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Micelle-like particles formed by carboxylic acid-terminated polystyrene and poly(4-vinyl pyridine) in chloroform/methanol mixed solution

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Abstract

Preparation and characterization of isolated particles and clusters of carboxylic acid-terminated polystyrene (CPS) and poly(4-vinyl pyridine) (P4VP) blends in chloroform/methanol (9/1, v/v) solution are reported. In chloroform CPS–P4VP blends form graft-like structure due to the interaction between terminal carboxylic acid and 4VP units. Upon addition of methanol, isolated particles and clusters with micelle-like structure were prepared. Dynamic light scattering (DLS) results and transmission electron microscopy (TEM) images both suggest the existence of isolated particles and clusters with micelle-like structure in the mixed solution. The effects of weight ratio of CPS to P4VP and addition of copper ion on the size of isolated particles and clusters were also investigated. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(4-vinyl pyridine); Carboxylic acid-terminated polystyrene; Dynamic light scattering

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1. Introduction

It is well known that block or graft copolymers have the potential to form micelles in selective solvents that are good for one block (or grafts) and a non-solvent for the other [1–5]. The core of a micelle basically consists of compact insoluble blocks (or grafts) and is surrounded by a corona of solvated blocks (grafts). In such systems, the driving force for micellization is mainly the repulsive interactions between one of the blocks (or grafts) and the solvent [6,7]. Recently, some research groups studied micellization of ion-containing block copolymers or hydrogen bonding involved block copolymers [8–13]. Eisenberg et al. examined micellization of ion-containing block copolymers in non-ionic solvents [8,9]. They found polystyrene-*block*-poly(metal methacrylate) diblock ionomer can form reverse micelles in solvents selectively good for the polystyrene block. In these systems the tendency for micellization is driven by ion pair associations that occur in the core of micelles. Zhao et al. studied monodisperse polystyrene-*block*-poly(*p*-hydroxystyrene) copolymer and found that the copolymer formed large aggregates with a hydrodynamic radius $R_h = 76$ nm in toluene by dynamic light scatting (DLS) [10]. In their experiments the hydrogen bonding in the micellar core is an additional driving force for the micelle formation. Kataoka et al. prepared stable and monodispersieve polyion complex micelles in an aqueous milieu through electrostatic interaction between a pair of oppositely charged block copolymers with common poly(ethylene glycol) (PEG) segments: poly(ethylene glycol)–poly(L-lysine) block copolymer and poly(ethylene glycol)–poly(α,β-aspartic acid) block copolymer [11–13]. These polyion complex micelles have a corona of hydrophilic PEG segments, which surround the core of the polyion complex of cationic and anionic segments.

In all the cases mentioned above, for a block copolymer chain, one block existing in core and the other in corona is connected by chemical bonds. Recently, our interests lie in some new approaches to macromolecular assembly of polymer blends in solution. In a previous paper, we reported association of sulphonated polystyrene/poly(4-vinyl pyridine) blends in tetrahydrofuran/methanol (1/10, v/v) mixed solvents [14], which is a precipitant for the former but solvent for the latter. It was found that in the solution the polymer blends formed stable isolated particles and their clusters, both of which are stabilized by solvated poly(4-vinyl pyridine) chains. Comparing with the micelles

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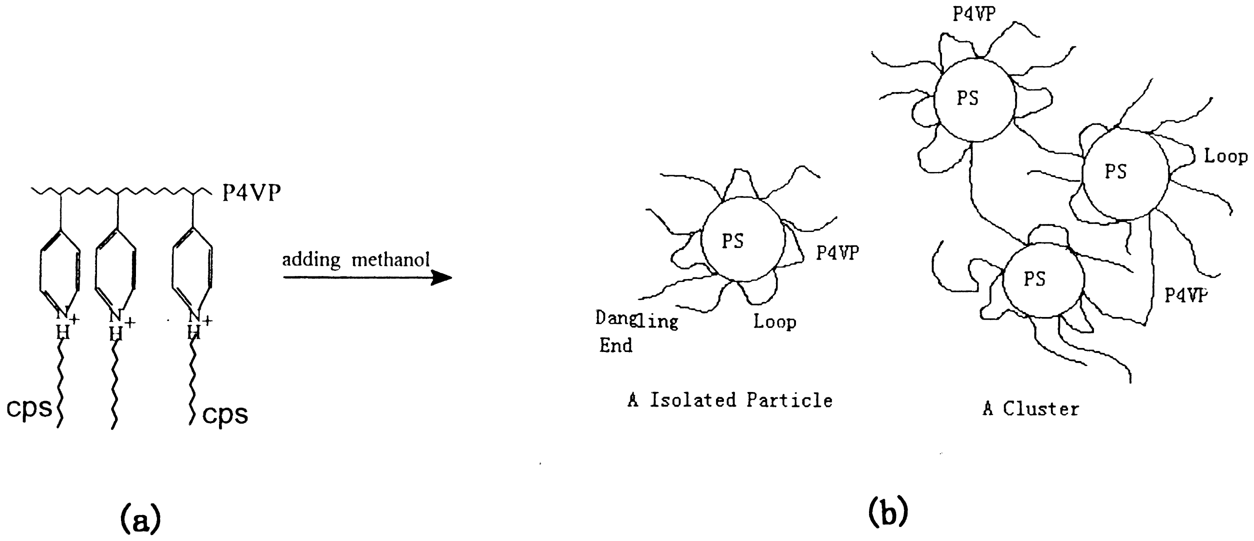

