Polym. Bull. (2010) 65:599–608
DOI 10.1007/s00289-010-0315-9

ORIGINAL PAPER

A facile preparative method for gold-containing vesicles from poly(styrene-*block*-2-vinylpyridine) block copolymer/$HAuCl_4$ complexes

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Received: 20 March 2010 / Accepted: 30 May 2010 / Published online: 6 June 2010

Abstract It is found that the complexes of PS-*b*-P2VP and $HAuCl_4$ in THF can form a compound vesicle when the THF solution is treated at 40 °C. The compound vesicle is composed of an insoluble wall formed by P2VP/$HAuCl_4$ complexes and a soluble PS shell. The vesicular character of the aggregates was investigated by dynamic light scattering (DLS) and transmission electron microscope (TEM). The decrease of the solubility of P2VP blocks in THF drives the PS-*b*-P2VP/$HAuCl_4$ complexes to aggregate into vesicles, which are stable upon dilution or crosslinking. Based on this study, the vesicles decorated with gold nanoparticles can be produced, which hold potential for the facile organization of the vesicle-supported precious metal catalysts.

Keywords Block copolymer · Vesicles · PS-*b*-P2VP

Introduction

Compared to conventional surfactant vesicles or liposomes, block copolymer vesicles have advantages in enhanced chemical, thermal, and mechanical stability [1–9]. In recent years, block copolymer vesicles have been extensively investigated due to their potential applications in numerous fields ranging from cosmetics to anticancer agent [1–10]. Block copolymer vesicles formed in aqueous media from

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various amphiphilic block copolymers and mixtures of block copolymers, such as polystyrene-*block*-poly-(ethylene oxide) (PS-*b*-PEO) and polystyrene-*block*-poly (acrylic acid) (PS-*b*-PAA), have been intensively studied [2–8, 11, 12] and reviewed by several authors [1–8, 11–14]. Recently, vesicles formed from stimuli-responsive such as pH-responsive and thermally responsive block copolymers have also been reported [14–17].

The typical method of forming vesicles from amphiphilic block copolymers involves the use of an organic solvent to prepare a polymer solution, followed by mixing of the organic solution with water, and then the purification processes [2–9, 11–13]. The morphology of the vesicles can be controlled by many factors, such as the copolymer composition, initial polymer concentration, nature of the solvent, temperature, and other additives [6, 14].

Amphiphilic block copolymers/low molecular-weight surfactants complexes have been proven to be useful precursors for the preparation of vesicles. In these systems, one block of the copolymer is complexed by the small molecular surfactants through specific noncovalent interactions resulting in the insoluble vesicular layer, while the remaining uncomplexed blocks point out toward the inner and the outer regions of the vesicle [18–20]. For example, hydrogen-bonding complexes of poly(vinylpyridine), P4VP or P2VP, with polyacids, including poly(acrylic acid), pentadecylphenol (PDP), poly(vinylphenol), poly(carboxylic acid)s, 2-(4′-hydroxybenzeneazo)benzoic acid (HABA), and other Lewis acids, can be used to manipulate the aggregate morphologies of block copolymer in selective media [21, 22]. The formation of various morphologies by the block copolymer–surfactant complexes demonstrates that the opportunities for the manipulation of morphology in these systems are much broader than those that have been previously considered [23–31]. Recently, the Jiang group reported that micellization of the complexes of PS-*b*-P4VP with a high polarity such as formic acid (FA) takes place in chloroform, leading to regular aggregates [23–27]. The direct formation of vesicles has been recently reported in mixtures of a PS-*b*-P4VP diblock with perfluorooctanoic acid (PFOA) in chloroform [32]. Stimuli-induced morphological transitions have been observed for block copolymer vesicles [32–36]. It is demonstrated that dilution can be used as a stimulus to trigger the reorganization of nonequilibrium spherical micelles into more stable vesicles for PS-*b*-P4VP/ perfluorodecanoic acid (PFDA) complexes in chloroform [35, 36].

