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

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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.1-3 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 interaction8 or hydrogen bonding9 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
Micellization of PS-b-P4VP/FA. The block copolymer was dissolved in CHCl₃ at designed concentrations for at least 2 days before use. Then, a stoichiometric amount of FA (in CHCl₃) 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-s digital time correlation (Malvern PCS7132) and a solid-state laser (LT 5500QSL, output power = 100 mW at λₒ = 532 nm) as light source was used. In dynamic LLS (DLS), the line-width distribution G(1) 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(1) can be converted into a transitional diffusion coefficient distribution G(D) or a hydrodynamic radius distribution R(h) via the Stokes–Einstein equation: R(h) = (kT/6πηD)⁻¹, where k is 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 (R(h)) 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.

H NMR Measurements. The 1H NMR measurements were performed on a Bruker DMX500 spectrometer in CDCl₃ 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. 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 tail and the polar nature of the acid are responsible for the different behavior in chloroform. However, the complexes of PS-b-P4VP with decanoic acid and acetic acid are soluble in chloroform, while the complex of PS-b-P4VP with stearic acid precipitates. The results are in agreement with the above considerations.
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)\(^a\)

<table>
<thead>
<tr>
<th>concn of PS-b-P4VP (mg/mL)</th>
<th>line 1 (〈R_b〉/\text{nm}, 〈h_b〉/\text{nm}^2)</th>
<th>line 2 (〈R_h〉/\text{nm}, 〈h_h〉/\text{nm}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>56; 0.06 41; 0.16 b / b</td>
<td>70; 0.10 68; 0.19 70; 0.2 144; 0.2</td>
</tr>
<tr>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50.0</td>
<td></td>
<td></td>
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</tbody>
</table>

\(^a\) \(〈R_b〉\) and \(〈h_b〉\): the average hydrodynamic radiiuses of the nanoparticles obtained without and with DA, respectively, measured at a scattering angle of 90° and 25 °C. \(〈R_h〉\) and \(〈h_h〉\): polydispersity index (PDI) of the size distribution; see ref 16.

LR was reported for the micellization of PAA-b-PS in the mixture of water and dioxane.\(^b\)

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 stochiometrically 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, \(I_s\) reaches its maximum for molecularly dispersed aggregates, followed by gradual precipitation. After 120 h, \(I_s\) 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-
We denote the complex of the copolymer with DA and DA and the complexation of DA with the copolymer). (a time sufficient for the completion of the diffusion of be quite different.

and the solubilization effect of the block copolymer. can change the balance between the aggregation effect 1 (line 2). It is also expected that the pyridine/DA units premixing of the copolymer with DA is shown in Table 1. The molar ratio of the pyridine units to DA of the former block copolymer is high. In fact, mixing the copolymer at the same concentration first 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-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 MRpy/DA and MRpy/DA/FA, respectively. In this study, MRpy/DA is 1/1 and MRpy/DA/FA is 1/1/1. Each of the 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 Iₜ 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 Iₜ (as well as in the (Rₜ) 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), (Rₜ) of the resultant aggregates depends on the structural parameters of the copolymer precursor and will not change remarkably with the variation of the concentration. 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 intra-chain aggregation and the interchain aggregation will have a great effect on the average size of the resultant aggregates. In these cases, the average size usually increases with the concentration since the interchain aggregation will become dominant when the concentration is high. In this study the concentration dependence of (Rₜ) of the resultant aggregates without DA is consistent with neither the thermodynamically controlled micellization nor the kinetically controlled one. (Rₜ) 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
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_p/F_A) of 1/1 and a higher concentration may be comparable to the system at a higher MR_p/F_A 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 (R_w) of the aggregates obtained at MR_p/F_A of 3/2 and the concentration of the copolymer of 1.0 mg/mL is 46 nm (comparable to that at MR_p/F_A of 1/1 and the concentration of 5.0 mg/mL, i.e., 41 nm, while that at MR_p/F_A 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 (R_w) of the resultant aggregates is constant at ca. 70 nm. Zhou et al. studied the concentration dependence of (R_w) of the aggregates produced from the micellization of poly(styrene-b-(2,5-bis(4-methoxyphenyl)oxyxycarbonyl)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 1H 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_p/F_A. Without the stabilization of the PS block, the complexation of the homopolymer P4VP with FA alone at MR_p/F_A 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_p/F_A 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 may be 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_p/F_A of 1/1/2 leads to the further replacement of pyridine/DA by pyridine/FA and the precipitation in the system (Table 2).

The 1H 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_p/F_A of 1/1/1 (spectrum D) are shown in

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Table 2. Solubility of P4VP/FA, P4VP/DA, and P4VP/DA/FA

<table>
<thead>
<tr>
<th>MR_p/F_A</th>
<th>P4VP/FA</th>
<th>P4VP/DA/FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/1</td>
<td>clear solution</td>
<td>clear solution with blue tint</td>
</tr>
<tr>
<td>2/1</td>
<td>precipitate</td>
<td>clear solution with blue tint</td>
</tr>
<tr>
<td>3/2</td>
<td>precipitate</td>
<td>clear solution with blue tint</td>
</tr>
<tr>
<td>1/1</td>
<td>precipitate</td>
<td>clear solution with blue tint</td>
</tr>
<tr>
<td>1/2</td>
<td>precipitate</td>
<td>precipitate</td>
</tr>
<tr>
<td>1/5</td>
<td>precipitate</td>
<td>precipitate</td>
</tr>
</tbody>
</table>

*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_p/F_A and MR_p/F_A/DA denote the molar ratios in P4VP/FA and P4VP/DA/FA, respectively.
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 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. 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 = 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 decreases 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 ^1H 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, <R_h> 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 slowed down. Therefore, the micellization of PS-P4VP/FA, with the premixing of the copolymer with DA, can be carried out at a concentration 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-P4VP/FA in chloroform can only be carried out at a concentration lower than 10.0 mg/mL; otherwise, a precipitate will be produced.

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References and Notes


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