Fig. 1. Schematic representation of the simplified model of formation of micelle-like particles. (a) Graft structure formed by CPS–P4VP blends in chloroform. (b) Isolated particles and clusters formed by CPS–P4VP in chloroform/methanol solution. In both cases, the core consists of collapsed PS chains and the corona consists of solvated P4VP chains.

prepared by block copolymers in selective solvents, there are not covalent bonds but specific interactions exist between the two components in the self-assembly structures.

In this paper we report association of carboxylic acid-terminated polystyrene (CPS) and poly(4-vinyl pyridine) (P4VP) blends in chloroform/methanol mixed solution. In chloroform, a common solvent for both CPS and P4VP, carboxylic acid groups and P4VP units not only form hydrogen bonds but also have proton transfer: some of the protons are shared by pyridine units and neighboring carboxylic groups [15], hence a graft-like structure will occur in the solution [16]. This structure was schematically shown in Fig. 1a. Upon adding methanol, a solvent for P4VP but a precipitant for CPS, into the solution dropwise, CPS chains will collapse. In the chloroform/methanol mixed solution (1/9, v/v), CPS chains still attach to P4VP chains, collapsed CPS chains form compact core and solvated P4VP chains form corona (Fig. 1b). Similar to micelles formed by block copolymers, the stable particles prepared by the above polymer blends may have two layers structure. However, the core and the corona of the particles are connected by specific interaction but covalent bonds. Solvated P4VP chains and interaction between carboxylic acid and P4VP units stabilize these particles with micelle-like structure. The formation of the particles with micelle-like structure in selective solvents by polymer blends is the distinguishing feature of this investigation.

2. Experimental part

2.1. Materials

Carboxylic acid-terminated polystyrene was synthesized by anionic polymerization initiated with *n*-BuLi in THF at −78°C. The polymerization was terminated by carbon dioxide and HCl solution, successively. The molecular weight (M_n) of the polymer is measured to be 2.0×10^3 (on PS standards). The polydispersity (M_w/M_n) was determined to be 1.1.

Poly(4-vinyl pyridine) was synthesized by free radical polymerization. The viscosity-average molecular weight of the polymer (M_η) is 4.00×10^4.

2.2. Preparation of micelle-like particles

Micelle-like particles were prepared by adding methanol drop by drop to a mildly stirred CPS–P4VP chloroform solution. Addition of methanol to the solutions result in slight blue to white milky solutions indicating appearance of aggregates. In the final solution, the volume ratio of methanol to chloroform is 9 : 1.

In order to examine the role of P4VP in the association of CPS in mixed solution, methanol was added dropwise to a CPS chloroform solution in the absence of P4VP. The immediate appearance of the CPS precipitate indicates that CPS aggregates are completely unstable without hydrogen bonding and stabilization of solvated P4VP.

