



Hierarchical composite microstructures fabricated at the air/liquid interface through multilevel self-assembly of block copolymers



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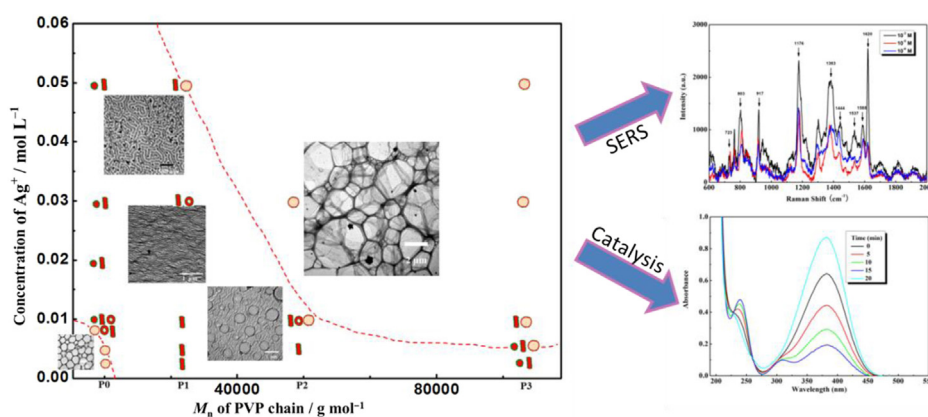
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HIGHLIGHTS

- Thin films of block copolymers with hierarchical microstructures were fabricated.
- The fabrication process involves in solution self-assembly and interface adsorption.
- The microstructures can be tuned finely by varying the experimental parameters.
- The length of the blocks affects the microstructures greatly.
- The SERS and catalytic properties of the microstructures were investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

Hierarchical composite microstructures of block copolymers, polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP)/Ag have been fabricated successfully at the air/liquid interface through a self-assembly and adsorption process. The films with various morphologies including foam, nanorod and nanowire array, hollow sphere, and nanosphere were obtained. These morphologies are closely related to the aggregates formed in the aqueous phase, such as microcapsules, cylindrical micelles, vesicles and spherical micelles, which can be controlled by tuning the critical packing parameters of the amphiphilic block copolymer molecules through changing the concentration of Ag⁺ ions in the aqueous solution. The length of the P2VP blocks in the PS-*b*-P2VPs exerts great influences on the self-assembly behavior of the polymers and the final microstructures, which provides a deep insight into the formation mechanism of the microstructures. Additionally, these hybrid films doped with silver nanoparticles provide potential application in surface enhanced Raman scattering (SERS) and catalysis.

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1. Introduction

Block copolymers composed of two or more chemically distinct polymer chains have received considerable attention due to their ability to microphase separation in bulk [1–3], in thin films [4–6] and in solutions. The level of complexity for block copolymers self-assembly in solution can be increased by solvent introduc-

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tion, where amphiphilic block copolymers can self-assemble into various aggregates including spherical and rod-like micelles [7,8], vesicles [9], capsules [10], and so on.

A wide variety of methods have been utilized in the preparation of block copolymer aggregates in solution. A dominant approach for preparing block copolymer assemblies, involves the addition of a selective solvent into a miscible common solvent containing the amphiphilic block copolymer to gradually decrease the solubility for one block, resulting in the formation of aggregates [11–13]. Another method is the direct dissolution method, in which the copolymer is simply added to the solvent at a concentration above the critical micelle concentration (cmc) and block copolymers are allowed to assemble into micelles [14]. If the copolymer is not readily soluble in water, the “emulsion and solvent evaporation” procedure can be utilized. Typically, the copolymers dissolved in a volatile non-water-miscible organic solvent is firstly dispersed in water to form an emulsion with the aid of a surfactant to stabilize the droplets, and upon gradual solvent removal by slow evaporation the copolymer dispersed in water are aggregated [15–18]. The next method is the film casting method which involves the dissolution of the copolymer in a volatile solvent which is then evaporated to leave a film with hierarchical structures in the bottom of a vial to be used, followed by solvent annealing under saturated organic solvent atmosphere. Finally, a certain selective solvent is then added with agitation to dissolve the polymer film to obtain the well-defined aggregates [19–21]. Recent works on the preparation of vesicles and micelles on the basis of amphiphilic block copolymers come up with the theory of the “Ouzo effect” [22–26]. The “Ouzo effect” or the spontaneous emulsification effect is a phenomenon observed when water is added to Ouzo (Greek liquor) forming a milky and highly stable oil-in-water emulsion. To make use of the Ouzo effect for the formation of nanoparticles, the polymer has to be soluble in an organic solvent which is miscible with water. Another recently developed strategy for micellization via self-assembly of polymer blends in solution is as follows [27–29]. If polymers A and B, which are able to interact with each other via molecular interactions such as hydrogen bonding, are dissolved in a solvent that is a precipitant for A but good solvent for B, A chains aggregate but macroscopic precipitation can be prevented by the soluble B chains. Therefore, micelle-like particles with a core of A chains surrounded by the corona of B chains are formed. Other techniques for the preparation of block copolymer aggregates include electro-formation [30], microfluidic techniques [31,32], and so on.

