



Hybridization of poly(4-vinyl pyridine)-*b*-polystyrene-*b*-poly(4-vinyl pyridine) aggregates in dioxane/water solution

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ABSTRACT

Self-assembly of binary blends of two triblock copolymers of poly(4-vinyl pyridine)-*b*-polystyrene-*b*-poly(4-vinyl pyridine), i.e., P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃ (P1) and P4VP₄₃-*b*-PS₃₆₆-*b*-P4VP₄₃ (P2), in dioxane/water solution was studied. These two triblock copolymers individually tend to form vesicles (P2) and cylindrical micelles (P1) in dilute solution. It was found that copolymer components in the blend, sample preparation method, and annealing time had significant effect on hybridization aggregate morphology. By increasing P1 content in the copolymer blends, fraction of looped and stretched cylinders increased, while fraction of bilayers decreased. Nearly no bilayer was observed when P1 content was above 85 wt%. On the other hand, fraction of cylinders decreased while fraction of bilayers increased with the increase of P2 content in copolymer blends. Lamellar structures were obtained, when P2 content was 60 wt% in the copolymer blends, whereas cylinders were seldom found when P2 content was above 80 wt%. These results indicate that P1 and P2 copolymer molecules cooperatively participate in the formation of cylinders and vesicles. Some exotic structures, such as lamellae with protruding cylinders (LPC), incomplete vesicles with protruding cylinders (VPC), and cylindrical bilayers, have been kinetically trapped. These structures may result from intramicellar fusion processes in cylindrical micelles. The striking structures represent a compromise between bilayer and cylindrical geometries.

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1. Introduction

Self-assembly of amphiphilic block copolymers in selective solvent into aggregates of a wide range of morphologies has been attracted considerable interest for several years [1–12]. The specific morphologies of aggregates can be attributed to a balance of three contributions to the free energy of the system: chain stretching in the core, interfacial energy, and repulsion among corona chains [13,14]. As with low molecular weight analogues, precise tailoring of molecular weight and component offers control over mor-

phological behavior of block copolymer aggregates [15,16]. The other powerful way to tune aggregate morphologies is by blending two or more block copolymers [17]. Blending of polymers offers attractive advantageous over single component formulation in achieving specific properties [18,19]. Theoretical and experimental efforts have been given to understand the effect of polydispersity on block copolymer self-assembly [17,20–24]. It was found that aggregate sizes and even morphologies could be changed by blending two block copolymers [17,25,26]. Recently, Bates and coworkers reported Y-junction and 3D network microstructures for poly(1, 2-butadiene-*b*-ethylene oxide) (PB-PEO) at weight fraction of PEO intermediate to those associated with cylinders and vesicles [27,28]. What happens, if we tune weight fraction of hydrophilic block to intermediate region of cylinders and vesicles via blending two copolymers with higher and lower hydrophilic block

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content? In this paper, we report systematic study on self-assembly of binary blends of cylinder-forming copolymer (P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃ i.e., P1; the subscript number represents degree of polymerization) [29] and bilayer-forming copolymer (P4VP₄₃-*b*-PS₃₆₆-*b*-P4VP₄₃, i.e., P2) [30] in dilute solution. Aggregate morphologies are expected to be tuned by blending, and some intermediate microstructures by hybridization and solution self-assembly of the block copolymers are expected to be obtained.

Great efforts have been devoted to understand kinetics and mechanisms of chain exchange between block copolymer micelles [22,31–35]. Due to slow chain exchange between micelles because of higher molecular weight of molecules, slow kinetics of block copolymer in solution hinders assembled microstructures from reaching global equilibrium state, thus forming a nonergodic (i.e., locally isolated) array of aggregates [15,27,28,36]. Some intermediate aggregate morphologies have been kinetically trapped which take advantage of the slow kinetics of intermicellar interactions through infrequent intermicellar single-chain exchange [28,36,37]. These kinetically trapped intermediate microstructures are very interesting and helpful for understanding of aggregate morphology transition and formation (for instance vesicle) mechanism [37–41]. We have studied kinetics of aggregates by using different sample preparation methods (post-mixing and pre-mixing) and tuning annealing time. It was found that these factors affected significantly on final aggregate morphologies of the block copolymer hybrids in dilute solution. Some intermediate exotic structures, such as lamellae with protruding cylinders, incomplete vesicles with protruding cylinders, cage-like structures, and cylindrical bilayers, were kinetically trapped. After being trapped and isolated through dialysis, these microstructures are stable in water because of inability of the system to thermodynamically equilibrate.

