Micellization of PS-*b*-P4VP/Formic Acid in Chloroform without or with the Premixing of the Copolymer with Decanoic Acid

Ximei Yao, Daoyong Chen,* and Ming Jiang

Department of Macromolecular Science and The Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China

Received February 8, 2004; Revised Manuscript Received February 27, 2004

ABSTRACT: Micellization of the stoichiometric complex of polystyrene-*b*-poly(4-vinylpyridine) with formic acid [(PS-*b*-P4VP)/FA] takes place in chloroform. When the concentration of the block copolymer is less than or equal to 5.0 mg/mL, the micellization leads to regular spherical micelles; while when the concentration of the copolymer is higher than or equal to 10.0 mg/mL, precipitates are produced. A stoichiometric complex of PS-*b*-P4VP/decanoic acid (DA) can be molecularly dispersed in chloroform, but introducing a stoichiometric amount of FA into the solution of PS-*b*-P4VP/DA leads also to the formation of regular spherical micelles. In this system, the pyridine/DA can be replaced by the pyridine/FA units, and the latter will associate. There is a balance between these two kinds of complexed units in the final mixture. It is thought that the preference of the pyridine units for DA will retard the complexation of the copolymer with FA and the resultant micellization; the remaining pyridine/DA complexed units will also retard the association among pyridine/FA units and change the balance between the aggregation effect of the complexed P4VP block and the solubilization effect of the PS block. As a result, the micellization can be conducted at the concentrations of PS-*b*-P4VP up to 50.0 mg/mL, resulting in regular micelles, and the micellization at the concentration of the copolymer lower than or equal to 10.0 mg/mL exhibits the thermodynamically controlled micellization.

Introduction

Micellization of block copolymers in their solutions has attracted both theoretical and applied research.[1] The micellization can provide us information on the interactions between the components in the system and is thought to have important implications for biological studies.[2] The resultant polymeric micelles are useful as nanocarriers for catalytic particles, molecules with electronic and photonic functions, and biological and medical species.[3]

Usually, the micellization of block copolymers takes place in selective solvents, resulting in nanoaggregates with different morphologies such as spherical micelles, vesicles, wormlike aggregates, nanotubes, and complexed micelles.[1,4] In the past decade, great efforts have also been made to search for new routes to micellization. It was found that the micellization of a block copolymer can be realized by (1) altering the temperature,[5] (2) changing the pH value,[6] and (3) chemically modifying one of the blocks in the copolymer.[7] In all these cases, including the micellization in selective solvents, the difference in the solubility between the blocks of a block copolymer is the driving force for the micellization, although the solubility difference in the numbered three cases results from the environmental changes or the chemical modification.

Interpolymer complexation due to electrostatic interaction[8] or hydrogen bonding[9] can also lead to the micellization. In this case, the driving force for the micellization is more complicated. First, taking an individual repeat unit into account, it may become insoluble on complexation. Second, the interpolymer complexation may lead to noncovalent cross-linking of the polymer chains. In principle, either the insolubility of the complexed units or the noncovalent cross-linking or both can be the driving forces for micellization. The micellization of a block copolymer resulting from the noncovalent cross-linking alone has been demonstrated by Yoshida et al. and Rotello et al.,[10] and the micellization induced by chemically cross-linking only one of the blocks has been reported by us.[11] In addition, it has been shown in our recent work that the complexation-induced change in the solubility of the repeat units alone can also lead to the micellization of a block copolymer.[12]

Recently, the behaviors of the complexes of block copolymers and low-molecular-mass compounds (LMC, including surfactants and other organic molecules with a polar head and a nonpolar tail) were studied. The micellization of block copolymers/LMC complexes can easily be controlled by the amount of LMC, a change in the environment which affects the binding between block copolymers and LMC, and the wide varieties of LMC to choose from.[13] This makes the systems of block copolymers/LMC promising in addressing various theoretical and practical problems. It is found that, in water, the complexation of a double hydrophilic block copolymer and LMC will lead to micellization of the complex, resulting in vesicles or micelles.[14] The aggregation between the hydrophobic tails of LMC in water is thought as the driving force for the micellization. However, in a low-polarity solvent, the behavior of the complex of a block copolymer and LMC is quite different, since the tails of LMC are soluble in the solvent. By a detailed analysis, we can see that the behavior is controlled by the two parts *contained in each of the complexed units* whose solubilities may be opposite to each other. In fact, the complexation takes place between the headgroup of LMC (such as the carboxylic group in a linear aliphatic acid) and its counterpart group in a repeat unit of the copolymer (such as the pyridine unit in PS-*b*-P4VP). The junction point (part

* Corresponding author: Fax 86 21 65640293; e-mail Chendy@fudan.edu.cn.