Langmuir monolayer technique has been widely applied to fabricate low dimensional supramolecular assemblies and ultrathin films of block copolymers at the air/water interface. By means of varying the experimental conditions such as the relative length of polymer blocks, temperature, molecular weight, and solvent etc., various aggregates including dots (circular aggregates), spaghetti (rod-like aggregates), and continents (planar aggregates) were obtained [33–36]. The circular micelles of PS-b-P2VP associates to form a laced network structure under low pH at the air/water interface as a balance of the hydrophobic attraction between the PS cores and the electrostatic repulsion between the ionized P2VP blocks submerged in the water [37]. Another recent work showed the mixed Langmuir monolayers of homo-PS and the symmetric PS-b-P2VP formed the necklace-network structures at the air/water interface [38]. Langmuir monolayers of PS-b-P2VP (with the same PS block length and different P2VP block lengths) spread with a nonselective solvent only exhibited isolated circular micelles, while those with a selective solvent exhibited quite different morphologies including planar structure, rodlike structure, circular micelles, and labyrinth pattern [39]. There are three mechanisms proposed to describe the aggregation phenomenon at the air/water interface: spontaneous surface aggregation [40], compression induced

surface aggregation [41,42], and simple deposition of the micelles formed in the spreading solution [43].

On the other hand, the composite microstructures of block copolymer/inorganic species have attracted great attention. The inorganic species can be embedded in the block copolymer microstructure through several approaches, such as in situ formation of nanoparticles within polymer material [44], directly mixing nanoparticles with polymers [45], self-assembly of nanoparticles and polymers through various supramolecular interactions, copolymerization of surface-modified NPs with polymers [46], and grafting of polymers onto nanoparticle surfaces [47]. These composite structures exhibit unique properties, for instance, electrical conductivity [48], luminescence [49,50], catalyst [51], and so on.

Very recently, we have developed a convenient, rapid and robust approach [52] to construct microstructures of block copolymers at the air/water interface. This method consists of several successive steps, i.e. phase transfer across the liquid/liquid interface, self-assembly in the aqueous solution, adsorption and organization at the air/water interface. Compared with the traditional Langmuir monolayer technique, this is a facile and rapid approach without use of expensive instruments. In addition, unique microstructures can be fabricated through this approach, which are different obviously from those obtained by using Langmuir monolayer technique. This is an effective method to fabricate hierarchical microstructures and composite thin films of block copolymers, which deserves to be investigated further.

Here, we studied the accessibility and versatility of this method using a series of PS-b-P2VPs with similar PS chain lengths and different P2VP chain lengths. It was found that various microstructures formed at the air/water interface. The molecular structure of the block copolymers and other experimental conditions, such as the concentration of Ag⁺ ions in the aqueous solution have great effects on the self-assembly behavior of the polymer molecules and the morphology of the formed microstructures. The fabrication mechanism was investigated and the regularities were summarized. In addition, silver nanoparticles were generated during the fabrication process and distributed on the surface of the microstructures. The SERS property of these composite microstructures was investigated, and the catalytic activity was evaluated by using the hydrogenation of nitroarenes in aqueous solutions.

2. Experimental section

2.1. Chemicals

The block copolymer PS-b-P2VP with two blocks with M_n values of 110000/12500 ($M_w/M_n = 1.09$, denoted as P0), 101000/29000 ($M_w/M_n = 1.09$, P1), 101000/52000 ($M_w/M_n = 1.06$, P2), and 102000/97000 g mol⁻¹ ($M_w/M_n = 1.06$, P3) were purchased from Polymer Source (Canada) and used as received. DMF ($\geq 99.5\%$) was obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), and used as received. Chloroform (analytical reagent) was obtained from Tianjin Guangcheng Chem. Co. The water used was highly purified using a UP water purification system (UPHW-IV-90T, Chengdu China) with a resistivity ≥ 18.0 M Ω cm. AgNO₃ (99 +%) and KBH₄ ($\geq 97.0\%$) were purchased from Zhanyun Chem. Co. Ltd. 4-nitroaniline (4-NA, $\geq 99.5\%$) was supplied by Tianjin Kemiou Chem. Reagent Co., Ltd. Crystal violet (CV) was purchased from Sinopharm Chemical Reagent Company (Chengdu, China).

2.2. Preparation of the composite thin film

The fabrication process of the composite thin film was described as follows. First, a certain amount of PS-b-P2VP was dissolved in DMF and then a certain amount of CHCl₃ was added to form a mixed

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