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In-situ monitoring of silica shell growth on PS-*b*-P4VP micelles as templates using DLS

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ABSTRACT

Polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) block copolymer (BCP) was used as a template for the preparation of PS-*b*-P4VP@SiO₂ core-shell particles using an acid catalyzed sol-gel process. The process of silica shell formation and development of shell morphology were studied using a combination of in-situ dynamic light scattering (DLS) and transmission electron microscopy (TEM). The results obtained reveal that shell formation and growth principally involve the following stages: (I) sol assembly around BCP micelles; (II) hydrolysis-condensation reaction accelerated by the protonated P4VP corona of BCP micelles; (III) shell densification; and (IV) shell growth. Present work provides insight into the sol-gel process which takes place in systems containing “reactive” templates, such as protonated PS-*b*-P4VP micelles, and discloses the mechanism and pathways of silica shell formation. We demonstrate that the whole process can be effectively monitored in-situ using conventional DLS. The results are of significant importance for fabrication of targeted core-shell nanostructures.

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1. Introduction

Among various templates, self-assembled block copolymer (BCP) structures are often used for the synthesis of novel functional nanomaterials and provide many benefits [1–5]. Having their periodicities in nanometer scale, these structures have been used for the fabrication of various “smart” materials, such as membranes for selective separation and purification, vesicles for drug delivery, controlled release materials, porous catalysts or proton exchange membranes, etc [6]. The degree of polymerization (N), volume fraction of the constituting blocks (φ) and Flory-Huggins interaction parameter (χ) determine the periodicity and morphology of self-assembled structures at equilibrium. Alteration of experimental conditions, for instance, solvent selectivity, also influence characteristics of self-assembled structures [7,8]. These self-assembled structures can be stabilized, e.g. by cross-linking of

one BCP component, and then disintegrated using an appropriately selected solvent to produce isolated hairy particles [9,10]. If the difference in solubility of BCP constituents in given solvent is large enough, it is possible to obtain isolated hairy particles using the so-called selective solvent approach, which does not require any additional stabilization (cross-linking). Through an appropriate selection of experimental conditions and precursors, multicomponent materials or multifunctional particles with controlled localization of functionalities can be prepared [5,6,11,12].

Polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) block copolymers are often used for the preparation of various functional nanostructures. Due to the reactive nature of pyridine units, P4VP-based block copolymers can be complexed with small molecules, metal precursors, or directly loaded with nanoparticles [13–16]. The lone pair of electrons renders the 4VP unit a strong ligand able to coordinate with electron-deficient species, such as transition metals [17]. The ability of 4VP units to undergo hydrogen bonding is also well known and has been widely exploited in various supramolecular systems. In addition, in protonated or quaternized state 4VP units can electrostatically interact with charged molecules, particles and substrates [18]. At the same time, comparably high χ

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value for PS/P4VP pair [19] allows disassembly of the matrix forming components with selective solvent without affecting the shape of domains formed by the minority component. The feasibility of using non-crosslinked PS-*b*-P4VP hairy particles as templates was demonstrated in our previous works. In particular, we have shown that PS-*b*-P4VP hairy particles, either cylindrically or spherically shaped, can be coated with silica or titania shell and further converted into hollow structures by oxidative pyrolysis [20,21].

Experimental work on preparation of core-shell type particles via a sol-gel process on P4VP-based polymeric templates was also carried out by other research groups in the past [22–25]. Liang and co-workers used symmetric PS-*b*-P4VP for the fabrication of PS-*b*-P4VP/SiO₂ core-shell particles by acid catalyzed sol-gel synthesis [22]. Depending on whether selective or non-selective solvent was used as reaction medium, spherical particles having silica in the core or coated with a silica shell were obtained. In the case of PS-selective solvent (THF), silica deposition took place within the protonated P4VP core of the micelles. In the case of non-selective solvent (DMF), micellization of PS-*b*-P4VP was induced upon addition of aqueous oxalic acid followed by silica shell formation atop of PS-*b*-P4VP micelles. Another example of using PS-*b*-P4VP micellar templates for the fabrication of various nanoobjects, such as gold or titania nanodots and nanowires, was recently reported by Cho and co-workers [23]. The authors used THF/ethanol and THF/water solvent mixtures of different ratios to obtain PS-*b*-P4VP micellar structures of various morphologies. Different aggregation morphologies, such as cylindrical and spherical micelles (PS core), vesicular structures, or reverse spherical micelles (P4VP core) were obtained, depending on the type of added solvent (ethanol or water) and solvent ratio. Apart from block copolymer micelles, spherical microparticles prepared from pyridine-based random copolymers or P4VP homopolymer were also used as templates for silica shell deposition. Zhang and co-workers used P4VP microspheres for fabrication of hierarchically structured core-shell particles under acidic conditions, which were then converted into hollow silica microspheres [24]. In other work, the same group reported on the preparation of polymer/silica hybrid particles using PS-*co*-P4VP microspheres as templates [25].