10.1021/ma0497308 CCC: $27.50
Published on Web 04/28/2004

1), thought to contain the two groups only, may be of a high polarity and insoluble in the low-polarity medium, while the nonpolar tails of LMC (part 2) are soluble in the medium. Shortening the tails will make the insoluble part dominant and lead to micellization of the complex; otherwise, the copolymer/LMC complex can be molecularly dispersed in the low-polarity solvent. Our previous work[12] studied the behavior of complexes of PS-*b*-P4VP/linear aliphatic acids in chloroform. It was demonstrated that only when the lipophilic tails of the acids were removed did the complex self-assemble, forming vesicles. This is one of few examples, to our knowledge, to obtain regular nanoaggregates in low-polarity media through the micellization of a block copolymer/LMC complex.

The efficiency of producing polymeric micelles is very low. This limits the practical applications of the micelles. The block copolymer micellization, especially the complexation-induced micellization, is usually conducted at a concentration not higher than 5.0 mg/mL; otherwise, irregular aggregates or even precipitates will be produced.[2] This is because the micellization at a relatively high concentration occurs so rapidly that the soluble block chains have no time to be disentangled from each other and to adjust their conformation so as to surround the aggregated insoluble block; thus, irregular aggregates or precipitates are produced. Recently, through cross-linking one of the blocks of a diblock copolymer in its common solvent, we succeeded in preparing narrow size distributed core−shell polymeric micelles at a concentration as high as 20% (w/v).[11] Here, we believe, the aggregation due to the cross-linking can proceed very slowly by controlling the speed of the cross-linking reaction. Therefore, even at a high concentration, there is enough time for the soluble block chains to disentangle, stretch out, and surround the aggregated block and to play a role as a shield localizing the cross-linking-induced aggregation. This suggests that slowing down aggregation of the insoluble block may be helpful to carry out the micellization at high concentrations.

It seems difficult to control the micellization process of a block copolymer in its selective solvent. Although we can make the rate of micellization as low as desired by selecting the temperature and the pH, our experiments indicated that the micellization at a concentration higher than or equal to 10.0 mg/mL results in irregular aggregates. It is thought that the micellization still occurs in an uncontrolled manner like the precipitation in a supersaturated solution. In the present study, we will report that through introducing decanoic acid (DA) first and formic acid (FA) second into PS-*b*-P4VP solution in chloroform, the micellization process of PS-*b*-P4VP/FA can be controlled. We believe that (1) the preference of the P4VP block for DA will form a temporary sheath for the block and make it less reactive to form complex with FA and (2) the soluble pyridine/DA complexed units may coexist with the pyridine/FA complexed units at the early stage or through the whole micellization process. Both will have a great effect on the process and the results of the micellization.

Experimental Section

Materials. PS-*b*-P4VP was synthesized and characterized according to procedures described in ref 15. The weight-average molecular weights of the PS block and the P4VP block and the molecular weight polydispersity index of the PS precursor are 51 000, 25 800, and 1.09, respectively. The length ratio (LR) of the PS block to the P4VP block is ca. 2/1. FA was distilled after refluxing in phthalic anhydride for more than 12 h before use. DA was purchased from Aldrich Chemical Co. Inc. and used without further purification. Chloroform of analytical grade was used as received. The homopolymer P4VP was synthesized via radical polymerization.

Micellization of PS-*b*-P4VP/FA. The block copolymer was dissolved in $CHCl_3$ at designed concentrations for at least 2 days before use. Then, a stoichiometric amount of FA (in $CHCl_3$) was added (ca. 2 μL/s) into each of the copolymer solutions under ultrasonic. The concentrations of the block copolymer in the final solutions are 1.0, 5.0, 10.0, and 50.0 mg/mL, respectively.

Micellization of PS-*b*-P4VP/DA/FA. A stoichiometric amount of DA (in chloroform) was added into each of the block copolymer solutions before the addition of FA. Several hours after the addition of DA, FA was added into each of the solutions to the molar ratio of FA to the pyridine units of 1:1. The final concentrations of the block copolymer in the resultant solutions are 1.0, 5.0, 10.0, and 50.0 mg/mL, respectively.

In addition, the P4VP solution in chloroform, at 2.0 mg/mL, was mixed with FA and DA or first with DA and then with FA. In the mixtures of PS-*b*-P4VP/DA/FA, the molar ratio of DA to the pyridine units was fixed at 1:1, while that of FA to the pyridine units was changed.

