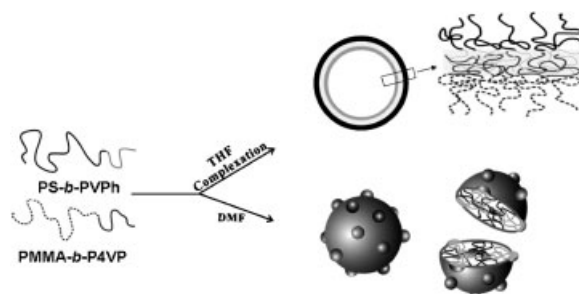


Supramolecular Micellization of Diblock Copolymer Mixtures Mediated by Hydrogen Bonding for the Observation of Separated Coil and Chain Aggregation in Common Solvents

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This paper describes a new approach towards preparing self-assembled hydrogen-bonded complexes that have vesicle and patched spherical structures from two species of block copolymer in non-selective solvents. The assembly of vesicles from the intermolecular complex formed after mixing polystyrene-*block*-poly(4-vinyl phenol) (PS-*b*-PVPh) with poly(methyl methacrylate)-*block*-poly(4-vinylpyridine) (PMMA-*b*-P4VP) in tetrahydrofuran (THF) is driven by strong hydrogen bonding between the complementary binding sites on the PVPh and P4VP blocks. In contrast, well-defined patched spherical micelles form after blending PS-*b*-PVPh with PMMA-*b*-P4VP in *N,N*-dimethylformamide (DMF): weaker hydrogen bonds form between the PVPh and P4VP blocks in DMF, relative to those in THF, which results in the formation of spherical micelles that have compartmentalized coronas that consist of PS and PMMA blocks.



Introduction

Strong interactions through hydrogen bonds has attracted great interest in polymer science because of strong economic incentives that arise from their potential applications.^[1–4] It has been demonstrated that poly(4-vinyl

pyridine) (P4VP) is able to interact strongly with polymers of a wide variety of structures through hydrogen bonding, such as poly(vinyl phenol) (PVPh),^[5–8] poly(vinyl alcohol),^[9] and phenolic resin.^[10] It is well known that the nature of the solvent medium can control complex formation.^[5–7] For instance, a mixture of PVPh/P4VP yields a precipitate of the complex in tetrahydrofuran (THF). However, no precipitation is observed in *N,N*-dimethylformamide (DMF) since the DMF molecule can also participate in hydrogen bonding and competes with P4VP for the hydroxy groups in PVPh. DMF is a much stronger hydrogen-bond acceptor relative to THF, therefore, the presence of such a strong hydrogen-bond breaking solvent does not allow the formation of the inter-polymer complex.^[5,6] Polymer coils are well separated for the PVPh/P4VP mixture in DMF solution and the polymer chains are rather extended prior to solvent evaporation because the inter-association hydrogen bonding between PVPh and DMF is stronger than between PVPh

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and P4VP. Hence, the higher hydrogen-bonding strength of PVPh/P4VP in THF tends to induce polymer complex aggregation.

However, direct observation of a separated coil in DMF and chain aggregation in THF of a PVPh/P4VP blend and complex has never been reported based on our knowledge. Neither macro nor micro-phase separation contrast in electron microscopy imaging is expected because the PVPh/P4VP is a well-known miscible polymer blend system. Herein, we report a facile method to confirm images of different chain behaviors of PVPh/P4VP in DMF and THF solutions by using a mixture of polystyrene-*block*-poly(vinyl phenol) (PS-*b*-PVPh) and poly(4-vinylpyridine)-*block*-poly(methyl methacrylate) (P4VP-*b*-PMMA) because of their ability to self-assemble into well-defined nanostructures.

The mixing of two diblock copolymers with non-covalent bond interactions between two blocks is a convenient approach to explore their morphological behaviors through inter-polymer hydrogen bonding,^[11–15] electrostatic interaction,^[16] and metal-ligand coordination bonding.^[17] The general shapes of the supramolecular structures in this case can be classified into three categories: i) core-shell spherical micelles with an insoluble complex core and a soluble block as the corona,^[13,15] ii) onion-type (core-shell-corona micelles, CSC) with an insoluble core, a shell layer composed of an inter-polymer complex, and a corona formed by a soluble block,^[11] and iii) vesicles from two block copolymers that have two insoluble segments and mutually interacting blocks.^[12,16] Therefore, we expect to see different images of the PVPh/P4VP complexes that correspond to the different supramolecular nanostructures in both THF and DMF. The self-organized supramolecular structure and chain behavior of a mixture of two diblock copolymers mediated by the intermolecular hydrogen bonds between the PVPh and P4VP blocks in different common solvents (THF and DMF) are discussed in this study.

