# Self-Assembly of Perfluorooctanoic Acid (PFOA) and PS-*b*-P4VP in Chloroform and the Encapsulation of PFOA in the Formed Aggregates as the Nanocrystallites

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The complexation of perfluorooctanoic acid (PFOA) and pyridine (as the model for the complexation of PFOA and polystyrene-*b*-poly(4-vinyl pyridine) (PS-*b*-P4VP)) in deuterated chloroform leads to an unusual low field shift of the $^{13}$C NMR signal of the carbon atoms in the carboxyl groups of PFOA. Unlike the complexes of block copolymers with other small molecular surfactants in low-polarity organic solvents, the complexes of PFOA/PS-*b*-P4VP self-assemble in chloroform, forming vesicles when the molar ratio of PFOA to the pyridine units is greater than or equal to 1/5 and less than or equal to 1/1. When the molar ratio is 2/1, the PFOA molecules that are unconnected to P4VP chains are encapsulated in the aggregates rather than solubilized in the solvent, leading to a solid spherical morphology of the resultant aggregates. Moreover, the PFOA molecules both connected and unconnected to the P4VP chains are crystallized within the aggregates and melt at different temperatures.

## 1. Introduction

Self-assembly of block copolymers in solutions and the resultant polymeric nano-objects have attracted considerable interest in a great range of research fields of both theory and applications.[1−7] While, in most cases, the self-assembly occurs in a selective solvent due to the difference in the solubility between the two blocks, it can also be induced by interpolymer complexation.[8−11] In recent years, much attention was drawn to the complexation of a block copolymer with a small molecular surfactant and the self-assembly of the resultant complex. It was reported that the complexation in water could lead to the self-assembly of the complex forming vesicles, driven by the aggregation of the surfactant tails.[12,13] However, in a low-polarity organic solvent, the surfactant tails are soluble and the complexation usually increases the solubility of the block copolymer.[14,15] To our knowledge, no regular aggregates resulting from the self-assembly of such a complex *in an organic solvent (or a solvents mixture)* have been reported. In this article, we will report the self-assembly of the complexes of perfluorooctanoic acid (PFOA) and polystyrene-*block*-poly(4-vinylpyridine) (PS-b-P4VP) in chloroform. Although both the PFOA and the block copolymer can be molecularly dispersed in the solvent, the mixing of them leads to vesicles or the “PFOA-filled aggregates” depending on the molar ratio of PFOA to the pyridine rings (MR) in the block copolymer.

## 2. Experimental Section

**Materials and the Preparation of Aggregates.** $PS_{317}$-*b*-$P4VP_{276}$ (the subscripts are the *average* number of the repeat units of the PS and the P4VP blocks, respectively; the $M_w/M_n$ of the block copolymer is 1.37) was synthesized and characterized by GPC and $^1$H NMR according to procedures described in ref 16. Perfluorooctanoic acid was purchased from Aldrich. Chloroform and methanol used in this study are of analytical grade and were used without further purification.

The solutions of the aggregates were prepared by adding PFOA/$CHCl_3$ solution (1% v/v) into a PS-*b*-P4VP/$CHCl_3$ solution dropwise under ultrasonic treatment, leading to the formation of aggregates. The concentration of PS-*b*-P4VP in the final solutions was 1.0 mg/mL.

**Analysis.** A modified commercial light scattering spectrometer (ALV/SP-125) equipped with an ALV-5000 multi-$\tau$ digital time correlator and an ADLAS DPY425 II solid-state laser (output power = 400 mw at $\lambda = 532$ nm) was used. In static light scattering (SLS), the angular dependence of the excess absolute time-averaged scattered intensity of a dilute dispersion, that is, the Rayleigh ratio $R_{vv}(q)$, can lead to the weight-averaged molar mass $M_w$, the second virial coefficient $A_2$, and the *z*-averaged root-mean square radius of gyration $\langle R_g^2\rangle_z^{1/2}$, where $q$ is the scattering vector. In this study, the concentration is as low as $10^{-3}$ g/mL, so the extrapolation to infinite dilution was avoided to prevent any changes in the structure of the aggregates due to dilution. In dynamic light scattering (DLS), the Laplace inversion of a measured intensity−intensity−time correlation function $G^{(2)}(t, q)$ in the self-beating mode can result in a line-width distribution $G(\Gamma)$. For a pure diffusive relaxation, $\Gamma$ is related to the translational diffusion coefficient $D$ by $\Gamma/q^2 = D$ or a hydrodynamic radius $R_h$ by $R_h = k_BT/6\pi\eta D$ with $k_B$, $T$, and $\eta$ being the Boltzmann constant, absolute temperature, and solvent viscosity, respectively.