Laser Light Scattering (LLS). A commercial laser light scattering (LLS) spectrometer (Malvern Autosizer 4700) equipped with a multi-τ digital time correlation (Malvern PCS7132) and a solid-state laser (ILT 5500QSL, output power = 100 mW at λ_0 = 532 nm) as light source was used. In dynamic LLS (DLS), the line-width distribution $G(\Gamma)$ can be calculated from the Laplace inversion of intensity−intensity time correlation function $G^{(2)}(q,t)$, The inversion was carried out by the CONTIN program supplied with the Malvern PCS7132 digital time correlator. $G(\Gamma)$ can be converted into a transitional diffusion coefficient distribution $G(D)$ or a hydrodynamic radius distribution $f(R_h)$ via the Stokes−Einstein equation. $R_h = (k_B T/6\pi\eta)D^{-1}$, where k_B, T, and η are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively. All the DLS measurements were performed at 25 ± 0.1 °C and at a scattering angle 90° as only a little of scattering angle dependence of the $\langle R_h \rangle$ of the micelles was observed. All the micelle solutions at different concentrations were measured directly without dilution, and the solutions were clarified using a 0.45 μm Millipore filter before the measurements.

Scanning Electron Microscopy (SEM). SEM observations were conducted days after the mixing of the copolymer (or the copolymer/DA) with FA on a Philips XL30 at an accelerating voltage of 25 kV. The specimens for SEM observations were prepared by depositing a drop of the solutions (ca. 5 μL) onto a glass slide.

Transmission Electron Microscopy (TEM). The TEM observations were carried out days after the mixing of FA with the block copolymer (or the copolymer/DA), performed with a Philips EM400 microscope at an accelerating voltage of 80 kV. The samples for TEM observations were prepared by depositing a drop of the solution on copper grids, which was coated with thin films of Formvar and carbon successively, and were observed without being stained.

^{1}H NMR Measurements. The ^{1}H NMR measurements were performed on a Bruker DMX500 spectrometer in $CDCl_3$ using TMS as an internal reference.

Results and Discussion

In our previous study, we have demonstrated that the *stoichiometric complexes* of PS-*b*-P4VP/linear aliphatic acids form in chloroform due to the hydrogen bonding between the pyridine units and the carboxylic groups.[12] The stoichiometric complexes of PS-*b*-P4VP with stearic acid, decanoic acid, and acetic acid can be molecularly dispersed in solution, while the complexes of PS-*b*-P4VP with formic acid will self-assemble in chloroform, forming regular nanoaggregates. The lack of the hydrocarbon

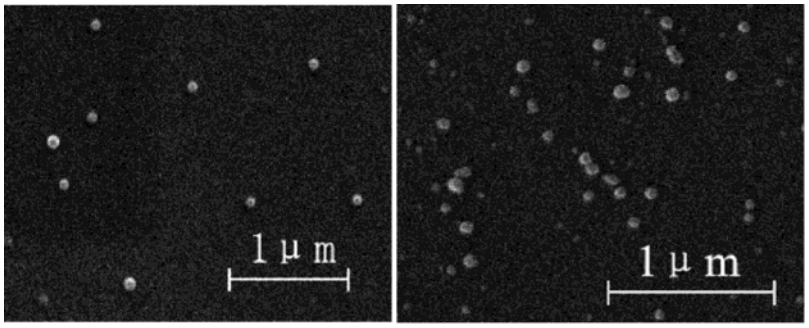


Figure 1. SEM images of aggregates at the concentrations of the copolymer of 1.0 mg/mL (a) and 5.0 mg/mL (b) obtained from the micellization of the stoichiometric complex of PS-*b*-P4VP/FA

Table 1. DLS Characterization Data of the Aggregates Obtained through Mixing PS-*b*-P4VP at Different Concentrations of PS-*b*-P4VP with FA (Line 1) or Firstly with DA and Secondly with FA (Line 2)[a]

		concn of PS-*b*-P4VP (mg/mL)			
		1.0	5.0	10.0	50.0
line 1	$\langle R_h\rangle$/nm; $\mu_2/\langle\Gamma\rangle^2$	56; 0.06	41; 0.16	*b*	*b*
line 2	$^{DA}\langle R_h\rangle$/nm; $\mu_2/\langle\Gamma\rangle^2$	70; 0.10	68; 0.19	70; 0.2	144; 0.2

[a] $\langle R_h\rangle$ and $^{DA}\langle R_h\rangle$: the average hydrodynamic radiuses of the nanoparticles obtained without and with DA, respectively, measured at a scattering angle of 90° and 25 °C. $\mu_2/\langle\Gamma\rangle^2$: polydispersity index (PDI) of the size distribution; see ref 16. The molar ratio of the pyridine units to FA molecules in PS-*b*-P4VP/FA (MR^{py}/FA) is 1/1, and that of the pyridine units to DA to FA in the mixture of PS-*b*-P4VP/ DA/ FA (MR^{py}/DA/FA) is 1/1/1. [b] Precipitate.

tails and the higher acidity of FA (as compared with other aliphatic acids) make the complexed units of pyridine/FA insoluble in the low-polarity media, leading to micellization.

