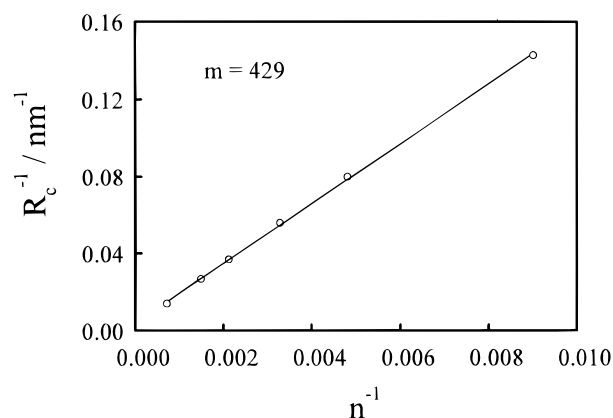* To whom the correspondence should be made.

Figure 1. Replot of the data presented in Table 3 of ref 14 for the self-assembly of the block copolymer poly(ethylene oxide)-*b*-poly(propylene oxide) (E$_m$P$_n$) in water at 25 °C where R_c is the radius of the core and *n* is the number of the repeating units of the insoluble block.

the numbers of the repeating units of the soluble and insoluble blocks are *m* and *n*, respectively. For a short soluble block, the shell made of the packed blocks can be viewed as a polymer brush, or in other words, it can be treated as a quasi-planar (one-dimensional) problem. If a core−shell nanostructure is made of *N* copolymer chains, the mass of the core should be proportional to both *N* and *n*, i.e.,

$$\rho_c(4/3)\pi R_c^3 \propto Nn \tag{1}$$

where ρ_c is the density of the core. On the other hand, the surface area of the core ($4\pi R_c^2$) is related to the average surface area (*s*) occupied per soluble block by

$$4\pi R_c^2 \propto Ns \tag{2}$$

Considering the soluble block as a polymer chain grafted on the core with a random coil conformation, we know that *s* should be proportional to the cross section of the coil, i.e., $s \propto r^2$ with *r* being the radius of the coil. Further considering that the soluble blocks packed on the surface are in the Flory Θ-state, we know that the cross section of a random coil is proportional to the chain length, i.e., $r^2 \propto m$. Therefore, we can rewrite eq 2 as

$$4\pi R_c^2 \propto Nm \tag{3}$$

The ratio of eqs 3 and 1 leads to a simple scaling,

$$R_c^{-1} \propto m/n \tag{4}$$

where we assumed that ρ_c is a constant for a given type of the insoluble block. It shows that for a given length of the insoluble block $R_c^{-1} \propto m$, i.e., the larger the soluble block, the smaller the core, while for a given length of the soluble block, $R_c^{-1} \propto n^{-1}$, i.e., the size of the core increases as the length of the insoluble block, which is reasonable.

Experimental Evidence

Figure 1 shows a replot of the data presented in ref 14. It is clear that, for a given series of block copolymers
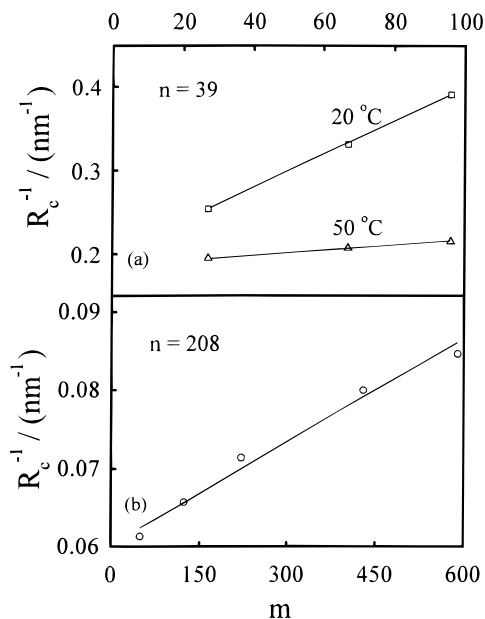
Figure 2. (a) Replot of Figure 11 in ref 13 for the self-assembly of the block copolymer poly(ethylene oxide)-*b*-poly-(propylene oxide) ($E_mP_nE_m$) in water at 20 and 50 °C. (b) Plot of the results in Table 3 in ref 14 for the self-assembly of the block copolymer poly(ethylene oxide)-*b*-poly(propylene oxide) (E_mP_n) in water at 25 °C, where R_c is the radius of the core and *m* is the number of the repeating units of the soluble block.