2.3. Dynamic light scattering measurements

Dynamic light scattering experiments were performed to measure the hydrodynamic diameter of the particles. The scattered light of a Argon laser ($\lambda = 514.5$ nm) was measured at 90° and collected on a Brookhaven BI 9000AT correlator at 25°C. The translational diffusion coefficient D and the hydrodynamic radius R_h were obtained from the average decay rate Γ and Stokes–Einestein

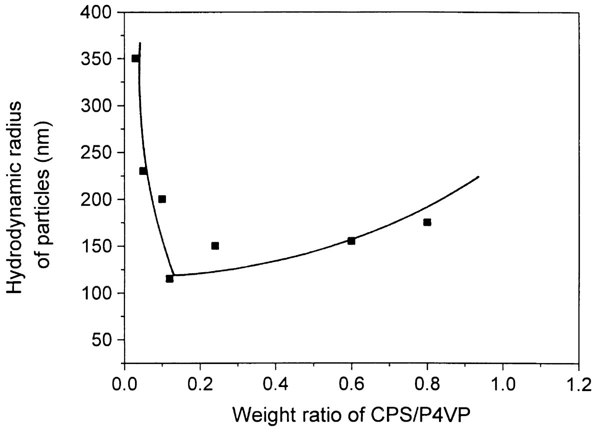

Fig. 2. The relationship between the hydrodynamic radius (R_h) of the particles in chloroform/methanol solution (1/9, v/v) and weight ratio of CPS to P4VP.

formula,

$$D = \Gamma/q^2 \tag{1}$$

and

$$R_h = kT/6\pi\eta D \tag{2}$$

where the scattering vector

$$q = 4\pi n/\lambda \sin(\theta/2) \tag{3}$$

In Eqs. (1)–(3) θ, λ, k, T, η and n are the scattering angle, the incident wavelength in vacuum, the Boltzmann constant, temperature, solvent viscosity and solvent refractive index, respectivly. The polydispersity of the particles (μ_2/Γ^2, where μ_2 is the second cumulant of the decay function) could be obtained using CONTIN V5.0 software supplied by Brookhaven.

2.4. Transmission electron microscopy

Transmission electron microscopy (TEM) was used to observe the morphology of the particles. Species were prepared by freeze-drying dilute solutions on a copper grid covered with a thin carbon film, and then staining in iodine vapor. In this way P4VP units could be stained. TEM observations were proceeded on a Philips EM400ST transmission electron microscopy at an accelerating voltage of 80 kV.

3. Results and discussion

The dependence of the average hydrodynamic radius of the particles on the initial weight ratio of CPS to P4VP is shown in Fig. 2. Initially, the average hydrodynamic radius of the particles decreases with the increase of the CPS/P4VP weight ratio. When the ratio reaches 0.12, the particles with the smallest radius can be achieved. However, with further increase of the ratio, the average hydrodynamic radius increases. Webber et al. studied micelle formation of poly(acrylic acid)-*graft*-polystyrene in aqueous solution [17], where the grafts collapse forming core and the solvated backbone act as the corona. They observed that the higher the grafting density of the hydrophobic polystyrene grafts, the smaller the diameter of the micelles when the grafting density lies between 2 and 10 mol%. This tendency is consistent with our experimental result when the weight ratio of CPS to P4VP is smaller than 0.12.

The stabilization of the particles can be attributed to the specific interaction between vinyl pyridine units and terminal carboxylic acid groups, and solubility of P4VP in the mixed solution. At low weight ratio, fewer CPS chains attach to a P4VP chain and the formation of particles is an enthalpy-driven process, so with the increase of the ratio the average hydrodynamic radius of the particles decrease. However, at high ratio more CPS chains are attached to a P4VP chain. In the formation of isolated particles and clusters the coronal chains must form loops in order to bring the neighboring CPS chains into the core (Fig. 1b), hence the entropic penalty resulting from the loops in the corona should be severe. For circumventing this penalty, a cluster structure, connecting of isolated particles by solvated chains (cluster), may appear.

Fig. 3 shows two typical distributions of the hydrodynamic diameter of the particles with different initial weight ratio measured by dynamic light scattering. All the cases present a broad distribution. For the CPS–P4VP solutions with weight ratio of 0.12 and 0.24, the polydispersities of the size distributions are about 0.11 and 0.16, respectively. Fig. 3a represents the DLS result of the CPS–P4VP solution with a weight ratio of 0.12, two peaks can be observed in the figure. One peak from 106 to 151 nm should be related to the isolated particles, and the other from 213 to 329 nm corresponds to the association of isolated particles (cluster). Fig. 3b is the DLS result of CPS–P4VP solution with a weight ratio of 0.24, in which also two peaks can be observed, one is in the range 130–183 nm, and the other in 336–476 nm. Comparing Fig. 3a and b, it is observed that with increase of the CPS–P4VP weight ratio, the sizes of the isolated particles and clusters both increase, which means at high ratio more CPS chains enter into an isolated particle and more isolated particles get involved in a cluster.