Nevertheless, as for the micellization of block copolymers in their selective solvents,[2] the micellization of the PS-*b*-P4VP/FA complex can only be carried out at low concentrations. We carried out the micellization of the stoichiometric PS-*b*-P4VP/FA complex in chloroform at different concentrations. The characterization data obtained by dynamic light scattering (DLS) measurements are given in Table 1.

From the data in Table 1 (line 1) one can see that, when the concentrations of the block copolymer are lower than or equal to 5.0 mg/mL, mixing the copolymer with FA leads to micellization, forming nanoaggregates. DLS measurements show that the resultant aggregates have a spherical morphology and a relatively narrow size distribution as indicated by the small polydispersity indexes and almost no dependence of the size on the measurement angles. This is supported by our SEM observations (Figure 1).

In our previous work, a copolymer with the length ratio of the PS block to the P4VP block (LR) of 1.15/1 was used,[12] and the micellization of PS-*b*-P4VP/FA led to vesicles, while in this study, LR is 2/1; it results in solid micelles, as indicated in Figure 1. The increase in LR leads to the change in the morphology of resultant nanoaggregates from vesicles to solid micelles. This phenomenon can be understood by considering a balance between three major forces acting on the system: the stretching of the core-forming blocks, the interfacial tension between the core and the solvent, and the intercorona repulsion, according to Eisenberg.[17] An analogous change in morphology due to the change in LR was reported for the micellization of PAA-*b*-PS in the mixture of water and dioxane.[18]

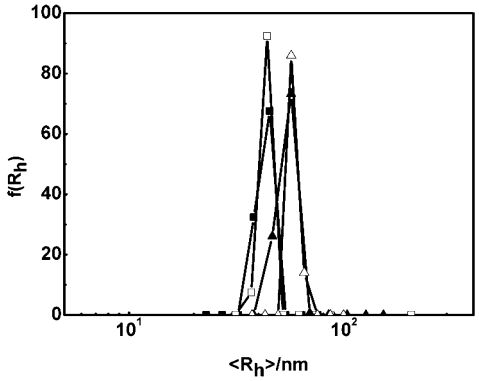


Figure 2. Hydrodynamic radius distributions $f(R_h)$ of the aggregates obtained from the micellization of PS-*b*-P4VP/FA in chloroform at the concentration of the block copolymer of 1.0 mg/mL measured several hours (▲) and 27 days (△) after the mixing and at 5.0 mg/mL measured several hours (■) and 27 days after the mixing (□).

The stability of the aggregates resulting from the micellization of the stoichiometric complex of PS-*b*-P4VP/FA in chloroform was studied by DLS measurements. It is proved that aggregates formed at the concentrations of the block copolymer of 1.0 and 5.0 mg/mL are stable, as indicated in Figure 2.

However, mixing PS-*b*-P4VP with FA stoichiometrically at the concentration of the copolymer of 10.0 mg/mL leads to unstable aggregates. The stability of the aggregates formed at such concentration was followed by the change in the light-scattering intensity (I_s) of the solution. The result is presented in Figure 3 as curve 1. Curve 1 of I_s vs time (t) indicates that, at the concentration of the block copolymer of 10.0 mg/mL, the aggregation occurred before the DLS measurements started. (Timing begins on mixing of the copolymer (or the copolymer/DA for curve 2) with FA. At the initial point of either curve 1 or curve 2, t is ca. 0.5 h.) I_s keeps changing in this system. When $t = 2.3$ h, the I_s reaches its maximum for molecularly dispersed aggregates, followed by gradual precipitation. After 120 h, the I_s fluctuates wildly. When the concentration of the block copolymer is 50.0 mg/mL, mixing the copolymer with FA will lead to instantaneous precipitation.

As mentioned above, linear aliphatic acids can form stoichiometric complexes with PS-*b*-P4VP, and these complexes except for PS-*b*-P4VP/FA can be molecularly dispersed in a low-polarity solvent such as chloroform; slowing down the speed of aggregation of the core-

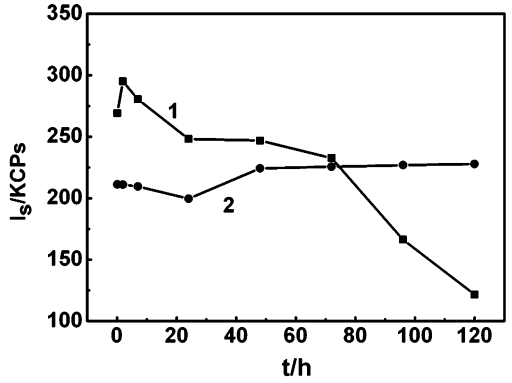


Figure 3. Light-scattering intensities (I_s) of the aggregates solutions vs mixing time (t): curve 1, mixing the PS-*b*-P4VP with FA only; curve 2, mixing the copolymer with DA first and FA second. The concentration of the PS-*b*-P4VP is 10.0 mg/mL. t = timing upon beginning of the mixing with FA.

