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A new approach to self-assembly of polymer blends in solution

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Abstract

A new approach to self-assembly of polymer blends in solution was studied by dynamic light scattering and transmission electron microscopy. Stable isolated particles and their clusters were obtained by dropping sulfonated polystyrene/THF solution into poly(4-vinyl pyridine)/methanol solution. The particles and clusters are stabilized by soluble poly(4-vinyl pyridine). The concentration of poly(4-vinyl pyridine) in methanol plays an important role in the self-assembly of polymer blends. Only in a suitable concentration range, stable particles can be prepared. Gelation appears at high poly(4-vinyl pyridine) concentration, while precipitation of sulfonated polystyrene occurs at low poly(4-vinyl pyridine) concentration. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Self-assembly of polymers leading to nano-structures became one of the most prevalent research subjects in polymer science during the past decades [1]. Among the different approaches to self-assembly, micellization of block copolymers is the most common one and has been investigated extensively [2–4]. A block copolymer in a selective solvent, i.e., being a good solvent for one block but a non-solvent for the other, will form spherical aggregates composed of a compact core of the insoluble blocks and a corona of the soluble blocks. In recent years, Eisenberg et al. [5–9] reported various morphologies of micelles obtained from the so-called crew-cut block copolymers consisting of a long hydrophobic block and a very short hydrophilic ionic block.

Hydrocarbon polymers bearing a few percent of the hydrophilic groups such as carboxylic acid, sulfonic acid or their salts are usually insoluble in a aqueous medium. However, Jiang et al. [10–12] found that via a special preparation procedure, the polymers can spontaneously aggregate to stable nano-size particles in water.

In this communication, we propose a new approach to self-assembly of multicomponent polymers in solution. Here polymers A and B may self-assemble into a micelle-like structure in a solvent mixture which is a precipitant for A but good solvent for B. The compact core of polymer A is stabilized by soluble B chains surrounding the core. Obviously, there are no covalent bonds but specific interactions only existing between the two components A and B. This differs from the micelles of block copolymers where the corona and the core are chemically bonded.

2. Experimental

2.1. Materials

Polystyrene was synthesized by anionic polymerization. The number-average molecular weight (M_n) and the polydispersity (M_w/M_n) of the polymer were measured to be 6.0×10^5 and 1.3 determined by size exclusive chromatography on PS standards, respectively. Sulfonation of polystyrene was carried out according to the method developed by Weiss et al. [13,14]. The degree of sulphonation was 1 mol% as determined by anionic chromatography.

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 particle dispersion

As an example of this approach, we report preparation of the stable particles made of slightly sulfonated polystyrene (SPS, sulfonic acid 1 mol%) and poly(4-vinyl pyridine)

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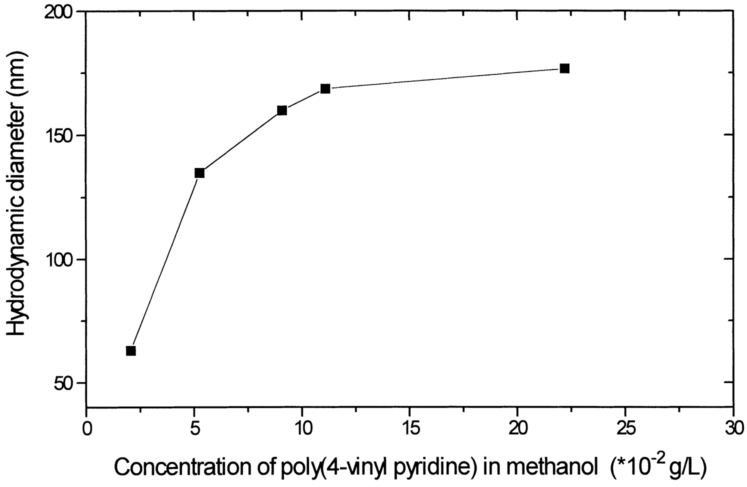

Fig. 1. Hydrodynamic diameter of particles as a function of concentration of P4VP in methanol.

(P4VP). Proton-transfer from the sulfonic acid to pyridine units causes ion–ion interactions between them [15,16]. The micelle-like particles were prepared by adding 1 ml dilute solution of SPS in THF (10 g/l) dropwise to 10 ml of P4VP/methanol solutions of different concentrations with mild stirring. The final solution of methanol/THF (10/1, v/v) was a precipitant for SPS but good solvent for P4VP. This procedure resulted in slightly blue to white milky solutions depending on the size of the particles.