Scanning electron microscope (SEM) observations were conducted on a Philips XL300 electron microscope at an accelerating voltage of 25 kV. The specimens were prepared by depositing a drop of the solutions onto a glass slide. The $^1$H NMR and $^{13}$C NMR measurements were performed on a Bruker DMX500 (125 and 500 MHz for $^{13}$C and $^1$H, respectively) spectrometer in $CDCl_3$ using TMS as an internal reference. Differential scanning calorimetry (DSC) measurements were performed using a Perkin-Elemer Pyris 1 differential scanning calorimeter at a heating rate of 10 °C/min. The liquid nitrogen was used as the coolant. The signals were recorded from −10 to 52 °C.

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**TABLE 1: Characterization Data of the Aggregates in $CHCl_3$ Measured by Both SLS and DLS at 25 °C**

| | MR = 1/5 | MR = 1/2 | MR = 1/1 | MR = 2/1 |
|---|---|---|---|---|
| $M_{w,particle}{}^a$ | $1.97 \times 10^6$ | $2.30 \times 10^6$ | $7.36 \times 10^6$ | $1.96 \times 10^7$ |
| $\langle R_g \rangle$/nm | 98.8 | 84 | 66 | 55 |
| $\langle R_h \rangle$/nm | 84 | 87.5 | 79 | 98 |
| $\langle R_g \rangle / \langle R_h \rangle$ | 1.18 | 0.96 | 0.83 | 0.56 |
| $\mu_2/\langle \Gamma \rangle^{2\ b}$ | 0.26 | 0.15 | 0.20 | 0.20 |
| $\rho^c$ (g/cm$^3$) | 0.0008 | 0.0015 | 0.0101 | 0.0467 |

[a] Average weight of each aggregate. [b] The polydispersity index of the size distribution.[18] [c] The average density of the aggregates. $\rho = M_{w,particle}/NV$ ($N$ is the Avogadro constant, $V$ is calculated from $4/3\pi\langle R_g \rangle^3$). The concentration of PS-*b*-P4VP in the final solutions is 1.0 mg/mL.

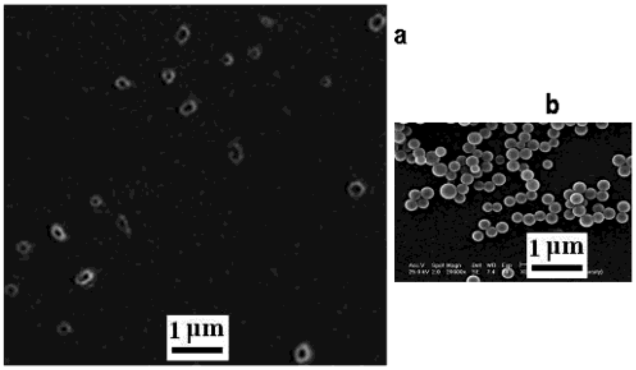

**Figure 1.** Morphologies of discrete aggregates at MR = 1 (a) and MR = 2 (b) observed by SEM (the two scale bars are of equal length).

## 3. Results and Discussion

Chloroform[17] is a common solvent for $PS_{317}$-*b*-$P4VP_{276}$ and a solvent for PFOA, since no aggregation was detected by DLS in their respective solutions even though the concentrations of PFOA and the block copolymer were high, up to 40 and 80 mg/mL, respectively. However, aggregation took place when the solutions of the block copolymer and PFOA were mixed at a MR greater than or equal to 1/5, as indicated by the data in Table 1.

The resultant aggregates have a regular spherical shape, as almost no dependence of the sizes on the scattering angles was observed.

The values of $\langle R_g \rangle / \langle R_h \rangle$ ($\langle R_g \rangle$ is the average radius of gyration measured by SLS, and $\langle R_g \rangle$ is the average hydrodynamic radius measured by DLS) are also presented in Table 1. Theoretically, for a uniform nondraining solid sphere and a nondraining thin shell vesicle the ratios of $\langle R_g \rangle / \langle R_h \rangle$ are about 0.774 and 1.0, respectively.[19,20] While experimentally, for a polymeric micelle, $\langle R_g \rangle / \langle R_h \rangle$ is often less than 0.774, since the density of the core is remarkably larger than that of the shell;[21,22] for a polymeric vesicle, $\langle R_g \rangle / \langle R_h \rangle$ may be a little larger or less than 1.0 depending on the thickness and density of its wall.[10] From Table 1 one can see that, in the cases of MR being 1/5, 1/2, and 1/1, the ratios are obviously larger than 0.774, so the resultant aggregates can be assumed to be vesicles. It is interesting to see that when 2 times the stoichiometric amount of PFOA is used (MR = 2/1), $\langle R_g \rangle / \langle R_h \rangle$ becomes 0.56, much less than 0.774. In addition, the average density of the aggregates obtained at an MR of 2/1 is four times that at an MR of 1/1. Therefore, it is assumed that the excess PFOA molecules are encapsulated in the aggregates. This assumption is further supported by SEM observations. The images of the collapsed vesicles and the PFOA filled aggregates are shown in parts a and b, respectively, of Figure 1. The difference between the aggregates in Figure 1a (MR = 1) and that in Figure 1b (MR = 2/1) is significant. Figure 1a shows a typical vesicle structure while Figure 1b shows the structure of rather homogeneous spheres. It is noted that the average size of the aggregates in the SEM images seems larger than that measured by DLS. One of the causes is that the average size of the aggregates measured by DLS is that of their equivalent nondraining spheres. Due to the drainable nature of the shells of the aggregates, the size may be smaller than that observed by SEM based on the outline of the aggregates.