Gold nanoparticles have been receiving great attention because of their potential applications as biomedical, optic, and electronic materials [37, 38]. Thiol-functional molecules are frequently employed as stabilizers [39–41]. It is also reported that some copolymers without thiol functionality can act as both reducing agent and stabilizer simultaneously in the formation of gold nanoparticles [42–44]. A new class of amphiphilic poly(styrene-*block*-cysteine) block copolymers was utilized as surface stabilizers to conjugate with Au nanoparticles [45]. However, gold nanoparticle decorated polymer vesicles have been reported scarcely. The McMormick group has reported that thermally responsive vesicles are prepared from the self-assembly of a poly[2-(dimethylamino)ethylmethacrylate-*block*-(*N*-isopropylacrylamide)] ($PDMAEMA_{73}$-*b*-$PNIPAM_{99}$) block copolymer. Simply mixing the vesicle solution with a solution of $NaAuCl_4$, without the necessity of an external reducing agent, leads to the formation of gold nanoparticle decorated vesicles [46]. Very recently, luminescent vesicles from ruthenium–bipyridine block copolymers are reported by Sleiman group [47]. These assembled metal/copolymer hybrids provide a means to potential uses in delivery biomolecules, catalysts, and drugs.

Usually, the vesicles from PS-*b*-PAA, PS-*b*-PEO, and PS-*b*-P2VP, or PS-*b*-P4VP have a wall consisting of the insoluble PS block and a shell consisting of the soluble block such as PAA, PEO, or PVP. It is well known that PS-*b*-P2VP/$HAuCl_4$ in toluene form spherical micelles having a core consisting of the P2VP/$HAuCl_4$ and a corona consisting of PS blocks. In this article, we introduce a sample and facile method to prepare vesicles containing gold by combining the self-assembly and hydrogen bonding methods just by changing the solvent quality. THF is a good solvent for PS and P2VP blocks. Hydrogen-bonding complexes of P2VP with $HAuCl_4$ can change the solubility of P2VP in THF and self-assemble into vesicles, in which the insoluble P2VP/$HAuCl_4$ complexes forms a wall and the soluble PS block forms a corona. To the best of our knowledge, this is the first example of the vesicular morphology of PS-*b*-P2VP/$HAuCl_4$ aggregates that is brought about by the binding of hydrogen bonds to the pyridine unites in organic solvent. The formation of the desired morphology in solution is crucial step in using these aggregates. The formation of gold-decorated vesicles in this study demonstrates that the opportunities for the manipulation of morphology in the system are much broader than has been previously considered. The vesicles hold potential for the facile organization of the vesicle-supported precious metal catalysts and sensing.

Materials and methods

Materials

Polystyrene-*block*-poly(2-vinyl pyridine) (PS-*b*-P2VP, the average degrees of polymerization of the PS and P2VP block are 528 and 177, respectively). Copolymers with a polydispersity index of 1.07 and P2VP homopolymer with molecular weight of 3,000 were purchased from Polymer Source, Inc. Tetrachloroauric(III) acid ($HAuCl_4 \cdot xH_2O$, $M_w = 333.79$), 1,4-dibromobutene and anhydrous THF ($\geq$99.9%) were purchased from Sigma-Aldrich and used as received.

Preparation of the complexes

Solutions of the PS-*b*-P2VP copolymers, the $HAuCl_4$ were prepared in THF at different concentrations. Calculated amounts of PS-*b*-P2VP copolymers and $HAuCl_4 \cdot xH_2O$ were dissolved in THF at 40 °C and stirred at least for 24 h to make a homogeneous solution (1.0 wt%). The molar ratio (MR) of $HAuCl_4$/2VP was varied from 0.2 to 0.5. The mixture solutions were equilibrated for one night before characterization. The initial mixture solutions were then diluted by addition of known amounts of THF.

Characterization methods

Dynamic light scattering (DLS)

DLS results were measured with a Zetasizer Nano system (Nano ZS), Malvern Instruments, Ltd., UK. The apparatus equipped with a He–Ne laser with a wavelength of 633 nm. The DLS data were analyzed using the Malvern Zetasizer software.