2.3. Dynamic light scattering measurements

Dynamic light scattering experiments (DLS) were performed to measure the hydrodynamic diameter of the particles. Before measurements, the solutions were clarified by filtering through 0.5 μm Millipore filters directly into the cleaned scattering cell. Dynamic light scattering measurements were made using an argon ion laser with a wavelength of 514.5 nm and output power of 10–200 mW. All the DLS was measured at 90° and collected on a Brookhaven BI 9000 AT correlator at 25°C. The output power of the laser and the channel diameter were optimized so as to overcome the possible multiple scattering. The measurement for each solution was repeated at least three times.

The translational diffusion coefficient D and the hydrodynamic radius R_h were obtained from the average decay rate Γ and Stokes–Einestein formula,

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

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

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, Boltzmann constants, temperature, solvent viscosity and solvent refractive index, respectively. Using Eqs. (1)–(3) the hydrodynamic diameter $2R_h$ can be calculated. The polydispersity of the particles (μ_2/Γ, 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 P4VP units with iodine vapor. TEM observations were performed on a Philips EM400ST TEM at an accelerating voltage of 80 kV.

3. Results and discussion

Solutions of the particles with different average size were obtained by changing the initial concentration of P4VP in methanol. The average hydrodynamic diameter of the particles as a function of P4VP concentration in methanol is shown in Fig. 1. The particle size increases significantly from 63 to 160 nm as the P4VP concentration varies from 2.06×10^{-2} to 9.09×10^{-2} g/l, but only a small increment of 16 nm is shown as the concentration increases further to 0.222 g/l. The solutions of the particles with a large diameter such as 168 and 178 nm were not very stable and precipitation was observed after being kept for several days. However, those with a diameter less than 150 nm were very stable and no precipitation was observed even being kept after several weeks.

Two typical distributions of the hydrodynamic diameter of the particles obtained using P4VP solutions of different concentrations are shown in Fig. 2. Both cases present quite broad distributions with a bimodal character.

