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Flower like micellar assemblies in poly(styrene)-block-poly(4-vinyl pyridine)/poly(acrylic acid) complexes

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ABSTRACT

The formation of rare flower like micelles in poly(styrene)-block-poly(4-vinyl pyridine)/poly(acrylic acid) (PS-*b*-P4VP/PAA) diblock copolymer/homopolymer complexes is reported. The self-assembly as well as the morphological changes in the complexes were induced by the addition of a high molecular weight PAA/ethanol solution into the PS-*b*-P4VP solution in dimethyl formamide followed by dialyses. The composition-dependent micelles were varying in size and shape with increase in PAA concentration in solution. The complex aggregates in solution were characterized by dynamic light scattering (DLS) whereas morphologies in the solid complexes were observed using transmission electron microscopy (TEM). Flower like micelles are formed in complexes at 20 wt% PAA concentration followed by 'spiky' micellar assemblies at 40 wt% PAA. The size of the micelles was found to be increased upon the addition of PAA into the block copolymer solution. Infrared studies revealed the intermolecular hydrogen bonding interactions between the complementary binding sites on PAA and the P4VP block of the block copolymer. Finally, a model was proposed to explain the self-assembly and morphological transitions in these complexes based on the experimental results obtained.

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1. Introduction

Micelles and vesicles created from block copolymers and block copolymer containing systems have become attractive and promising research objects in biology, chemistry and physics and found numerous practical applications in various branches of science and technology [1–4]. In fact, block copolymers are known to self-assemble into various ordered morphologies [5–6], and these morphologies can be controlled by varying the structural parameters of the block copolymer, solvent, temperature, concentration and pH of the solution [7]. The final morphology of the system will be the balance between interfacial energies and entropy loss due to the insoluble blocks packed into aggregate domains [8,9].

Micelles are used to encapsulate and transport macromolecules into the blood stream or through the skin, leading to the widespread use of these structures in cosmetics and extensive research into the potential use for drug delivery [10–12]. Block copolymers can be designed in a way to fit well to create micelles. Moreover, block copolymers, which have the same basic architecture of

lipids, mimic the lipid amphiphilicity [9]. Therefore, micelles have been widely used as model systems for in vitro explorations such as the study of membrane proteins [7]. The first observation of simple block copolymer micelles and vesicles was done by Eisenberg and co-workers who proposed the aggregations of the block copolymer with small hydrophilic fractions as crew-cut micelles [13,14]. Other than the conventional synthetic block copolymer micellar aggregates, micelles formed by the self-assembly of oppositely charged components are gaining enormous attention recently due to many potential applications [15]. Such micelles formed from polyelectrolyte and block copolymers are given different names like "block ionomer complexes" [16], polyelectrolyte complex(PEC), or "polyion complex micelles" (PIC) [17–19].

In this article, we describe formation of sunflower like micelles and a composition-dependent micellar development generated from the self-assembly in complexes of poly(styrene)-block-poly(4-vinyl pyridine) (PS-*b*-P4VP) block copolymer and a high molecular weight ($M_w=750,000$) PAA. The strong intermolecular hydrogen bonding between PAA and P4VP leads to the formation of various self-assembled micelles. Sunflower like micelles have been hardly reported due to the complexity in the formation of these architectures. The hydrogen bonding interactions in the complexes was investigated by Fourier transform infrared (FTIR) spectroscopy. The hydrodynamic diameter (D_h) of the aggregates

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in solution was detected by dynamic light scattering (DLS) and the microphase morphology of the complexes was examined using transmission electron microscopy (TEM).

2. Results and discussion

In amphiphilic block copolymer systems, the aggregates were prepared by first dissolving the block copolymer in a solvent common for both blocks. This was followed by the addition of a non-solvent which is a precipitant for the core-forming block but a good solvent for the corona-forming block [14]. The same method can be adopted in selected block copolymer/homopolymer systems. The complexes were prepared by the drop-wise addition of PAA/ethanol solution into PS-*b*-P4VP/DMF solution, which induced the formation of micelles. Due to the insolubility of PS in aqueous solvents, micellar aggregation can be induced by changing the solvent quality from a good solvent (i.e., DMF) for both blocks to a selective solvent (ethanol). At a particular ethanol content, the PS blocks start to aggregate to form the micelles, i.e. core-shell micelles with neutral PS chains as the core and hydrogen bonded PAA/P4VP pair as the shell. There are various reports regarding the nature of interactions in poly(carboxylic acid) complexes. Fujimori et al. [19] and Abe et al. [20] investigated the hydrogen bonding interaction between PAA and P4VP (P2VP) whereas evidence for ionic interactions between these polymers is also reported [21–23].

The morphology of the complexes was observed using TEM which has been widely used to observe the formation of micelles and vesicles. The pure PS-*b*-P4VP block copolymer possesses a self-assembled morphology of uniform spherical micelles as shown in Fig. 1. Addition of ethanol into block copolymer/DMF mixture results in the confinement of PS blocks to the core of the micelles. Fig. 1 also shows the hydrodynamics diameter (D_h) distribution of the aggregates in solution measured by DLS. The PS-*b*-P4VP block copolymer forms micelles with an average diameter 150 nm in solution.

