



Soft patchy micelles



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ABSTRACT

Colloids with patches, which refer physically or chemically distinct domains at their surface, have broadened the range of complex superstructures that can be achieved by self-assembly. Similarly, patches are recently introduced on micelles which are called “soft patchy micelles”. Due to soft interaction potential between patches on micelles, it holds great potential to form unique soft superstructures at nanoscale. In this review, we first describe a recent development in the synthesis of soft patchy micelles. Diblock amphiphilic copolymers are encapsulated into uniform emulsion which are then aggregated and reformed into patchy micelles with surfactants at interface. Alternatively, triblock amphiphilic copolymers are assembled into uniform spherical patchy micelles via stepwise micellization process. For cylindrical or platelet micelles, block copolymers with crystallizable core-forming blocks are introduced for monodisperse cylindrical or platelet patchy micelles by sequential growth of core blocks. Finally, we discuss how those soft patchy micelles are assembled into two or three-dimensional superstructures by hydrophobic-hydrophobic interaction, electrostatic attraction or coordination between patches, showing potentials of micellar structure as a soft designer micelles.

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1. Introduction

Patchy colloids were introduced a few decades ago for colloidal superstructures [1], of which main motivation was building up better photonic crystals other than face-centered cubic crystals. In comparison to colloidal spheres with isotropic interaction, patchy colloids provide pre-determined directional interaction between them which enables designing of non-conventional superstructures with low coordination superlattices. In early works using colloidal spheres, various types of colloidal clusters have been assembled with homopolymers or small nanoparticles to conceal the main body of clusters leaving edges of particles exposed [2]. This strategy is further developed for the colloidal patchy particles with chemically distinct patches, and finally, DNA has been selected as a programmable patch [3] which opens a new era for realizing colloidal architectures theoretically for any kinds of crystal structures. Concept of patchy particle has also been investigated for patchy nanoparticles toward nanoscale self-assembled structures (Fig. 1a). For instance, gold nanorods are synthesized which are mainly decorated with surfactant around side due to preferential adsorption of surfactants on less dense crystal plane and then polymer ligands are later coated selectively on both ends (Fig. 1b) [4]. They could form

small clusters, linear chains with branch and other complex structures by either end-to-end assembly [4] or side-by-side assembly [5–7].

Molecular aggregates of amphiphilic molecules such as surfactant form soft colloids by themselves called ‘micelles’, in which insoluble blocks form core and soluble blocks form shell or corona. When amphiphilic block copolymers (BCPs) are organized into micelles, soft colloids can be formed in which molecular architectures of BCPs such as volume ratio between blocks, number of blocks, and interaction parameters that can determine the structures. Interestingly, when molecules at surface are organized forming chemically or physically distinctive patches (Fig. 1c), such structured molecular assemblies are called as ‘soft patchy micelles’ [8].

The aggregation process toward micelles depends on the type of amphiphilic molecules and the solvent. As concentration of amphiphilic molecules increases, they form colloidal aggregates and forms stable micelles above their certain concentration called critical micelle concentration (CMC), in which physicochemical properties can be abruptly changed. The difference between micelles and other colloids is that micelles are in dynamic equilibrium with monomers in the solution. Therefore, micelles represent dynamic association-dissociation equilibria and it could be advantageous for building energetically stable or metastable self-assembled structures in situ. However, for patchiness, micellar structure should be structurally more stable rather than dynamic or metastable. Nevertheless, micellar structures are still deformed and intrinsically very flexible when they are bound and

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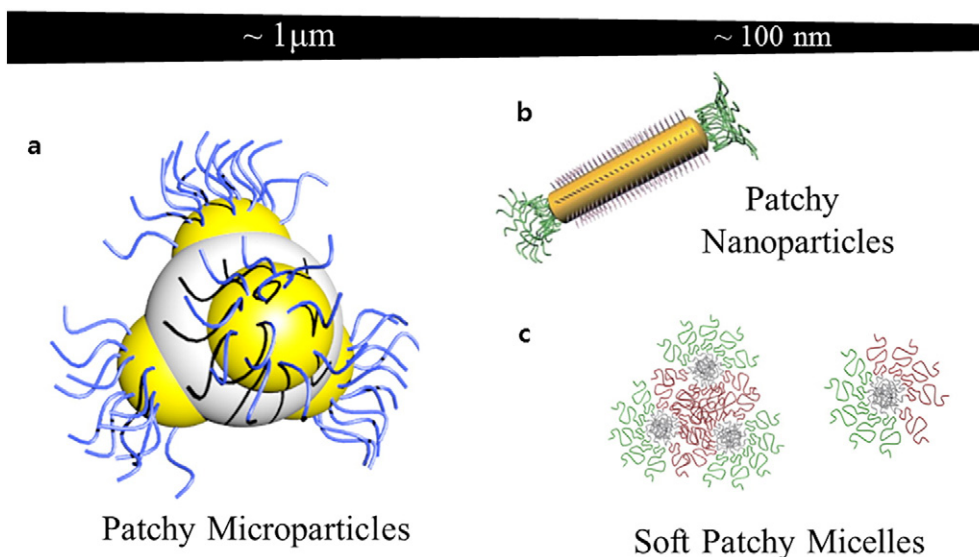