forming block is helpful to carry out the micellization of a block copolymer at high concentrations. But what will happen if we mix in chloroform PS-*b*-P4VP with a linear aliphatic acid other than FA and then add FA to the mixture? FA may have to interact with the pyridine units occupied by the linear aliphatic acid, so the formation of the PS-*b*-P4VP/FA complex and the resultant aggregation among pyridine/FA units will be delayed. Besides, soluble pyridine units complexed with DA with its hydrocarbon tail existing at the early stage or in the whole process of the micellization can also retard the aggregation among the pyridine/FA complexed units. The characterization of the aggregates obtained via the micellization of PS-*b*-P4VP/FA with the premixing of the copolymer with DA is shown in Table 1 (line 2). It is also expected that the pyridine/DA units can change the balance between the aggregation effect and the solubilization effect of the block copolymer. Therefore, with the premixing of the copolymer with DA, the behavior and the result of the micellization should be quite different.

In all the cases when DA was used, the mixing of the copolymer with DA was hours before the addition of FA (a time sufficient for the completion of the diffusion of DA and the complexation of DA with the copolymer). We denote the complex of the copolymer with DA and the mixture of the copolymer with DA and FA by PS-*b*-P4VP/DA and PS-*b*-P4VP/DA/FA, respectively. The molar ratio of the pyridine units to DA of the former and that of pyridine units to DA to FA in the latter is denoted by $MR^{py/DA}$ and $MR^{py/DA/FA}$, respectively. In this study, $MR^{py/DA}$ is 1/1 and $MR^{py/DA/FA}$ is 1/1/1. Each of $\langle R_h \rangle$ values listed in Table 1 is based on the measurement made weeks after the preparation of the aggregates solution, which is believed to be sufficient for the system to reach its equilibrium.

From the data in Table 1, one can see that the addition of a stoichiometric amount of FA into the complex of PS-*b*-P4VP/DA in chloroform leads to nanoaggregates. Obviously, the pyridine/DA complexed units can be replaced or partially replaced by the pyridine/FA units. It seems that the effect of preexistence of the copolymer/DA complex on the subsequent micellization of PS-*b*-P4VP/FA complex is not remarkable when the concentrations of the copolymer are 1.0 and 5.0 mg/mL. A remarkable effect is found when the concentration of the copolymer is high. In fact, mixing the copolymer at the concentration of 10.0 mg/mL with a stoichiometric amount of FA solely will lead to precipitation, while mixing the copolymer at the same concentration first with DA and then with FA in chloroform results in stable nanoaggregates. The stability of thus-prepared aggregates was also studied by following the change in I_s with mixing time. As indicated in curve 2 (Figure 3), although there is a fluctuation at the early stage, no further changes can be observed in I_s (as well as in the $\langle R_h \rangle$ value) about 48 h later. This shows that the aggregates obtained at 10.0 mg/mL with the premixing of the copolymer with DA are quite stable.

We believe that the complexation of PS-*b*-P4VP with FA and the resultant micellization will be retarded by the preoccupation of the pyridine units by DA. However, at the early stage of the mixing (e.g., t is less than 0.5 h), the diffusion of FA in the system, the replacement of pyridine/DA by pyridine/FA, and the resultant micelles may be entangled. This makes the characterization of the micellization process at the very initial stage difficult. Actually, the data obtained at $t < 0.5$ h cannot be replicated.

SEM and TEM observations demonstrate that the aggregates obtained at the concentration of the block copolymer of 10.0 mg/mL in the presence of DA are regular spherical micelles. The images are presented in Figure 4.

We conducted the micellization of PS-*b*-P4VP/DA/FA at a concentration of PS-*b*-P4VP of 50.0 mg/mL. In this case, regular aggregates are produced. The resultant aggregates are quite stable in the solution, and no precipitation was observed weeks after the preparation, while mixing the block copolymer at such a concentration with FA alone will lead to instantaneous precipitation. The micellization of a block copolymer, especially that of a block copolymer/LMC complex, conducted at such a high concentration has been seldom reported.

In a system of a block copolymer in its selective solvent, when there is balance between the solubilization effect of the soluble block and the aggregation effect of the insoluble block, the micellization of the block copolymer will exhibit thermodynamically controlled micellization. In this system, when the concentration of the block copolymer is higher than the cmc (but not too high), $\langle R_h \rangle$ of the resultant aggregates depends on the structural parameters of the copolymer precursor and will not change remarkably with the variation of the concentration.[19] Whereas, in some cases the micellization of a block copolymer is kinetically controlled (roughly speaking, when the aggregation effect of the insoluble block is much stronger than the solubilization effect of the soluble block, the core of the formed aggregates is frozen), the competition between intrachain aggregation and the interchain aggregation will have a great effect on the average size of the resultant aggregates.[20] In these cases, the average size usually increases with the concentration since the interchain aggregation will become dominant when the concentration is high.[20] In this study the concentration dependence of $\langle R_h \rangle$ of the resultant aggregates without DA is consistent with neither the thermodynamically controlled micellization nor the kinetically controlled one. $\langle R_h \rangle$ decreases from 56 to 41 nm when the concentration of the block copolymer increases from 1.0 to 5.0 mg/mL. This is assumed to be due to the competition between the complexation of the block copolymer with FA and the micellization of the resultant complex. When the concentration is high, the micellization may take place