Experimental Part

Diblock copolymers of polystyrene-*block*-poly(4-vinyl phenol) (PS₃₆₀-*b*-PVPh₃₆, PDI = 1.10) and poly(methyl methacrylate)-*block*-poly(4-vinylpyridine) (PMMA₁₅₀-*b*-P4VP₄₀, PDI = 1.18) were synthesized by sequential anionic polymerization using *sec*-butyl lithium as the initiator.^[18] To obtain the solution assembly of PS-*b*-PVPh (SVPh) and PMMA-*b*-P4VP (MVP), these two diblock copolymers were dissolved in common solvents (THF and DMF), and then filtered through a membrane with a nominal pore size of 0.2 μm to remove dust before mixing.

Infrared spectra were recorded at a resolution of 1 cm^{-1} on a Nicolet AVATAR 320 FTIR spectrometer using polymer films cast onto KBr pellets from THF or DMF solution and then vacuum dried. Transmission electron microscopy (TEM) was performed on a Hitachi H-7500 Transmission Electron Microscope at an acceleration voltage of 100 kV. A drop of the very dilute solution was placed onto a carbon-coated TEM copper grid. After 3 min, excess solution was blotted away using a strip of filter paper. The samples were allowed to dry in atmosphere at room temperature and then stained with ruthenium tetroxide (RuO₄) for 30 min or iodine (I₂) for 24 h. It is known for several simple cases that P4VP, PVPh, PS, and PMMA show deep, intermediate, light, and very light contrasts, respectively, with RuO₄ staining, which would enable one to distinguish the phase behavior in this blend system.

Results and Discussion

Figure 1 shows the IR spectra of the hydroxy group stretching of a SVPh/MVP = 1/1 mixture cast from THF and DMF solutions recorded at room temperature. Pure PVPh shows two unresolved bands in the hydroxy-stretching region, which correspond to the free hydroxy group at 3 525 cm^{-1} and a broad band centered at 3 400 cm^{-1} for the absorption of self-associated hydroxyl-hydroxy groups. The peak frequency of the broad band shifts to lower wavenumbers of the diblock copolymer blends (SVPh/MVP = 1/1), which reflects that a new distribution of hydrogen bonds results from the competition between the hydroxyl-hydroxy group interactions within pure PVPh and the hydroxyl-pyridine group interactions between PVPh and P4VP. The THF system has a lower intensity signal for the free hydroxy groups and lower wavenumbers for the broad band in comparison to the DMF system,

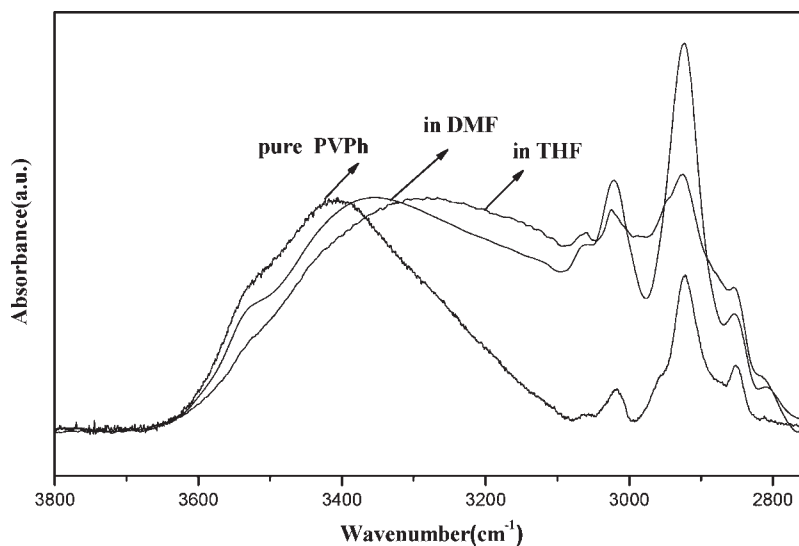


Figure 1. IR spectra of the hydroxy region for pure PVPh and SVPh/MVP = 1/1 diblock copolymer mixtures in both THF and DMF.