Transmission electron microscopy (TEM)

TEM was performed on an H-800 electron microscopy (Hitachi, Japan) operating at 80 kV. The samples were prepared by depositing a drop of the solutions on a carbon-coated copper grid and dried in air.

UV–Vis spectra

UV–Vis spectra of were recorded on a UV2450 spectrometer (Shimadzu Co., Japan). Dilute solutions of the aggregates were measured in quartz cuvettes, using pure solvent as a reference.

Results and discussions

Formation of vesicles

The solubility parameters of THF, PS, and P2VP are 19.4, 17.8–18.6, and 20.6 $(\mathrm{MPa})^{1/2}$, respectively [48]. The values demonstrate that THF is a common solvent for the PS and P2VP blocks, as well as a solvent for $HAuCl_4$. No aggregated species were detected for pure PS-*b*-P2VP copolymers (Fig. 1a), indicating that the copolymers are molecularly dissolved in THF [32].

It is well known that $HAuCl_4$ and the pyridine units can form complexes [49, 50], which can induce the micelles formation in THF. We prepared gold nanoparticles (AuNPs) with block copolymer shell structures by UV irradiation of the micellar solution of PS-*b*-PVP/$HAuCl_4$ complexes in THF [51]. When the micellar solution of the PS-*b*-P2VP/$HAuCl_4$ complexes in THF was kept at 40 °C for several hours and then characterized by DLS, aggregates with the hydrodynamic diameters ranging from several tens of nanometers to several hundreds of nanometers were detected (Fig. 1b). The morphology of the aggregates of the PS-*b*-P2VP/$HAuCl_4$ complexes was examined under TEM. Figure 2 shows a TEM image of the aggregates of PS-*b*-P2VP/$HAuCl_4$ complexes at a concentration of 1.0 wt%. The vesicular structure is evidenced from a higher transmission in the center of the aggregates than around their periphery. The average diameter of the vesicles measured from Fig. 2 is about 230 nm. Although there is no direct correlation between the size of the vesicles as measured by TEM and their diameters as measured by DLS [36], these results can illustrate that the complexes of PS-*b*-P2VP

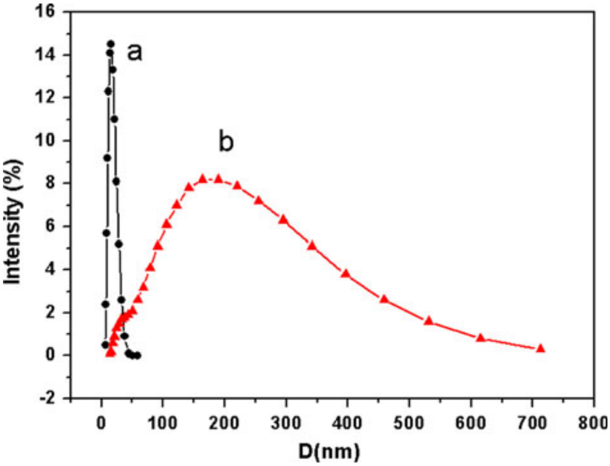

Fig. 1 Hydrodynamic diameter distributions of PS-*b*-P2VP (*a*) and PS-*b*-P2VP/$HAuCl_4$ (MR = 0.2) complexes (*b*) at concentration of 1.0 wt%