2. Experimental

2.1. Materials

The copolymers used in this study were two triblock copolymers of P4VP-*b*-PS-*b*-P4VP which were purchased from Polymer Source, Inc. Canada. Detailed information of the triblock copolymers is listed in Table 1. Distinction of the two triblock copolymers is the difference of middle block (PS) length.

2.2. Sample preparation

To prepare aggregates solution, the triblock copolymer (or block copolymer binary blends with predetermined component) was first dissolved in 1,4-dioxane, which is a

common solvent for both PS and P4VP blocks. Initial copolymer concentrations in organic solvent were kept at 1 wt% for all of the samples. The solutions were kept stirring overnight to make the copolymers dissolve into the solvent by single molecule form. Then, a predetermined amount of deionized water (25 wt% of the solution) was slowly (ca. 0.2 wt%/30 s) added into the copolymer solution with stirring. After that, the micellar solution were kept stirring for 3 days. Then, a large amount of water (ca. 600 wt%) was added to the resulting solutions in order to quench the aggregate morphologies. At this water content range, structures of the aggregates became kinetically locked over experimental time scale [13]. Subsequently, the resulting solution was placed in dialysis tubes (Cut off: 12,000–14,000, DM27 EI9004, USA) and dialyzed against deionized water for a few days to remove all of the organic solvent from the micellar solutions. During dialysis process, pH of the distilled water was adjusted to 4 by hydrochloric acid (HCl) to keep the micellar solutions from precipitating [29,42,43]. Aggregates morphology was stable during dialysis process and after dialysis. The length of time between water addition reaching predetermined amount and subsequent large amount water addition is named annealing time.

Preparation method effect on aggregate morphology was studied by preparing samples in two different methods: premixing and postmixing method. For premixed samples, calculated amounts of dry triblock copolymers blends were dissolved in dioxane and formed 1 wt% homogeneous solution. After stirring overnight, predetermined deionized water (25 wt%) was added to the homogeneous solution slowly to induce self-assembly of the copolymers in the solution. Following procedures were kept the same as that given above. The postmixed samples were prepared by pouring together predetermined amounts of two copolymer micellar solutions (immediately after water content reached 25 wt% and without further annealing). This aforementioned two micellar solutions were prepared by dissolving two block copolymers in dioxane and adding predetermined deionized water (25 wt%) to induce the self-assembly separately. The other experimental procedures were kept the same as that given above. It should be noted that all of the results given in this paper were samples prepared from premixing method if not given particular illustration.

For premixed solution of P1/P2 = 1/1, samples from the aggregates solutions were extracted and quenched by large amount of water at varied time for kinetic studies.

2.3. Transmission electron microscopy (TEM)

It is most suitable to adopt TEM to directly observe morphologies of complicated, irregular, and polydisperse

Table 1
Molecular characteristic of triblock copolymers

Triblock copolymers	Mn	PDI	P4VP content (%)	Microstructure ^a
P1: P4VP ₄₃ - <i>b</i> -PS ₂₆₀ - <i>b</i> -P4VP ₄₃	4500–27,000–4500	1.09	25	C, R
P2: P4VP ₄₃ - <i>b</i> -PS ₃₆₆ - <i>b</i> -P4VP ₄₃	4500–38,000–4500	1.10	19	V

^a Note: C, R, V represent cylinders, ring-shaped structures, and vesicles, respectively.

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