Coleman et al. studied hydrogen bonding in polymer blends containing methacrylic acid and vinyl pyridine groups [18]. They quantitatively measured the fraction of pyridine groups that are hydrogen bonded to carboxylic acid groups and drew a conclusion that in the formation of hydrogen bonding there is a competing equilibrium among the species of acid–pyridine complex, acid dimmer, acid monomer, and uncomplexed pyridine. In the present system, not all carboxylic acid take part in the formation of hydrogen bonding. The absence of peaks corresponding to the unassociated molecules is presumably due to the fact that the signal is dominated by scattering from the particles.

A TEM image of the particles formed by CPS–P4VP (0.1, w/w) in chloroform/methanol mixtures is shown in

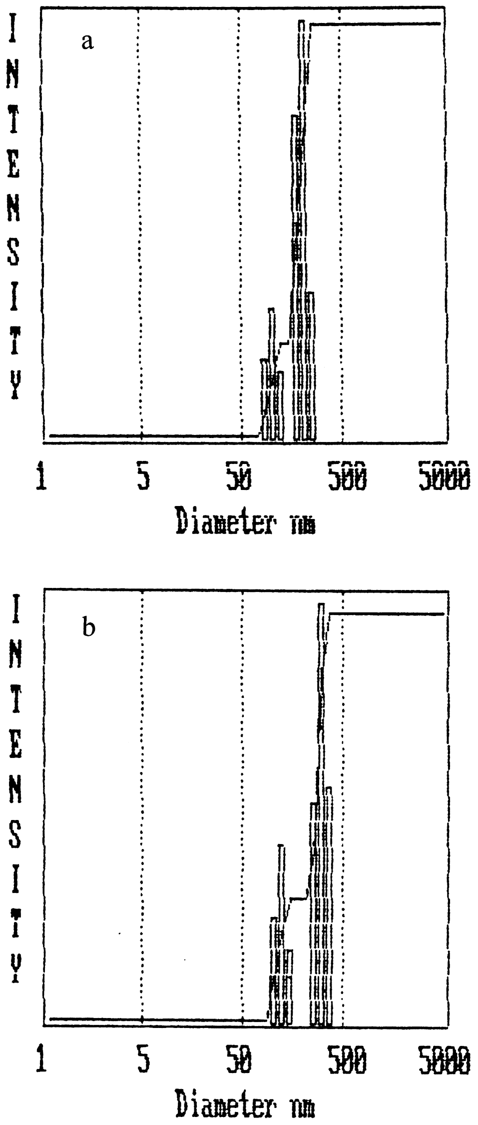

Fig. 3. Histograms showing the size distribution of (a) 1 mg/ml CPS–P4VP (0.12, w/w) in chloroform/methanol solution (1/9, v/v); (b) 1 mg/ml CPS–P4VP (0.24, w/w) in chloroform/methanol solution (1/9, v/v).

Fig. 4. In the picture not only isolated particles but also aggregation of particles can be observed. It is noted that some isolated particles with core–shell structure are observed (arrow 1). The white core consists of collapsed PS chains and the black shell is formed by stained P4VP chains.

In the past micellar aggregation are often observed by several groups. Semenov et al. proposed a theory for the equilibrium and dynamic properties of a solution of telechelic polymers in the limit of high aggregation number. Their theory showed that at some polymer concentration telechelic polymers have the potential to produce flower structure, in which micelles are bridged by polymer chains [19]. Watanabe et al. studied the rheology of solutions of a series of styrene–butadiene diblock copolymers dissolved in a selective solvent *n*-tetradecane [20]. They found that in some cases micelles in the solution are spontaneously arranged to form a regular three-dimensional array referred to as a macrolattice. By TEM Webber et al. found if the concentration of PAA-*g*-PS added to water is sufficiently high, the micelles consist of multiple polystyrene cores surrounded by PAA loops [17]. In our system aggregation of isolated particles with densely packed flowers structure (arrow 2 in Fig. 4) or densely packed globe structure (arrow 3 in Fig. 4) indicate that just similar to aggregation of micelles, in the aggregation of isolated particles the neighboring particles are bridged by P4VP chains.