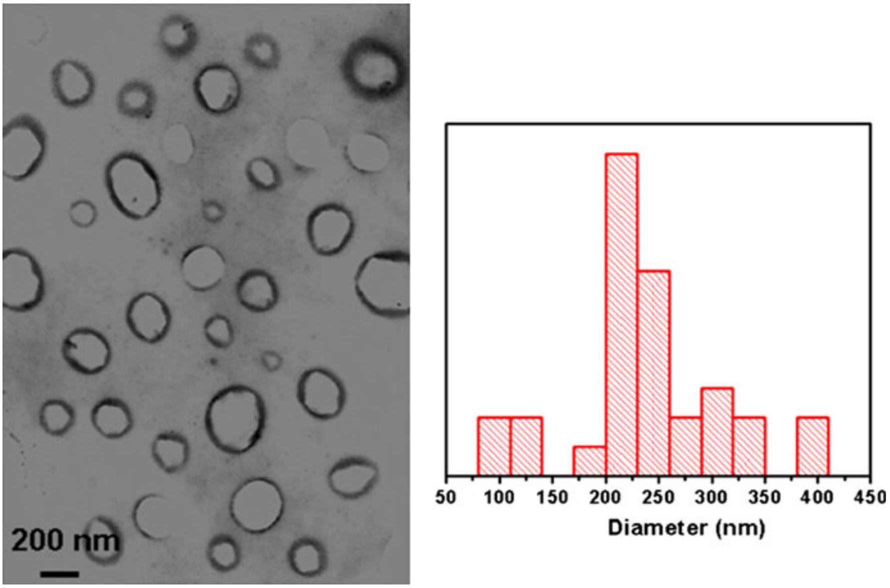

Fig. 2 TEM image of PS-*b*-P2VP/$HAuCl_4$ (MR = 0.2) complexes at concentration of 1.0 wt%

with $HAuCl_4$ in THF can self-assemble into vesicles. It has been reported that the complexes of PS-*b*-P4VP with FA or PFOA lead to the formation of vesicles in chloroform [32, 35, 36]. The vesicles of block copolymers containing the metal complexes are generated by the self-assembly of the block copolymers containing metal transition metals synthesized living (ring-opening metathesis) polymerization

[52–56] or by attaching the complexes/nanoparticles to a preformed vesicle. For example, vesicles containing ruthenium are obtained directly from the self-assembly of ruthenium–bipyridine block copolymers in organic solvent [47]. Metal–nitrilotriacetic acid (NTA)-functionalized block copolymer vesicles are prepared by self-assembly of the poly(butadiene)-*block*-poly(ethylene oxide) copolymers with terminal M(II)–NTA groups (copper or nickel) [57]. Gold-decorated vesicles can be obtained by mixing the vesicle solution with a $NaAuCl_4$ solution at 50 °C [46].

Vesicle formation mechanism

In order to understand the vesicle formation mechanism, different experiments were carried out. In a first control experiment, it is found that mixing of the P2VP homopolymer solution with the $HAuCl_4$ solution in THF under the identical condition leads to precipitation. This demonstrates that the hydrogen-bonding complexation of $HAuCl_4$ to the pyridine units changes the interactions between P2VP blocks and PS blocks or THF molecules. In addition, the PVP block becomes stiffer due to the increase of the interactions between PVP blocks after complexation, which facilitates the vesicle formation. PS-*b*-P2VP/$HAuCl_4$ (MR = 0.2) complexes can not be molecularly dissolved in THF [49, 50]. Therefore, it is reasonable to conclude that the complexed P2VP chains are organized to form the wall, while the soluble PS chains will adjust their conformation to stretch out to surround the wall, forming the inner and the outer shells. The wall contains gold components, which is consistent with the morphology observation (Fig. 2).

In a second experiment, the effect of dilution on the aggregates of PS-*b*-P2VP/$HAuCl_4$ complexes was investigated. In general, dilution can induce vesicle-to-micelles transition in block copolymer micelles [58]. However, Hu et al. found that dilution could induce the reorganization of spherical micelles into more stable vesicles for PS-*b*-P4VP/PFDA complexes in chloroform [35, 36]. If the vesicular PS-*b*-P2VP/$HAuCl_4$ solution is diluted from 1.0 to 0.5 and 0.25 wt%, then the hydrodynamic diameters of the aggregates decrease, and the size distributions of the aggregates become narrow (Fig. 3a). Combined with the TEM image (Fig. 3b), it is evident that the vesicular morphology is still retained after dilution. This may be understood as follows. Following dilution of the 1.0 wt% solution, small amounts of the formed P2VP/$HAuCl_4$ complexes can be resolubilized, which leads to the decrease of the number of the aggregation. However, due to the low solubility or low chain mobility of the P2VP/$HAuCl_4$ complexes in THF, the vesicular structures formed at a concentration of 1.0 wt% are kinetically frozen. Therefore, dilution does not lead to the morphological change from vesicles to spherical micelles.