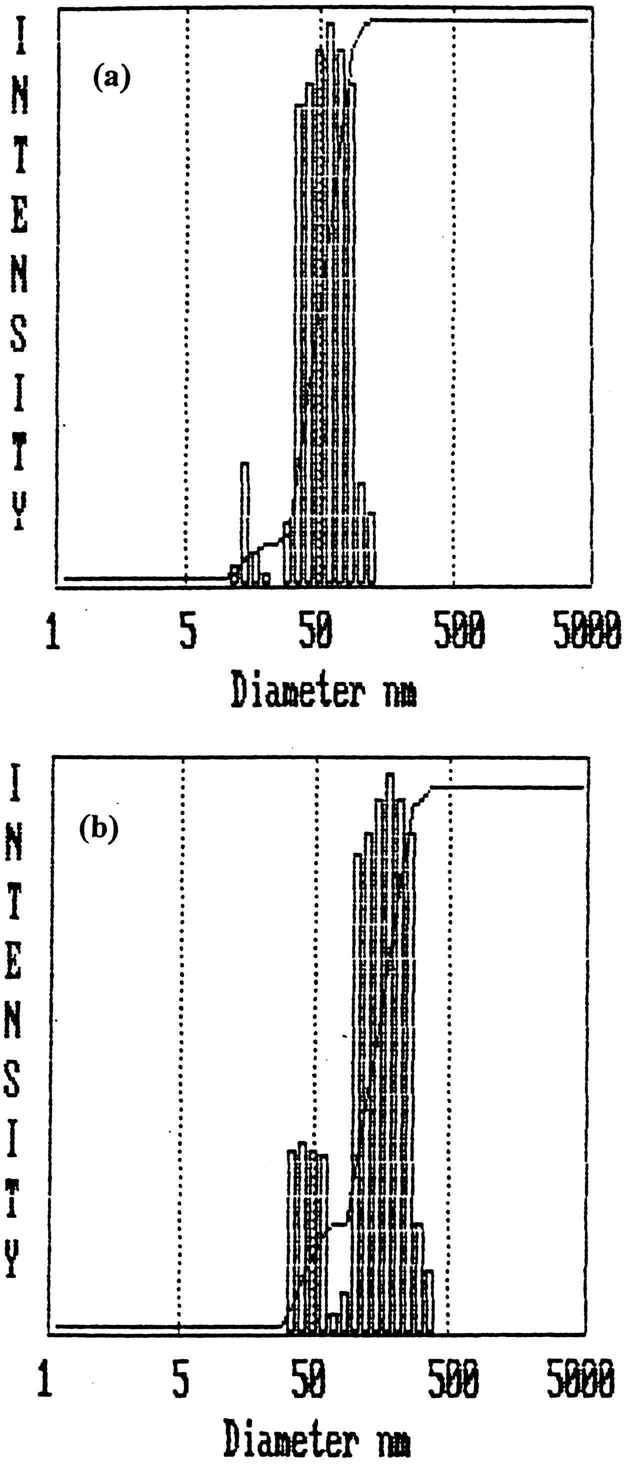

Fig. 2. Histograms showing the size distribution of the particles prepared by dropping 1 ml 10 g/l SPS/THF into (a) 10 ml 2.06×10^{-2} g/ P4VP/methanol; (b) 10 ml 0.111 g/l P4VP/methanol.

Considering that each pyridine unit in P4VP chains provides an interaction site, one P4VP chain is able to connect with many SPS chains which may exist in one particle or neighboring particles. In the latter case, the P4VP chain bridges the particles forming a cluster. Therefore, in the final solutions, four kinds of species may exist, i.e., free SPS chains, P4VP chains, isolated particles and clusters of the particles. In Fig. 2, the absence of peaks at several nanometers corresponding to the free homopolymer chains is presumably because of the fact that the single chains are too small to make detectable signal of scattering compared to that of the particles and clusters [17].

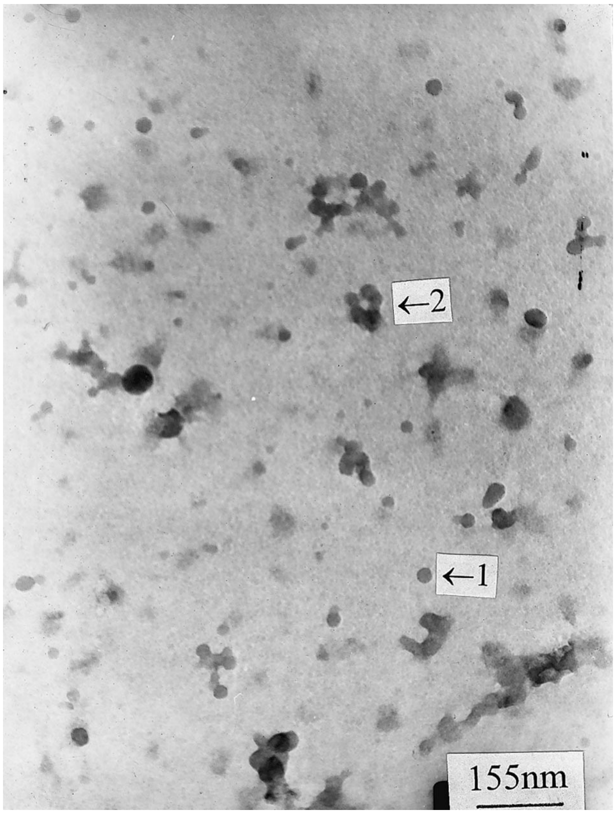

Fig. 3. A TEM image of the specimen prepared by dropping 1 ml 10 g/l SPS/THF solution into 10 ml 2.06×10^{-2} g/l P4VP/methanol solution.

In Fig. 2(a), the small peak located at about 20 nm can be attributed to the isolated particles. The large peak having the diameter ranging from 38 to 150 nm should be associated with the formation of clusters. As the P4VP concentration is increased to 0.111 g/l, the hydrodynamic diameter of both isolated particles and clusters shift to higher values (Fig. 2(b)). In Fig. 2(b) the peak of the cluster is located at about 200 nm and the largest ones reach about 412 nm.