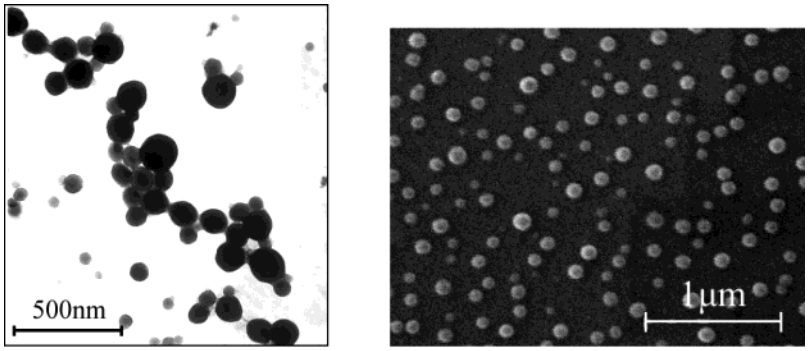


Figure 4. TEM image (a) and SEM image (b) of the nanoaggregates obtained in the system of PS-*b*-P4VP/DA/FA in chloroform at the concentration of PS-*b*-P4VP of 10.0 mg/mL. $MR^{py/DA/FA}$ is 1/1/1.

Table 2. Solubility of P4VP/FA, P4VP/DA, and P4VP/DA/FA[a]

$MR^{py/FA}_{P4VP}$ $MR^{py/DA/FA}_{P4VP}$	3/1 3/3/1	2/1 2/2/1	3/2 3/3/2	1/1 1/1/1	1/2 1/1/2	1/5 1/1/5
P4VP/FA	clear solution with blue tint	precipitate	precipitate	precipitate	precipitate	precipitate
P4VP/DA/FA	clear solution with blue tint	clear solution with blue tint	clear solution with blue tint	clear solution with blue tint	precipitate	precipitate

[a] The concentration of P4VP is 2.0 mg/mL. The results listed are based on the observations conducted 24 h after the mixing with FA. Then, the systems were observed for weeks; no further changes in the systems were observed. $MR^{py/FA}_{P4VP}$ and $MR^{py/DA/FA}_{P4VP}$ denote the molar ratios in P4VP/FA and P4VP/DA/FA, respectively.

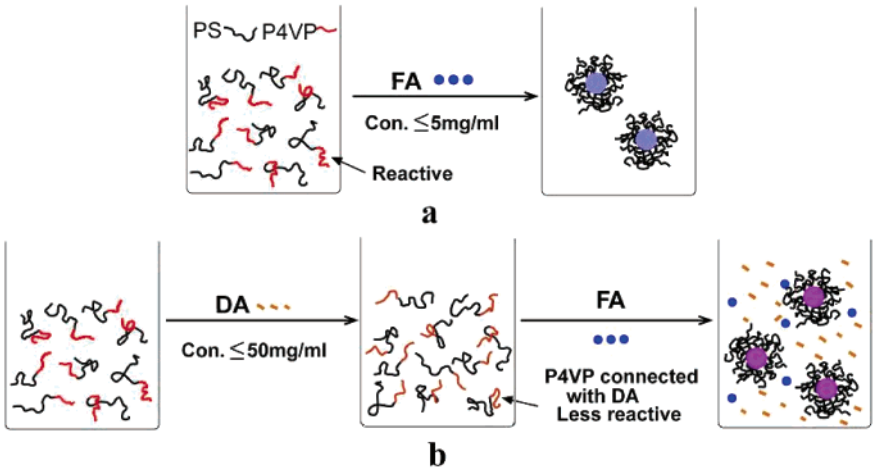
before the completion of the complexation, so that the micelles initially formed should contain more "free" pyridine units (without DA). (This is easy to understand by supposing that there is a cmc based on the concentration of pyridine/FA units.) This suggests that in the early stage the behavior of the micellization at a molar ratio of the pyridine units to FA ($MR^{py/FA}$) of 1/1 and a higher concentration may be comparable to the system at a higher $MR^{py/FA}$ but a lower concentration. In addition, it is assumed that the process of the micellization without DA is kinetically controlled and the core of the aggregates is frozen, so that the outline of an aggregate, which should determine the size of the aggregate, may be fixed at the early stage. These considerations are supported by the fact that $\langle R_h \rangle$ of the aggregates obtained at $MR^{py/FA}$ of 3/2 and the concentration of the copolymer of 1.0 mg/mL is 46 nm (comparable to that at $MR^{py/FA}$ of 1/1 and the concentration of 5.0 mg/mL, i.e., 41 nm, while that at $MR^{py/FA}$ of 1/1 and the concentration of 1.0 mg/mL is 56 nm). However, the micellization of PS-*b*-P4VP/FA with DA, when the concentration of the block copolymer is less than or equal to 10.0 mg/mL, seems to be thermodynamically controlled, since the $\langle R_h \rangle$ of the resultant aggregates is constant at ca. 70 nm. Zhou et al. studied the concentration dependence of $\langle R_h \rangle$ of the aggregates produced from the micellization of poly(styrene-*b*-(2,5-bis(4-methoxyphenyl)oxycarbonyl)styrene) (PS-*b*-PMPCS) in *p*-xylene; the results indicate that, with an increase in the length ratio of the soluble block (PS) to the insoluble block (PMPCS), the dependence becomes weaker.[20b] This indicates that the increase in the solubilization effect (for example, the increase in the length ratio of the soluble block to the insoluble block) should improve the mobility of the core of the aggregates and lead to the balance between the solubilization effect and the aggregation effect; thus, the micellization can change from a kinetically controlled micellization to a thermodynamically controlled one.