with a given length of the soluble block (i.e., *m* is a constant), R_c^{-1} is indeed proportional to n^{-1}. On the other hand, Figure 2 shows a replot of the results shown in refs 13 and 14. It confirms the prediction of eq 4. It should be noted that the chain connectivity in $E_mP_nE_m$ only affects the prefactor, not the scaling exponents. It is interesting to note that the slope of the line at 20 °C is larger than that at 50 °C, which is reasonable because at lower temperatures, water is a better solvent for the soluble PEO block so that it is more expanded and able to stabilize a larger surface area. To create more total surface of the core, the core must be smaller. Therefore, for a given PEO/PPO composition, lower temperature led to a smaller core. Further, it has been known that, for short polymer chains densely grafted or anchored on a surface, the thickness (δ) of the polymer layer is related to the number density (σ) of the chain on the surface by $\delta \propto m\sigma^{1/3}$.[1,13,15,16] For the self-assembly of *N* diblock copolymer chains, the number density (σ) of the soluble blocks on the surface of the core is

$$\sigma \propto N/(4\pi R_c^2) \qquad (5)$$

A combination of eqs 3 and 5 leads to $\sigma \propto m^{-1}$. Therefore,

$$\delta \propto m^{2/3} \qquad (6)$$

Figure 3 shows that, for a set of block copolymers with a given length of the insoluble blocks, δ is indeed a linear function of $m^{2/3}$.

In summary, using a simple structural model and assuming that the surface area occupied per stabilizer (soluble block) is a constant for a given polymer/solvent system, we obtained a scaling for the core−shell nano-
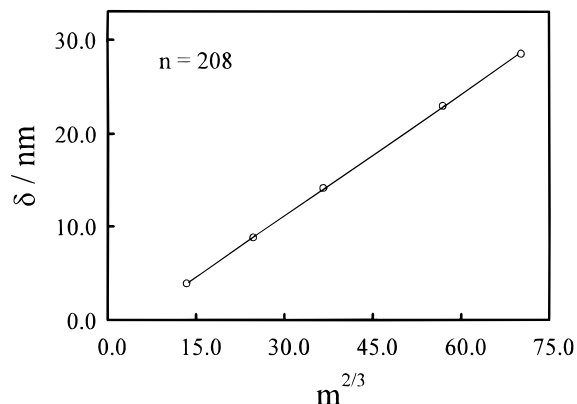

Figure 3. Replot of the data in Table 3 in ref 14 for the self-assembly of the block copolymer poly(ethylene oxide)-*b*-poly-(propylene oxide) (E_mP_n) in water at 25 °C, where δ is the thickness of the soluble shell, *m* is the number of the repeating units of the soluble block, and R_c is the radius of the core.

structure formed through the self-assembly of block copolymers in a selective solvent; namely, the radius of the core (R_c) and the thickness of the shell (δ) can be scaled to the copolymer composition, i.e., $R_c^{-1} \propto m/n$ and $\delta \propto m^{2/3}$, where *m* and *n* respectively are the numbers of the repeating units of the soluble and insoluble blocks in a A_mB_n or $A_mB_nA_m$ type block copolymers. Note that the model presented here should not conform with a very small core (e.g., starlike polymers) because it is no long a quasi-planar (one-dimensional), but a spherical (three-dimensional), problem.

References and Notes

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