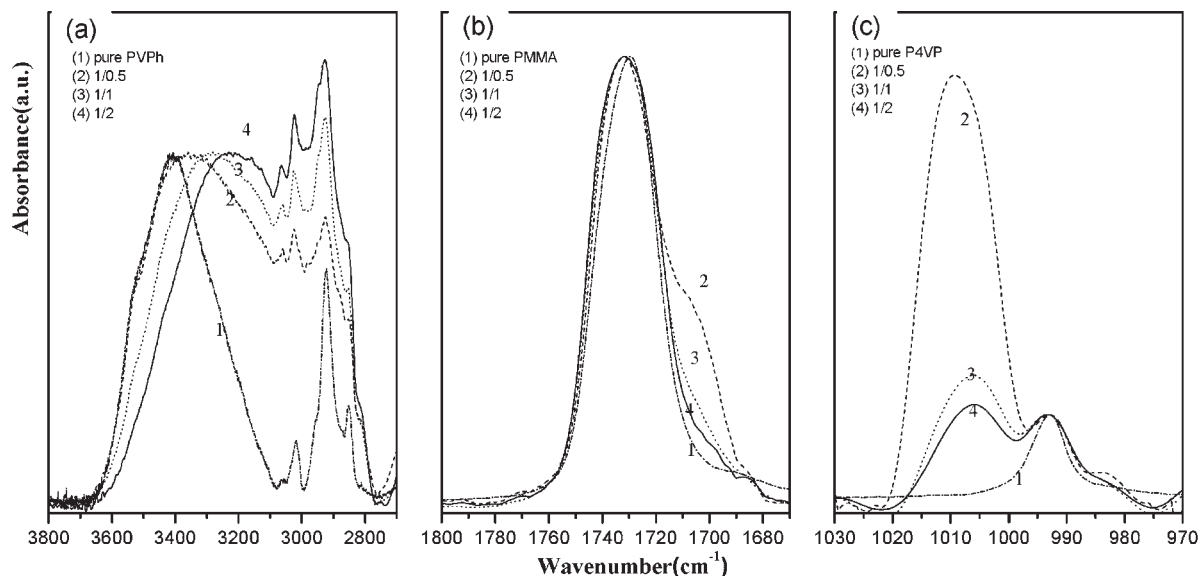


Figure 2. FT-IR spectra of SVPh/MVP in THF at room temperature: a) hydroxy stretching band ($2700\text{--}3800\text{ cm}^{-1}$), b) carbonyl stretching band ($1670\text{--}1760\text{ cm}^{-1}$), and c) pyridine ring absorption ($970\text{--}1030\text{ cm}^{-1}$).

which suggests that the PVPh/P4VP hydrogen-bonding interactions in THF are stronger than in the DMF system.^[19]

Figure 2 presents several regions of the IR spectra recorded at room temperature for various SVPh/MVP mixtures, namely the a) hydroxy stretching ($2700\text{--}3800\text{ cm}^{-1}$), b) carbonyl stretching ($1670\text{--}1760\text{ cm}^{-1}$), and c) pyridine ring absorption ($970\text{--}1030\text{ cm}^{-1}$) regions, which are all influenced by hydrogen-bonding interactions. Clearly, the hydroxy stretching intensities of the SVPh/MVP mixtures shift to lower wavenumbers upon increasing the MVP content, as indicated in Figure 2(a). Figure 2(b) shows the carbonyl stretching region ($1670\text{--}1760\text{ cm}^{-1}$) of the IR spectra of PMMA at various SVPh/MVP 35–65 molar ratios in THF. For the non-covalently bonded complex micelles, Figure 2(b) indicates that the

location of this band was highly dependent on the SVPh/MVP molar ratio. The peaks at 1730 and 1706 cm^{-1} are those of the free and hydrogen-bonded carbonyl groups, respectively. As the molar ratio of MVP to SVPh increased, the fraction of hydrogen-bonded carbonyl groups is decreased, which indicates that the hydrogen-bonding interaction between the PVPh and P4VP blocks is stronger than the interaction between the PVPh and PMMA blocks.