In the system of PS-*b*-P4VP/DA/FA in chloroform, the pyridine/DA complexed units can be replaced by the pyridine/FA complexed units, and the latter will associate, leading to micellization. However, an amount of the soluble pyridine/DA complexed units may exist at the early stage or through the whole process of the micellization, although the amount may change with the progress of complexation and micellization. The existence of pyridine/DA complexed units in the system of PS-*b*-P4VP/DA/FA is proved by the behavior of the complexes of P4VP/DA, P4VP/FA, and the mixtures of P4VP/DA/FA (FA was added into the P4VP/DA solutions several hours after the addition of DA) and the ^{1}H NMR measurements (see Table 2).

The data in Table 2 indicate that the complexation of FA with the homopolymer P4VP without DA in chloroform leads to soluble aggregates or precipitate depending on $MR^{py/FA}_{P4VP}$. Without the stabilization of the PS block, the complexation of the homopolymer P4VP with FA alone at $MR^{py/FA}_{P4VP}$ smaller than or equal to 2/1 leads to precipitation. The situation is changed in the presence of DA. The fact that stable nanoaggregates formed at $MR^{py/DA}_{P4VP}$/FA of 1/1/1 demonstrates that the complex of P4VP/DA is only partially replaced by that of P4VP/FA. It seems that there is a balance between pyridine/FA and pyridine/DA complexed units (although the former maybe dominant due to the higher acidity of FA), and there should be a competition between the two kinds of complexation, since increasing the relative amount of FA in the mixture to $MR^{py/DA/FA}_{P4VP}$ of 1/1/2 leads to the further replacement of pyridine/DA by pyridine/FA and the precipitation in the system (Table 2).

The ^{1}H NMR spectra in deuterated chloroform of pure block copolymer (spectrum A), the stoichiometric complexes of PS-*b*-P4VP/FA (spectrum B) and PS-*b*-P4VP/DA (spectrum C), and the mixture of PS-*b*-P4VP/DA/FA with $MR^{py/DA/FA}$ 1/1/1 (spectrum D) are shown in

Scheme 1. Schematic Description of the Micellization of the Complex of PS-*b*-P4VP/FA (a) without and (b) with the Premixing of PS-*b*-P4VP with DA



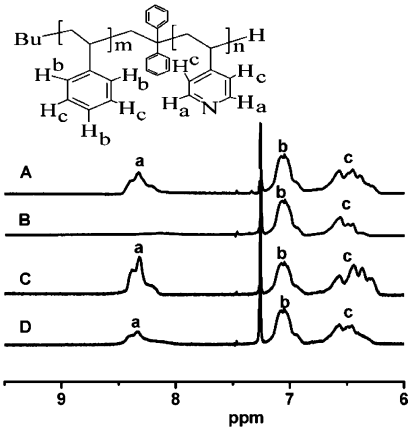


Figure 5. ^{1}H NMR spectra of pure PS-*b*-P4VP (A), PS-*b*-P4VP/FA (B: $MR^{py/FA} = 1/1$), PS-*b*-P4VP/DA (C: $MR^{py/DA} = 1/1$), PS-*b*-P4VP/DA/FA (D: $MR^{py/DA/FA} = 1/1/1$) in $CDCl_3$. The concentration of the block copolymer is 1.0 mg/mL. TMS at a fixed concentration was used as the internal standard.