The TEM picture in Fig. 3 is for the particles prepared using P4VP at concentration of 2.06×10^{-2} g/l. The main feature of the micrograph is the coexistence of isolated spheres and clusters with multicore structure as indicated by arrow 1 and arrow 2, respectively. In the TEM picture the diameters of isolated particles range from 12 to 30 nm and the diameters of clusters range from 45 nm to more than 100 nm. The results are in good agreement with the DLS data as shown in Fig. 2(a). Based on all the results described earlier, a schematic representation for the isolated particles

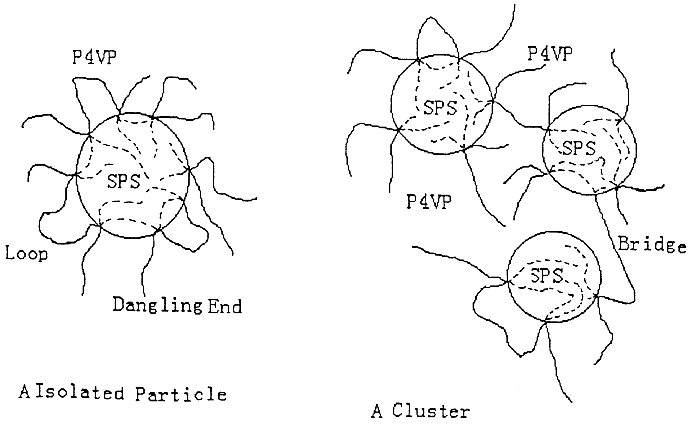

Fig. 4. Schematic representation of the simplified model of formation of particles and clusters by SPS and P4VP in solution.

and clusters is suggested as shown in Fig. 4. For the isolated particles, collapsed SPS chains form the core surrounded by the solvated P4VP chains and the ion–ion interaction sites are located at the interface. At corona of the isolated particles P4VP chains may form loops and dangling ends, both of which can stabilize the particles. The clusters are consisted of insoluble SPS domains linked by P4VP chains.

This communication emphasized the effect of P4VP concentration on particle size and its distribution. It is worth noting two extreme cases as follows: First, addition of a SPS/THF solution into methanol without P4VP resulted in precipitation of SPS immediately. The same phenomenon was found using P4VP solution with a low concentration of 6×10^{-3} g/l. Second, gelation occurred when P4VP solution with high concentration, e.g., 1 g/l, was employed. It seems that stable dispersion of the micelle-like particles can only be obtained when the concentration of P4VP is between a low (C_1*) and a high critical (C_2*) concentration, as schematically shown in Fig. 5. The formation of the stable particles needs a sufficient of P4VP to stabilize the particles and, of course, too many P4VP chains bridging the particles will produce an infinitely large three-dimensional network (gel). Now, the exact values of C_1* and C_2*, and the effects of many factors, such as degree of sulfonation of SPS, molecular weight of P4VP and PH etc. on the structure of the stable particles are being investigated in our laboratory.

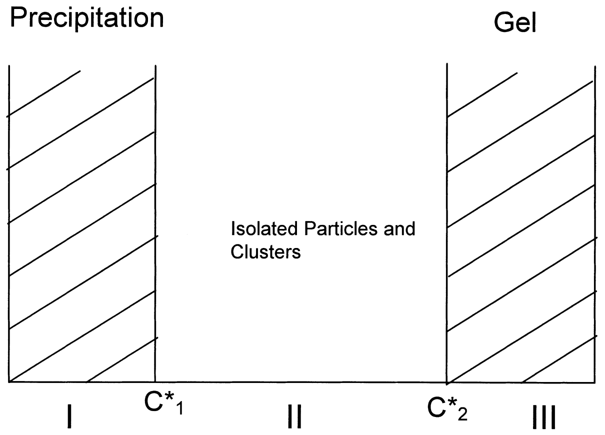

Fig. 5. The effect of concentration of P4VP upon self-assembly of SPS/P4VP in THF/methanol mixed solvents. In area I and III, precipitation and gel can be observed upon adding SPS/THF solution into P4VP/methanol solution. In area II, isolated particles and clusters form.

4. Conclusions

We have examined a new approach to self-assembly of polymer blends in solution. Stable particles consisting of sulfonated polystyrene and poly(4-vinyl pyridine) in THF/methanol mixed solvents were prepared. The size of the particles increases with increasing P4VP concentration in methanol. DLS and TEM results both show that in the solution not only isolated particles but also clusters exist. At high P4VP concentrations, gel formation appears. In this way we have developed a new self-assembly structure, which possesses potential applications in drug delivery, water treatment etc.

Acknowledgements

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