Development of various PS-*b*-P4VP micellar morphologies: Fabrication of inorganic nanostructures from micellar templates

Heesook Cho [a], Hyungmin Park [a], Soojin Park [a,*], Heungyeal Choi [b], Haiying Huang [b], Taihyun Chang [b]

[a] *Interdisciplinary School of Green Energy, Ulsan National Institute of Science and Technology, Banyeon-ri 100, Ulsan 689-798, Republic of Korea*
[b] *Department of Chemistry, POSTECH, Pohang 790-784, Republic of Korea*

ABSTRACT

We demonstrate a simple route for preparing various micellar nanostructures, like spheres, cylinders, and vesicles, by spin-coating or drop-casting process of polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) copolymer solutions in pure tetrahydrofuran (THF), THF/water, and THF/ethanol mixture. Upon drying, a solvent selectivity plays an important role in determining micellar nanostructures in thin films. In solution, micellar sizes and shapes of these PS-*b*-P4VP copolymers were investigated by dynamic and static light scattering. Immediately after spin-coating the polymer solutions, surface and internal morphologies of the films were observed by atomic force microscopy and transmission electron microscopy. As the polymer concentration in THF or the amounts of water or ethanol added in THF solutions was varied, a remarkable difference in the PS-*b*-P4VP micellar morphologies was observed, from which spherical or cylindrical or vesicular micelles were developed. These micellar films were used as scaffolds or templates for fabricating metal nanodots or nanowires arrays.

© 2011 Elsevier Inc. All rights reserved.

1. Introduction

Block copolymers (BCPs) with two immiscible blocks can self-assemble to form ordered arrays of nanostructures in selective solvent, which is a good solvent for one of the blocks, but a poor one for the other, to produce well-organized micellar aggregates, like spheres, cylinders, vesicles, and more complex architectures [1–5]. The most common micellar structures, spherical micelles, are composed of a spherical core surrounded by corona chains whose characteristics depend on chemical composition, molecular weight, molecular architecture, and block affinity [6–9]. The micelle formation of BCPs is driven by the unfavorable interactions between the selective solvent and the insoluble blocks, which are willing to aggregate to minimize their contact with the solvent [10]. Other specific micellar aggregates, like cylindrical micelles, vesicles, crew-cut micelles, and micelles with multi-compartment, can also be realized by controlling various factors, such as composition, ionic strength, polymer concentration, sample preparation conditions, and solvent selectivity [11–18]. These well-defined nanostructures with the structural and chemical diversity make them attractive for the use in numerous applications, like solubilization of drugs or pollutants, nano-reactors, drug delivery, reinforcing nanofiller, a fabrication of one-dimensional nanostructured materials, and nanolithography [13,14,19–22]. The control of the micellar morphologies on the nanometer-sized dimension is of great importance to get the desired functionalities and properties.

Among various micellar nanostructures, spherical and cylindrical micelles can be used as templates or scaffolds for fabricating quantum dots or one-dimensional metal and/or metal oxide nanostructured materials. As examples of spherical micelles, spherical micelles of PS-*b*-P4VP or polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) copolymers consisting of a P4VP or PAA core surrounded by a PS shell were formed in toluene, a selective solvent for the PS block, at well above the critical micelle concentration. These micellar thin films have been used as templates for fabricating metal nanoparticles or quantum dots, like Au, Fe_2O_3, ZnO, TiO_2, Ag, and CdS [23,24].

In addition to spherical micelles, Manners' group reported on an interesting strategy for making cylindrical micelles in solution by introducing more rigid block in one of both blocks, which might have additional interactions, like hydrogen bonding or π–π interactions [25–28]. Interestingly, these micellar structures were produced via a living supramolecular polymerization process, as seen in other reports [12–15]. Well-defined cylindrical micelles were used as templates for preparing metal oxide or polymer nanowires via a sol–gel process. However, the examples above mentioned require complicated steps, such as dialysis process, addition of electrolytes, and pH control, for preparing various micellar structures. One underlying goal of BCP micelles is to construct spherical and/or cylindrical micelles in a simple manner.

* Corresponding author. Fax: +82 52 217 2909.
  E-mail address: spark@unist.ac.kr (S. Park).

Here, we report on a simple way for preparing PS-b-P4VP spherical, cylindrical, and vesicular micelles via solvent evaporation without the requirement of complicated steps. As the solvent selectivity for PS-b-P4VP copolymer was systematically changed, during spin-coating process, various micellar structures were obtained in thin films. A subtle change of solvent quality, combined a slight selective solvent with a strong selective solvent, enabled us to obtain a novel micellar structures. This approach may be applied to other systems, like colloids or emulsion. Well-defined micellar thin films were used as templates for preparing inorganic nano-objects, as illustrated in Scheme 1.