Figure 5. For clarity, only the spectra from 6.0 to 9.5 ppm are presented. The assignments of peaks a, b, and c are given as the inset. In the assignments, peak b is assigned to the hydrogen atoms H_b (inset) in the benzene rings only; peak a and peak c are associated with H_a in the pyridine rings and H_c in both the pyridine and benzene rings, respectively.

As mentioned above, for the systems of PS-*b*-P4VP/FA and PS-*b*-P4VP/DA/FA in $CDCl_3$, the complexed units of pyridine/FA are insoluble and associate to form the core of the aggregates, driving the micellization. These aggregated pyridine units will lose their mobility as well as their signals in the spectra. [6a] However, all the PS block chains, as the shell of the aggregates, should remain in a soluble state, and their signals' intensities do not change in all the spectra. This is demonstrated by the constancy of the relative intensity of peak b in all the spectra. In spectrum B ($MR^{py/FA}$ is 1/1), nearly all the pyridine units are seriously restricted and lose their signals in the spectrum, so the peak a disappears and the intensity ratio of b to c becomes close to 3/2, the number ratio of the H_b to H_c in the benzene rings. In spectrum C, since the stoichiometric complex of PS-*b*-P4VP/DA can be molecularly dispersed in $CDCl_3$, no remarkable change can be found in peak a and peak c, when compared with the spectrum of the pure block copolymer. In spectrum D, $MR^{py/DA/FA}$ is 1/1/1; the relative intensity of peak a deceases but not to zero. This shows that only a part of the pyridine units are bound with FA and are restricted, while the remaining pyridine units are still complexed with DA. The soluble nature of pyridine/DA complexed units makes the pyridine groups connected with DA and perhaps some neighboring pyridine rings bound with FA detectable by ^{1}H NMR. Therefore, in the mixture of PS-*b*-P4VP/DA/FA at $MR^{py/DA/FA}$ of 1/1/1, the pyridine block chains are complexed with both the DA and the FA. This is consistent with the results from the observations on the behaviors of the P4VP/FA complexes and the P4VP/DA/FA mixtures in chloroform (Table 2). The existence of pyridine/DA complexed units in the system of PS-*b*-P4VP/DA/FA will decrease the aggregation effect of the complexed P4VP block chains and help to reach the balance between the solubilization effect and the aggregation effect, so that the micellization, with the premixing of the copolymer with DA, exhibits thermodynamically controlled micellization.

Although the micellization with the preexistence of DA can be conducted at the concentration of the block copolymer of 50.0 mg/mL, yielding stable and regular nanoaggregates, $\langle R_h \rangle$ is much larger than that of the aggregates prepared at 1.0, 5.0, and 10.0 mg/mL. In the system of PS-*b*-P4VP/DA/FA at $MR^{py/DA/FA}$ of 1/1/1/ and the concentration of the copolymer of 50.0 mg/mL, the solid content is 86.3 mg/mL when FA and DA are taken into account. Since the viscosity of the solution is high, the diffusion of FA and DA in the system is retarded, affecting the competition between the complexations as well as the micellization process. Few examples of the micellization at such a high solid content have been reported. Further studies on the micellization process at high concentrations are needed.

Conclusions

This present work demonstrates that the micellization of the PS-*b*-P4VP/FA in chloroform can be controlled by premixing the copolymer with DA. It is proved that, with the addition of FA into the solution of PS-*b*-P4VP/DA, the pyridine/DA complexed units can be replaced by pyridine/FA, and the latter will associate in chloroform, leading to the micellization. It is also shown that when $MR^{py/DA/FA}$ is 1/1/1, pyridine/DA complexed units coexist with the pyridine/FA complexed units. We speculate that the preference of the P4VP block chains

for DA will make them less reactive to form a complex with FA, so the complexation and the resultant association among pyridine/FA complexed units will be retarded. Also, the existence of soluble pyridine/DA complexed units, which are randomly located among the pyridine/FA units, will retard the association. When considering a whole copolymer chain, we can see that the existence of the soluble pyridine/DA units can decrease the aggregation effect of the complexed P4VP block and help to reach a balance between this aggregation effect and the solubilization effect of the PS block. For these reasons, the micellization may be slown down. Therefore, the micellization of PS-*b*-P4VP/FA, with the premixing of the copolymer with DA, can be carried out at a concentration of the copolymer as high as 50.0 mg/mL (Scheme 1), and the micellization at the concentration of the copolymer less than or equal to 10.0 mg/mL exhibits thermodynamically controlled micellization. Without the premixing of the copolymer with DA, the micellization of PS-*b*-P4VP/FA in chloroform can only be carried out at a concentration lower than 10.0 mg/mL; otherwise, a precipitate will be produced.

Acknowledgment. The authors thank Professor Chi Wu and Professor Guangzhao Zhang of University of Science and Technology in China for their kind help in completion of this work. This work has been supported by National Science Foundation of China 50273006, 50333010.

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MA0497308