Fig. 1. (a) Patchy particles (b) Patchy nanoparticles with surfactant (ligand). Reprinted from ref. [4]. Copyright 2007 Nature Publishing Group. (c) Soft patchy micelles.

their interaction potentials are also very soft between patches unlike patchy particles with solid cores.

In this review article, we introduce recent advances of soft patchy micelles with spherical, cylindrical, or platelet shape in the aspects of theoretical background, experimental results on how amphiphilic BCPs are organized into micelles, state-of-the-art of soft patchy micelles, and finally, their self-assembled superstructures.

2. Monodisperse micelles of BCPs

In general, solubility of polymers in solvent depends on the type of repeating unit as well as molecular weight or the number of repeating

unit, which are significant enough to induce phase separation in solution or mixture melt. In the presence of surfactant, therefore, oligomers or polymers can be precipitated forming nuclei during dispersion polymerization. Otherwise, they can be polymerized on the pre-existing nuclei or surface. In the similar manner, mixture melts are separated into distinct multiple phases with the help of compatibilizer (or surfactants).

BCPs show unique self-assembly behaviors since two unfriendly repeating units are bounded together limiting total phase separation. As a result, well-defined polymeric nanostructures, including lamellae, bicontinuous gyroid, hexagonally packed cylinders, and body-centered cubic spheres, can be developed in mixture melts depending on their molecular topology structures (e.g., linear, graft, star-shaped) or

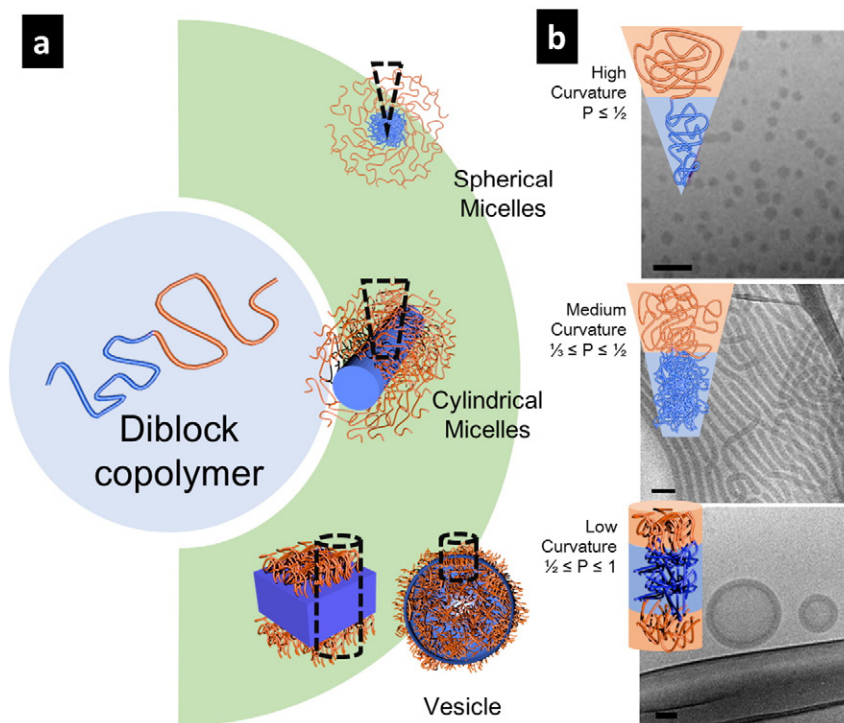


Fig. 2. (a) BCPs form various self-assembled micellar structures in solution. (b) Due to the inherent curvature of the molecule, spherical, cylindrical, bilayer (or vesicle) micelles formed which can be estimated through calculation of its packing parameter [9,10]. TEM images are reprinted from ref. [10]. Copyright 2013 Nature Publishing Group.

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