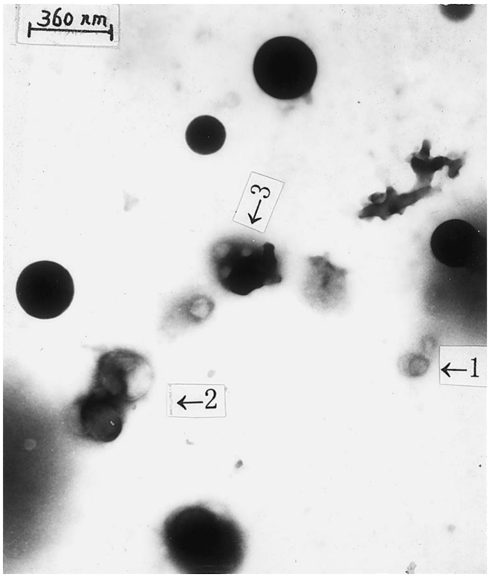

Fig. 4. A TEM image of the specimen prepared by dropping methanol into CPS–P4VP (0.1, w/w) chloroform solution.

The corona of the particles consists of P4VP chains, and

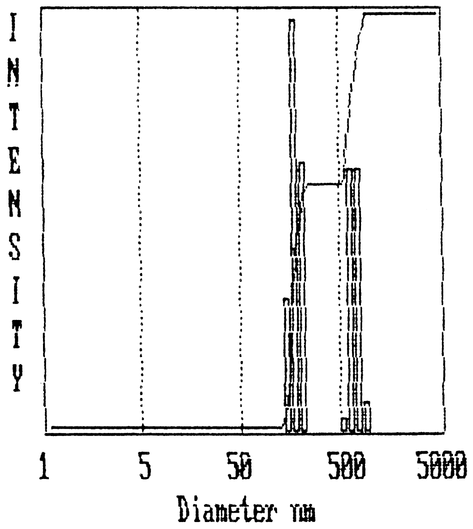

Fig. 5. Histograms showing the size distribution of 1 mg/ml CPS–P4VP (0.24, w/w) in chloroform/methanol solution (1/9, v/v) after addition of 0.1 ml 1.3 mg/ml $CuSO_4$ aqueous solution.

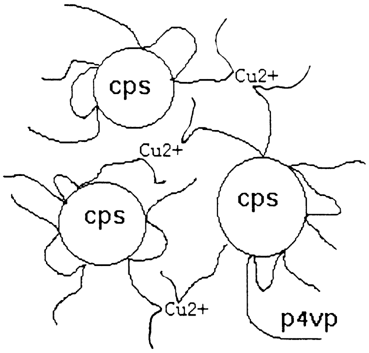

Fig. 6. Schematic representation of the simplified model of particles bridged by Cu^{2+}.

one copper ion can coordinate with two 4-vinyl pyridine units, so it is very interesting to investigate the effect of addition of Cu^{2+} upon the formation of particles. Fig. 5 shows the size distribution of 3 ml 1 mg/ml CPS–P4VP (0.24, w/w) solution after adding 0.1 ml $CuSO_4$ aqueous solution (1.3 mg/ml). Upon addition of 0.1 ml $CuSO_4$ solution, two peaks at 199–259 nm and 671–948 nm appear. Comparing with DLS result of the original solution (Fig. 3b), the shift of the two peaks means more isolated particles and clusters are bridged by Cu^{2+} (Fig. 6). With further addition of $CuSO_4$ solution, gel can be observed, indicating too many Cu^{2+} bridging the clusters or isolated particles will produce an infinitely large three-dimensional network. In a previous paper [21], we studied the effect of Cu^{2+} upon self-assembly of sulfonated polystyrene (SPS) and P4VP in THF/methanol (1/10, v/v) solution. In the selective solvents, SPS–P4VP can form stable particles, in which P4VP chains exist as the corona of the particles. So with addition of Cu^{2+}, more and more particles and clusters are further bridged by Cu^{2+} causing increase of the viscosity of the solution and the size of the particles. At high concentration gel can also be observed indicating appearance of large three-dimensional network.

4. Conclusions

We have examined formation of micelle-like particles by blends of carboxylic acid-terminated polystyrene and poly(4-vinyl pyridine) in methanol/chloroform mixed solution. In the formation of particles, weight ratio of CPS to P4VP exerts an important influence upon the size of particles. DLS and TEM results both show that in the solution not only isolated particles but also cluster exist. The higher the ratio of CPS to P4VP, the more isolated particles are involved in a cluster. Upon addition of Cu^{2+} into the solution, more isolated particles and clusters are bridged by Cu^{2+}.

Acknowledgements

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