There are several advantages of template-assisted sol-gel processes over conventional acid or base catalyzed processes. In particular, by using templates various hybrid particles with pre-determined size, shape and shell thickness can be prepared relatively easily. The core-shell particles can be further converted into hollow structures or yolk-shell type particles by pyrolytic removal or by selective etching [26]. Regarding “reactive” templates, those can be considered as such having building blocks, functional groups or other structural components which are chemically involved in sol-gel process. As will be discussed further, PS-*b*-P4VP micelles represent such a “reactive” case because of the localized catalytic effects of the protonated pyridine units. Although existing reports describe the structural and morphological aspects of template-derived core-shell particles, to the best of our knowledge, there are no studies on kinetics and mechanism of the sol-gel process which occurs in the presence of “reactive” templates, like PS-*b*-P4VP micelles or P4VP based particles.

It is well known that kinetics and mechanism of acid- or base-catalyzed sol-gel reactions depend on the temperature, pH, type of catalyst (acid/base), and composition of the reaction medium [27–29]. At a pH close to the isoelectric point of silica, the rate of the condensation reaction is very slow and the gelation time is high. Gelation time increases with an increase of precursor/solvent (alcohol) ratio. The variation of gelation time with respect to different precursor/water ratios is non-monotonic with a minimum which, in turn, depends on the precursor/solvent ratio and pH.

Thus, changes in pH and/or composition of reaction medium affect the kinetics and mechanism of the sol-gel process and, subsequently, may alter properties of the formed silica particles. Such changes, which may locally occur in the vicinity of PS-*b*-P4VP micelles upon addition of acidic silica sol, would alter the kinetics of the sol-gel reaction as compared to the rest of the solution. A thorough understanding of the sol-gel reaction taking place in the presence of “reactive” templates is necessary for the synthesis of core-shell nanostructures with pre-defined characteristics and properties. In the present work, we combined in-situ DLS and transmission electron microscopy to investigate the sol-gel process carried out in the presence of PS-*b*-P4VP micelles and to understand the mechanism and pathways of silica shell formation.

2. Experimental

2.1. Materials

PS-*b*-P4VP block copolymer with $M_n = 18500$ g/mol and $M_w = 40500$ g/mol for PS and P4VP, respectively, and a polydispersity index of 1.10, was purchased from Polymer Source (Canada). The calculated volume fractions of the PS and P4VP blocks were 0.3 and 0.7 respectively. Hydrochloric acid (37 wt%) was obtained from Merck. Tetraethyl orthosilicate (TEOS) was obtained from Sigma Aldrich. The solvents (chloroform, absolute ethanol, and methanol, analytical grade) were purchased from Acros Organics. Prior to use all solvents were filtered through a 0.2 μm pore size PTFE membrane filter to remove particulate impurities. Carbon coated TEM grids (300 mesh) were purchased from Plano GmbH (Germany). Highly polished single-crystal silicon wafers of {100} orientation were used as substrates. Silicon wafers were cleaned with dichloromethane in an ultrasonic bath for 20 min and then further in a 1:1:1 v/v mixture of 29% ammonium hydroxide (Acros), 30% hydrogen peroxide (Merck) and deionized water for 1.5 h at 65 °C, rinsed several times with water and finally dried under argon flow.

2.2. Characterization

SEM images were obtained using Neon40 FIB-SEM workstation (Carl Zeiss Microscopy GmbH, Germany) operated at 3 kV. The samples prepared on silicon substrates were viewed under the SEM without any additional coating. Tapping mode AFM imaging was performed using a Dimension 3100 Scanning force microscope (Digital Instruments, Inc., Santa Barbara, CA) using silicon cantilevers with a resonance frequency of 60–70 kHz and a tip radius of ca. 10 nm. Conventional and energy filtered TEM images (EFTEM) were obtained using Libra120 transmission electron microscope (Carl Zeiss Microscopy GmbH, Germany) equipped with an Omega-type energy filter and operated at 120 kV. EFTEM imaging was performed by 3-windows method using 20 eV window width. For elemental mapping, K-ionization edges of N and C, and L₂₃-ionization edge of Si were used. Specimens for TEM imaging were prepared on the carbon coated copper grids by drop casting method followed by immediate rinsing with absolute ethanol. Dynamic light scattering (DLS) measurements were performed at 25 °C using Zetasizer Nano S (ZEN 1600, NIBS Technology, Malvern Instruments, UK) equipped with 4 mW He-Ne-laser (632.8 nm, scattering angle 173°).

2.3. Synthesis of PS-*b*-P4VP@SiO₂ core-shell particles via sol-gel

PS-*b*-P4VP block copolymer was dissolved in chloroform to give a homogeneous solution with BCP concentration of 0.5 mg/mL and filtered through a 0.2 μm pore size PTFE membrane filter. An

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