Figure 2(c) presents scale-expanded infrared spectra in the range $970\text{--}1030\text{ cm}^{-1}$ measured at room temperature for various SVPh/MVP copolymer mixtures. Pure P4VP has a characteristic band at 993 cm^{-1} , which corresponds to the absorption of an uncomplexed pyridine ring. The new band at 1006 cm^{-1} is assigned to hydrogen-bonded pyridine units; its intensity increases upon the increase of PVPh blocks in comparison to P4VP blocks. The carbonyl

Table 1. Curve fitting of hydrogen-bonding results of SVPh/MVP at $25\text{ }^{\circ}\text{C}$.

SVPh/MVP ^{a)}	Free Carbonyl			Hydrogen-bonded Carbonyl			$f_b^{\text{C=O}}$
	ν	$W_{1/2}$	A_f	ν	$W_{1/2}$	A_b	
	cm^{-1}	cm^{-1}	%	cm^{-1}	cm^{-1}	%	
Pure PMMA	1730	25	100.0				
1/2	1732	26	88.7	1706	20	11.3	7.0
1/1	1732	26	87.6	1706	20	12.4	8.6
2/1	1732	26	76.4	1706	20	23.6	17.0

^{a)}SVPh/MVP = PS-*b*-PVPh/PMMA-*b*-P4VP.

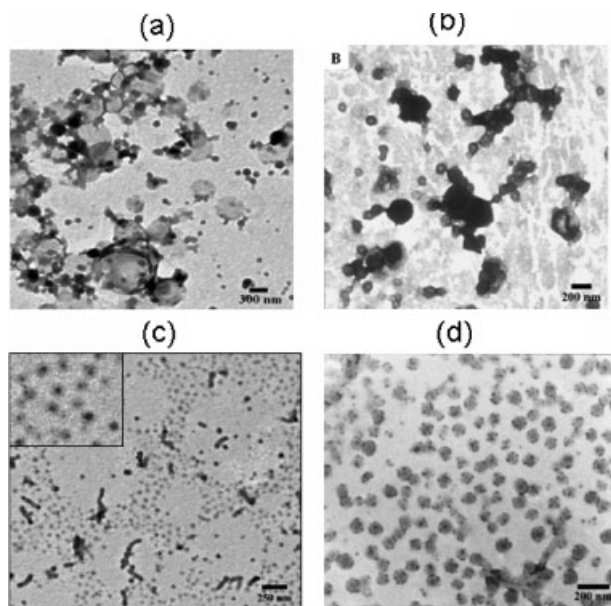
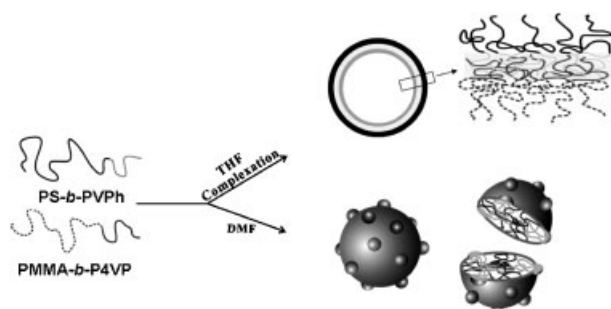


Figure 3. TEM images of SVPh/MVP hydrogen-bonded complexes in THF solution: a) 1/1 stained with I_2 , b) 1/1 stained with RuO_4 and in DMF solution, c) 1/1 stained with I_2 , and d) 1/1 stained with RuO_4 .

signal in Figure 2(b) is split into two bands that can be fitted well to a Gaussian function and results from curve fitting are summarized in Table 1. The hydrogen-bonding fraction of the carbonyl increases with the increase of PVPh content in these diblock copolymer blends. All IR spectra show the existence of hydrogen-bonding interactions between the pyridine group and the hydroxy group at all molar ratios, however, a greater fraction of hydrogen-bonding interactions exists between PVPh and PMMA at relatively high PVPh contents.

Figure 3(a) shows a TEM image of SVPh/MVP = 1/1 hydrogen-bonded complexes from THF, which reveals a wide distribution of hollow spheres upon staining with I_2 , but the contrast is rather poor. Thus, staining with RuO_4 was used and the comparative result is shown in Figure 3(b). The contrast of the complexed micelle staining images using RuO_4 is better than that with I_2 , and reveals that these complex micelles are in vesicular structure.



