

Multiple morphological micelles formed from the self-assembly of poly(styrene)-*b*-poly(4-vinylpyridine) containing cobalt dodecyl benzene sulfonate

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Abstract

A series of supramolecular block copolymers were prepared using poly(styrene)-*b*-poly(4-vinylpyridine)(PS-*b*-P4VP) which coordinated with cobalt dodecyl benzene sulfonate (Co(DBS)₂) in tetrahydrofuran (THF). Fourier transformation infrared spectroscopy (FTIR), UV–vis absorption spectroscopy (UV) and differential scanning calorimetry (DSC) showed that Co(DBS)₂ coordinated to the lone electron pairs of the pyridine nitrogens in the P4VP block and led to complexes. The supramolecular block copolymers could self-assemble into nanosized micelles with different shapes and dimensions in THF, depending on the number of Co(DBS)₂ groups per 4-vinylpyridine (repeat unit was denoted by *n*) and the ratio between PS block length and P4VP block length. Transmission electron microscopy (TEM) results showed that when the number of repeat units of P4VP was more than that of PS, micelles with different interesting shapes such as spheres, rods, vesicles, large compound vesicles (LCVs) and the large compound micelles (LCMs) were observed if increasing the content of the Co(DBS)₂ in PS-*b*-P4VP copolymer/THF solution; When the number of repeat units of P4VP was less than that of PS, the micelle morphologies changed from spheres to rods, bi-layer, and LCMs if the Co(DBS)₂ content was increased progressively.

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1. Introduction

Self-assembly of block copolymers in solutions and the resultant polymeric nano-objects have been receiving much attention both in the field of theory and in the field of applications [1–5]. Block copolymers play an important role in the preparation of nanosized polymer aggregates

or particles due to their well-defined structural and morphological behavior [6]. A wide range of amphiphilic block copolymers have been synthesized, and their solution behavior and self-assembly have been extensively characterized [7–9]. Some typical examples of self-assembly of amphiphilic block copolymers have been reported in specific solvent systems, which formed sphere and nonsphere micelles [10–26].

In most cases, the self-assembly occurs in a selective solvent due to the difference in the solubility between the two blocks, it can also be induced by the physical

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or chemical interaction between block copolymer and other small molecules. In recent years, much attention was drawn to the complexation of a block copolymer with an amphiphilic molecule and the self-assembly of the resultant supramolecular block copolymers [27–32]. It was reported that the complexation in water could lead to the self-assembly of the supramolecules forming vesicles [33,34]. Lysenko et al. [35,36] reported micelles and micellar clusters formed by poly(styrene)-*block*-poly(*N*-ethyl-4-vinylpyridinium) (PS-*b*-PE4VP) cations and bis(2-ethylhexyl) sulfosuccinate (AOT) anions in water and hexane. In another example, polymeric nanofibers were prepared from self-organized supramolecules formed by PS-*b*-P4VP and pentadecylphenol (PDP) [37]. More recently, Ming Jiang et al. reported the complexation of perfluorooctanoic (PFOA) and poly(styrene)-*b*-poly(4-vinyl pyridine) (PS-*b*-P4VP) self-assembly in chloroform, forming spheres and vesicles [38]. The reported interactions between block copolymer and amphiphilic molecule are almost all hydrogen bonds and electrostatic interactions [29–32,35,36]. Other types of interactions such as coordination complexation between transitional metal ions within amphiphilic molecules and block copolymers which have been reported are few [39,40], study of the self-assembly behavior of resultant supramolecules in solution is few too.