Upon the addition of PAA, which selectively swells the block copolymer, flower like micelles of various sizes were formed in complexes depending on the composition. The TEM images of various compositions and corresponding DLS curves are given in Fig. 2. Flower like micelles with an average size of 320 nm are formed at 20 wt% PAA concentration in the complex (Fig. 2a). Interestingly, as the concentration of PAA increases, the size and shape of the micelles change. This can be attributed to the adsorption of added PAA on to the surface of micelles due to strong interaction between the P4VP and PAA. The shape of the micelles in complexes is observed to change from flower like to more 'spiky' flower at 40 wt% PAA complex (Fig. 2b). It is noted that the micelle size is also increased to around 500 nm at this concentration. At 60 wt% PAA, the complexes form a more or like

deformed clusters of around 600 nm diameter as shown in Fig. 2c. At 80 wt% PAA, the complexes form larger cluster having D_h around 820 nm (Fig. 2d). The deformation of spherical micelles at higher PAA concentration can be attributed to reduction in the additional entropy associated with the increase of the degree of stretching of the core-forming PS blocks. At low PAA concentrations (20 and 40 wt%), the complex solution contains more uniform size micellar aggregates (Fig. 2a and b), which is identified by the single less broad peak in DLS graphs. However, D_h of aggregates increase and the peak becomes broader with increasing PAA concentration.

When block copolymer molecules are solubilized in homopolymer to form aggregates, various intra-aggregate interactions will be influenced, thus the shape and size of the aggregates are also changed with variation in the block copolymer fraction, composition, molecular weight, etc. The morphological transition can be regarded as the structural change due to the balance of various intra-aggregate interactions. Here, the shell region of the micelles is composed of bonded PAA/P4VP complex and the core is formed by PS. This is obvious because the PS blocks are insoluble in ethanol and will form the core of the micelle.

When interpolymer interaction outweighs polymer-solvent interaction, the two polymers precipitated to form highly associated systems known as polymer complexes and here the complexation of PAA/PS-*b*-P4VP is confirmed by the formation of a white precipitate upon mixing the individual polymer solutions. The hydrogen bonding between PAA and P4VP (or P2VP) was also reported by several authors [20,21]. It can be suggested that in PAA/PS-*b*-P4VP complexes, hydrogen bonding interaction also exists between pyridine groups and acrylic acid groups.

Fig. S1 illustrates the FTIR spectra of pure PAA, PS-*b*-P4VP block copolymer and 50/50 PAA/PS-*b*-P4VP complexes. Infrared studies show that the hydroxyl, carbonyl and pyridine ring peaks undergo important changes which can be attributed to the hydrogen bonding between them. Pure PAA exhibits a broad band (Fig. S1A) at 1710 cm^{-1} which can be attributed to the overlapping of two carbonyl stretching bands comprising of free as well as self-associated carboxylic groups in PAA and this band moves towards higher wavenumbers upon complex formation. This is due to the intermolecular interaction between the carboxylic group in PAA and pyridine groups in P4VP. The interaction between PAA and P4VP block can be further examined by analysing the $1550\text{--}1600\text{ cm}^{-1}$ region in the IR spectra of PAA/PS-*b*-P4VP complexes which is given in Fig. S1B. Pure P4VP exhibits two peaks at 1570 cm^{-1} and 1595 cm^{-1} , respectively, which are the ring modes of pyridine group. As the concentration of PAA increases, this band becomes broad and shift towards higher wavenumber region. This is due to the increase in stiffness of the pyridine ring as a result of hydrogen bonding [25]. The hydrogen bonding interaction between carboxylic groups and pyridine nitrogens is strong which causes the positive deviation in glass transition temperature of the complexes [24].

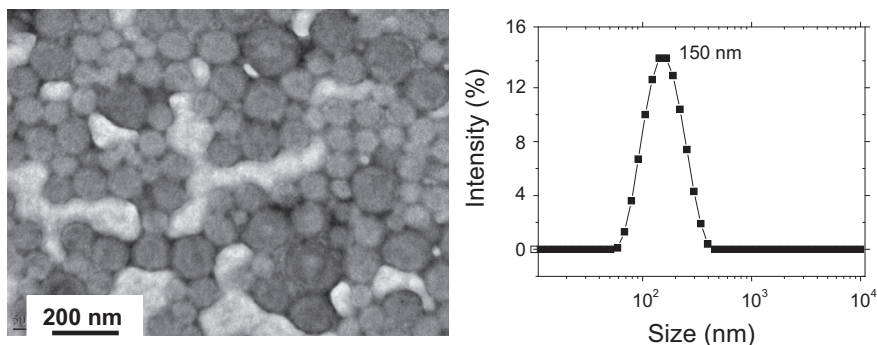


Fig. 1. The TEM image (left) and DLS curve of neat PS-*b*-P4VP block copolymer.

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