2. Experimental section

2.1. Materials and methods

A polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP) block copolymer was purchased from Polymer Source and was used without further purification (M_n^{PS} = 41.5 kg/mol, M_n^{P4VP} = 17.5 kg/mol, M_w/M_n = 1.07). PS-b-P4VP copolymers were dissolved in tetrahydrofuran (THF) at room temperature for 12 h to yield 0.005–1.5 wt.% polymer solutions. Subsequently, the PS-b-P4VP thin films were spin-coated at 2000 rpm for 60 s or drop-casted onto silicon substrates or carbon-coated copper grids. To investigate the effect of additional solvent, like water (H_2O) or ethanol (EtOH), on the PS-b-P4VP micellar morphologies, water (1, 2, 5, and 10 vol.%) or ethanol (1, 2, 5, 10, 30, 50, 70 vol.%) was added to pure THF solutions at a fixed total polymer concentration of 0.5 wt.%. Micellar thin films spin-coated from polymer solutions in THF/water or THF/ethanol were used as templates for preparing metal nanodots or nanowires. Hydrogen tetrachloroaurate ($HAuCl_4$) and titanium tetraisopropoxide precursors were purchased from Sigma–Aldrich and used without further purification.

2.2. Preparation of metal nanodots and nanowires

Cylindrical and spherical micellar thin films were immersed in gold precursor (0.3 wt.% $HAuCl_4$ in ethanol) solution for 5 min to let gold precursor bind with P4VP chains, and followed by oxygen plasma treatment (SPI Plasma Prep II, 50 W) to obtain pure gold nanoparticles and nanowires with the complete removal of polymers. A well-known synthetic process was used to make titanium oxide arrays. First, for titania sol, 4.2 g of titanium tetraisopropoxide was mixed with 12.1 M HCl, and the mixture was stirred vigorously at 25 °C for 10 min, then 5 mL ethanol was added. The micellar thin films were immersed in the titania sol solution for 10 min and rinsed with ethanol for several times to remove excess

sol precursors. Subsequently, the titania loaded films were heated to 400 °C in air for 2 h to degrade the BCP copolymer.

2.3. Characterization of PS-b-P4VP in solution

The micellar size and shape of PS-b-P4VP in pure THF, THF/EtOH, and THF/H_2O solutions were measured by dynamic light scattering (DLS). DLS experiment was performed at 22 °C using a Brookhaven Laser Light Scattering system equipped with a BI-200SM goniometer, a BI9000AT digital correlator, a diode pumped crystal laser (λ_o = 532 nm), and a photomultiplier detector. All polymer solutions were filtered through Millipore 0.45 μm PTFE filters. All samples were systematically studied at a scattering angle ranged from 30° to 120°.

2.4. Characterization of BCP thin films

The PS-b-P4VP micellar films, metal nanoparticles and nanowires on a silicon wafer were imaged by atomic force microscope (AFM, Digital Instruments, Nanoscope III) in the tapping mode. The measurements were performed using commercial Si cantilevers. For transmission electron microscopic (TEM) measurements, the PS-b-P4VP micellar films were spin-coated onto Formvar-coated copper grids. The films were stained with iodine to increase the contrast of P4VP blocks. Bright-field TEM was performed on a JEM-1400 TEM operating at an accelerating voltage of 120 kV. The crystal structures of the arrays of titanium oxide were measured by high power X-ray diffractometer (XRD) on a Rigaku D/MAX at 2500 V using Ni-filtered Cu Kα radiation with a graphite diffracted beam monochromator.

3. Results and discussion

3.1. PS-b-P4VP micellar structures in solution

The size and structure of PS-b-P4VP micelles in THF, THF/H_2O, and THF/EtOH solutions were studied by DLS. The autocorrelation functions were measured in different PS-b-P4VP solutions where the concentrations were varied from 0.1 to 1.5 wt.% in THF. THF is a good solvent for PS, but non-solvent for P4VP, in which spherical micellar structures are formed with PS shell and P4VP corona. Typical DLS results measured at a scattering angle of 90° were shown in Fig. 1a. Even though polymer concentrations were varied, the autocorrelation functions were almost the same, indicating that the micellar size of PS-b-P4VP made unchanged. From the autocorrelation functions, the hydrodynamic radii (R_h) measured at concentrations of 0.1, 0.5, 1.0, and 1.5 wt.% PS-b-P4VP
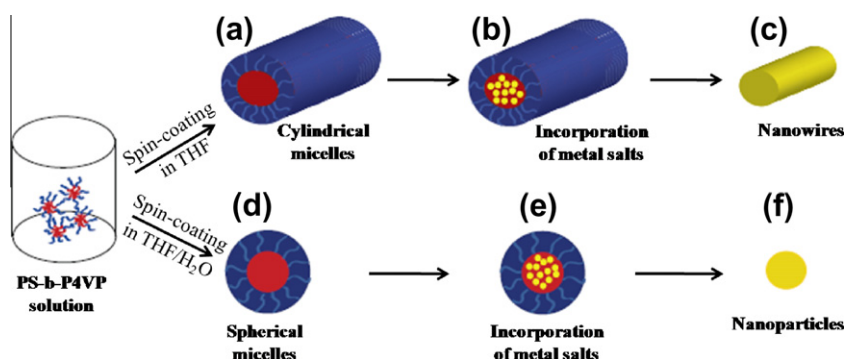
Scheme 1. Schematic illustration for preparing inorganic nanodots and nanowires from PS-b-P4VP micellar nanostructures. (a) Cylindrical micellar films prepared from spin-coating of THF or THF/EtOH solutions, (b) cylindrical micelles loaded with metal precursor, (c) inorganic nanowires prepared by oxygen plasma treatment with samples seen in (b), (d) spherical micellar structures prepared by spin-coating from THF/H_2O solution, (e) spherical micellar structure incorporated with metal precursor, and (f) inorganic nanodots prepared by plasma treatment with samples seen in (e).