In this article, diblock copolymers PS-*b*-P4VP are coordinated with Co(DBS)₂ to yield PS-*b*-P4VP[Co(DBS)₂] comb-coil supramolecules. The compositions of the copolymeric supramolecules are indicated as PS-*x*-*b*-P4VP-*y*[Co(DBS)₂]_{*n*}, where *x* and *y* are numbers of repeat units of the PS and P4VP blocks, respectively; *n* is the number of Co(DBS)₂ groups per 4-vinylpyridine. The self-assembly of resultant supramolecules in THF by varying the number of Co(DBS)₂ groups per 4-vinylpyridine (repeat unit was denoted by *n*) and the ratio between PS block length and P4VP block length is studied. The micelles formed by supramolecules can form nano-sized micelles with different sizes and shapes such as spheres, rods, vesicles, bi-layer, the large compound vesicles (LCVs) and the large compound micelles (LCMs).

2. Experimental section

2.1. Materials

Poly(styrene)-*b*-poly(4-vinylpyridine) copolymers (PS-*b*-P4VP) with different block size ratios were synthesized using ATRP as described in our previous report [41]. The molecular weight and molecular weight distribution of the block copolymer are summarized in Table 1.

Tetrahydrofuran (THF) was distilled before used. Sodium dodecyl benzene sulfonic (NaDBS) was analy-

Table 1
Characteristics of PS-*b*-P4VP block copolymer

Samples	M_n^a	PDI ^b	f_{P4VP}^c
PS ₈₂ - <i>b</i> -P4VP ₁₃₆	22800	1.23	0.62
PS ₈₂ - <i>b</i> -P4VP ₇₂	16100	1.18	0.47

^a Calculated by ¹H-NMR in CDCl₃.

^b Measured by GPC.

^c The molar ratio of each block was measured by ¹H-NMR in CDCl₃ and the mole fraction of P4VP(f_{P4VP}) was calculated from the results.

tical grade (Shanghai Chemical Reagent Corporation, China), and cobalt chloride hexahydrate (CoCl₂ · 6H₂O) was analytical grade (Shanghai Reagent Factory, China). The solvents used in all experiments were analytical grade. Deionized water was used in all experiments.

2.2. Synthesis

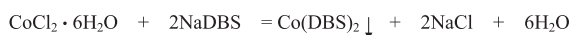
2.2.1. Synthesis of cobalt dodecyl benzene sulfonate

Co(DBS)₂ was prepared in H₂O from NaDBS and CoCl₂ · 6H₂O according to Scheme 1:

Two moles of NaDBS and 1 mol of CoCl₂ · 6H₂O powder was dissolved in water respectively. After CoCl₂ · 6H₂O/H₂O solution (20% w/w) was added dropwise into a NaDBS/H₂O solution (20% w/w) under vigorous mixing at 60 °C obvious pink precipitation was observed. The resultant deposition was filtrated and washed three times with water. The water was first evaporated at 60 °C on a hot plate, then the product was recrystallized three times from DMF (Shanghai Chemical Reagent Corporation, 99.5%). Finally, the Co(DBS)₂ was dried at 80 °C in a vacuum for 3 days. The resulting Co(DBS)₂ was glaucous powder. The UV–vis analysis (UV–vis spectrometer, Sahimadzu Corporation, Japan.) was applied to identify the synthesis of Co(DBS)₂. There were no absorbant peak in the visible region of NaDBS solution in THF, while Co(DBS)₂ appeared a peak from 580 nm to 680 nm due to the d–d transitions of cobalt salt.

2.2.2. Synthesis of PS-*b*-P4VP/Co(DBS)₂ polymeric supramolecules and self-assembly of polymeric supramolecules into micelles

PS-*b*-P4VP block copolymers under study were dissolved in THF (1 mg/ml), which is a good solvent for both PS blocks and P4VP blocks. Then Co(DBS)₂ was dissolved in THF(5% w/w), which is also a good solvent for Co(DBS)₂. Co(DBS)₂/ THF solution was added very slowly to the polymer solution under vigorous mixing, leading to formation of PSt-*b*-P4VP/Co(DBS)₂ supramolecular block copolymers, the concentration of



Scheme 1. Synthesis of Co(DBS)₂.

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