Scheme 1. Micelle formation model of SVPh/MVP diblock copolymer mixtures mediated by hydrogen-bonding interactions.

Because of the strong hydrogen bonding between the PVPh and P4VP blocks, the bound block possesses an extended conformation, which allows the bound copolymer chains to pack in parallel to form micelles with lamellae structures. Finally it turns into vesicles in solution to minimize the surface energy. Therefore, vesicular complexes are formed and are surrounded by PMMA and PS chains in THF solution. These micellar complexes can be predicted to be very stable since these soluble PMMA and PS chains enhance the stability of the vesicular complexes in THF solution. We believe that the inner and outer layer polymer chains of the vesicle are predominantly formed by PMMA and PS, respectively, because dark spots (PS staining with RuO_4) are outside the aggregates as shown in Figure 3(b). In addition, PS and PMMA segments are mutually incompatible and immiscible, and the PMMA can also undergo intermolecular hydrogen bonding with the PVPh based on FT-IR analysis in Figure 2(b). Therefore, the resultant vesicular complex is composed of an outer layer, the majority of which is the PS block, a PVPh/P4VP complex aggregated wall, and an inner layer that is predominantly PMMA block. The formation of the micellar complexes through hydrogen-bonding interactions between PVPh and P4VP in THF is schematically shown in Scheme 1.

As we mentioned earlier, the hydrogen bonding interaction between PVPh and P4VP in DMF is relatively weaker than that in THF solution as demonstrated by the FT-IR spectra in Figure 1. Therefore, the complex formed is expected to exhibit different morphologies compared to that in THF because of a lower degree of stretching of the PVPh/P4VP core chains and the stronger repulsion of the corona chains (PS and PMMA) in DMF. Figure 3(c) illustrates several TEM images of SVPh/MVP = 1/1 mixtures in DMF, which show the star-like micelles. A dark core surrounded by a halo shell is confirmed by the optical density profile stained by I_2 in large magnification in Figure 3(c). These dense cores are formed through the hydrogen-bonding interaction between PVPh and P4VP blocks and are surrounded by a soluble corona of PMMA and PS chains. This copolymer mixture in DMF possesses relatively weaker hydrogen bonding in the core and a better solubility of the corona chains. Because it has less stretching and more separated coils of PVPh/P4VP blocks in the core and a higher repulsion among the coronal chains (PS and PMMA blocks), this induces the formation of spherical (star-like) micelles. However, these spherical micelles have a mixed corona because of the presence of two different types of coronal blocks. In general, three categories of mixed coronal spheres can possibly exist: a) Janus (two-faced) spheres,^[20] b) patched spheres,^[21] and c) uniformed spheres.^[21,22] In this mixed diblock copolymer system, the coronal chains of the PS and PMMA blocks are immiscible, so it must form spheres with

chain-segregated corona. However, this category of chain-segregated corona can not be detected by using I₂ staining because of the poor selectivity between PS and PMMA chains. These micelles were further contrasted by RuO₄ staining in order to highlight phase selectivity between the PS, PVPh, and P4VP blocks of the micelles (Figure 2(d)). Small black spheres can now clearly be observed on the surface of spherical micelles because of the collapse of the PS coronal block on the PVPh/P4VP core, which indicates the mixed coronal sphere must be a patched form as shown in a schematic drawn in Scheme 1. Although PS and PMMA chains are strongly immiscible, the Janus sphere is not observed since DMF is a good solvent for both PS and PMMA chains in this case. It is well known that two immiscible binary polymer blends can become miscible through adding a large amount of good solvent, however, the PS and PMMA chains are still intrinsically immiscible. Therefore, the patched sphere is a compromise phenomenon between intrinsic immiscibility and miscibility enhancement upon adding a good solvent.

The main reason for the different morphologies of these diblock mixtures in THF and DMF is a result of the different chain behavior of the PVPh/P4VP block mixture. The greater hydrogen-bonding strength of the PVPh/P4VP block mixture in THF tends to induce polymer complex aggregation and forms the vesicle structure in the SVPh/MVP mixture. The more separated coils of the PVPh/P4VP block mixture as a result of a lower hydrogen-bonding strength in DMF solution leads to the formation of a patched sphere in the SVPh/MVP mixture.

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