Effect of the $HAuCl_4$ loading ratio

The effect of the $HAuCl_4$/2VP MR on the average hydrodynamic diameter of aggregates was also examined. As shown in Fig. 4, the peak associated with individual PS-*b*-P2VP molecules can be seen when the $HAuCl_4$/2VP MR is 0.2. However, if the $HAuCl_4$/2VP MR is increased to 0.5, then the peak corresponding to

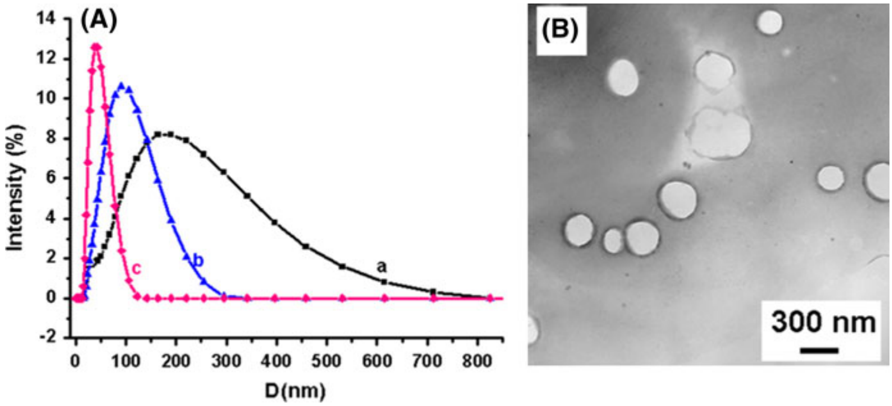

Fig. 3 **a** Hydrodynamic diameter distributions of PS-*b*-P2VP/$HAuCl_4$ (MR = 0.2) complexes at different concentrations. *a* 1.0, *b* 0.5, *c* 0.25 wt%. *b* and *c* were prepared by dilution *a* with pure THF. **b** TEM image of PS-*b*-P2VP/$HAuCl_4$ complexes after dilution to 0.25 wt%

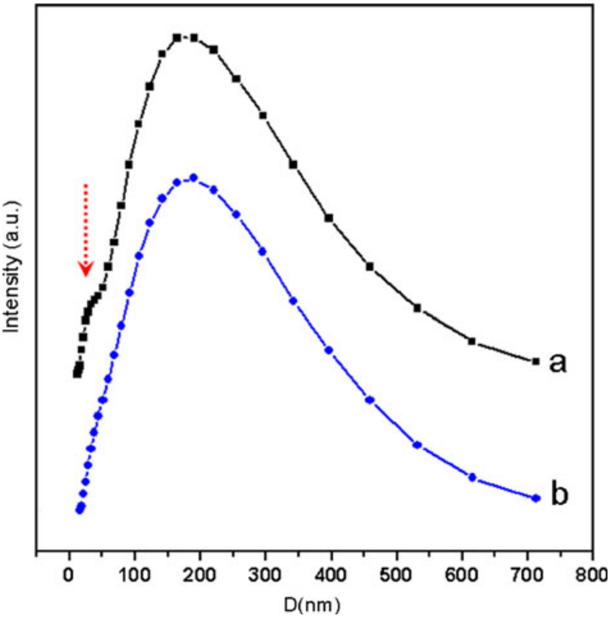

Fig. 4 Hydrodynamic diameter distributions of PS-*b*-P2VP/$HAuCl_4$ complexes with different $HAuCl_4$/VP MR. *a* MR = 0.2, *b* MR = 0.5

PS-*b*-P2VP unimers has not been detected, indicating that more $HAuCl_4$ molecules are complexed with the pyridine units on P2VP block. With the increase of the $HAuCl_4$/2VP MR, the solubility of the complexes in THF should decrease further, leading to the formation of aggregates. For amphiphiles, the two main contributions to the free energy are the interfacial energy of the hydrophobic–hydrophilic interface and the loss of entropy when the polymer chains are forced to fit into the aggregate microdomains [13]. In this system, the complex formation between pyridine units and $HAuCl_4$ restricts conformational entropy. Owing to the increase of the rigidity of the P2VP/$HAuCl_4$ blocks, the entropy loss of aggregation becomes smaller. The minimization of the interfacial area should dominate association thermodynamics, and the formation of vesicles is likely the result of the increase of rigidity and the decrease of solubility of the complexed P2VP/$HAuCl_4$ blocks.

Crosslinking of vesicles

In order to further prove the formation of vesicular structure in solution, we added 1,4-dibromobutene to crosslink the composite vesicles formed by PS-*b*-P2VP/$HAuCl_4$ complexes. Subsequent hydrazine hydrate was added to the solution to reduce the $HAuCl_4$ into Au atoms that coagulate to form an Au nanoparticle. One can see from TEM image (Fig. 5a) that a vesicular structure is retained after crosslinking. Au nanoparticles dissociate from the cross-linked copolymers. The similar result was obtained by the Jiang group [59]. This drawback can be overcome by a timely addition of HCl into the solution [59] or by other methods, such as photo-crosslinking. Further study is needed to optimize the reduction conditions. As shown in Fig. 5b, the formation of Au nanoparticles is confirmed by the UV–Vis absorption spectra of the vesicle solutions of PS-*b*-P2VP/$HAuCl_4$ complexes after crosslinking and reduction. Before reduction of $HAuCl_4$ precursors, the vesicular solution is pale-yellow and absorption is observed at 313 nm. After reduction, the solution is wine-red, and a broad absorption at about 530 nm is assigned to the surface plasma resonance of gold nanoparticles [60, 61].

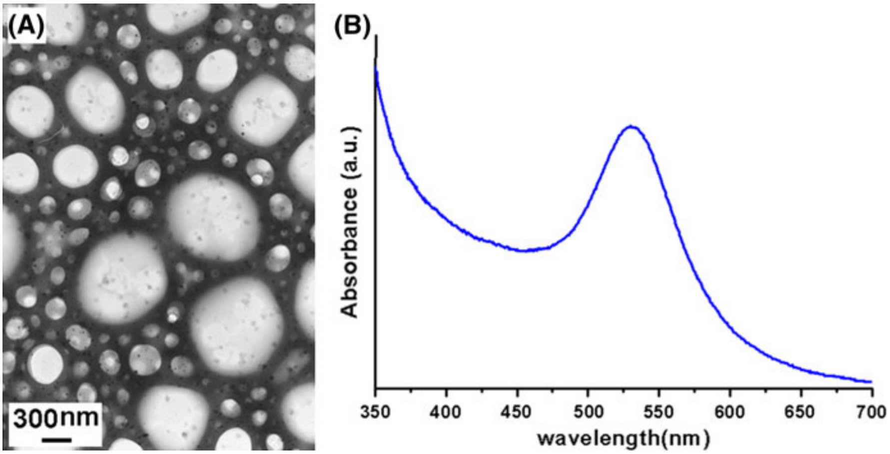

Fig. 5 TEM image (**a**) and UV–Vis absorption spectrum (**b**) of the vesicles of PS-*b*-P2VP/$HAuCl_4$ complexes after crosslinking with 1,4-dibromobutene and reduction $HAuCl_4$ with hydrazine hydrate

Conclusions

It is found that the temperature can induce the formation of the compound vesicles of PS-*b*-P2VP/$HAuCl_4$ complexes in solution. The compound vesicles are composed of an insoluble wall formed by P2VP/$HAuCl_4$ complexes and a soluble PS shell. The aggregation is mainly driven by the decrease of the solubility and the increase of the rigidity of the complexes of PS-*b*-PVP/$HAuCl_4$. After dilution or cross linking, the vesicular structures are still retained. The vesicles decorated with gold component hold potential for the facile organization of the vesicle-supported precious metal catalysts which may offer advantages in terms of catalyst recovery.

Acknowledgments This study was funded by the National Natural Science Foundation of China (20674030), Shandong Natural Science Foundation (Y2006B02), and the Doctorial Foundation of University of Jinan (B0541).

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