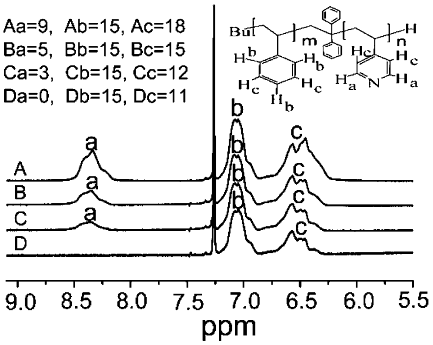

**Figure 2.** $^1H$ NMR spectra of PFOA/PS-*b*-P4VP in $CDCl_3$ at different MR values of 0 (A), 1/5 (B), 1/2 (C), and 1/1 (D). In the inset, $K_i$ refers to the peak area (*the relative intensity*) of peak $i$ in spectrum $K$. Dimethyl sulfoxide (DMSO) was used as an internal standard. All the measurements were conducted at room temperature.

The complexation due to hydrogen bonding between the carboxyl groups in PFOA and the pyridine rings in the block copolymer was proved by measuring the $^{13}C$ NMR spectra of the mixtures of pyridine and PFOA in deuterated chloroform (as the model for the complexation of PFOA and the block copolymer), as the peak associated with the carbon atoms in the carboxyl groups shifts from 159.6 to 163.3 ppm due to the complexation. Usually, in the cases where carboxyl groups act as the proton donor only, the formation of such hydrogen bonding will increase the electron densities surrounding the H atoms and carbon atoms in the carboxyl groups and lead to the high field shifts of their signals.[23] The low field shift in this case may be remarkable and worthy of being further studied.

The complexes of PFOA and the block copolymer at different MR values were characterized by $^1H$ NMR in deuterated chloroform. The spectra are shown in Figure 2. For clarity, only the spectra from 6.0 to 10.0 ppm are presented. The assignments are given in the inset.[24]

It is shown in Figure 2 that the relative intensity of peak b assigned to the hydrogen atoms $H_b$ (inset) in the benzene rings only does not change with the addition of PFOA. With addition of PFOA and an increase of the MR, the relative intensities of peak a and peak c, which are associated with $H_a$ in the pyridine rings and $H_c$ in both the pyridine and benzene rings, respectively, decrease. When the MR equals 1 (spectrum D), peak a disappears completely and the intensity ratio of peaks b to c becomes close to 3/2, which is the number ratio of the $H_b$ to $H_c$ in the benzene rings. These indicate that as the stoichiometric complexation between PFOA and the block copolymer takes place, the complexed pyridine rings aggregate, and their mobility is fully restricted, leading to complete disappearance of the signals.[25] In addition, it is noted that, in the cases of MR being 1/5 and 1/2, the decreases in the relative intensities of peaks a and c compared to those in the spectrum of pure PS-*b*-P4VP apparently exceed what were expected stoichiometrically. This implicates that not only the complexed pyridine rings but also their close neighboring ones lose their mobility and their signals in the spectra. However, the signals of the benzene rings remain

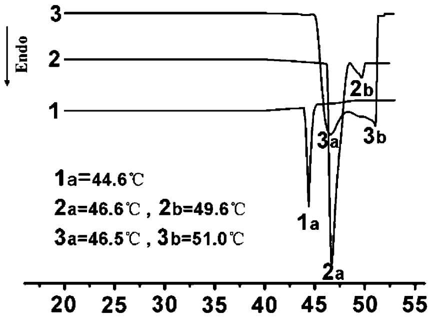

**Figure 3.** DSC traces of PFOA/PS-*b*-P4VP in chloroform at MR values of 1/5 (curve 1), 1/1 (curve 2), and 2/1 (curve 3). The concentration of the block copolymer in the solutions is 5.0 mg/mL, and the concentrations of PFOA at MR values of 1/5, 1/1, and 2/1 are 1.85, 9.22, and 18.5 mg/mL, respectively. The heating rate was 10 °C/min.

unchanged with the addition of PFOA, indicating that nearly all of them remain in the solvated state. Therefore, it is deduced that, during the process of forming a vesicle, the complexed pyridine rings and their close neighboring ones aggregate along with the bound PFOA molecules to form the wall of the vesicle, while the polystyrene chains (and possibly some of the unbound pyridine units that are movable enough to be detectable by $^1$H NMR in the cases of the MR being 1/5 and 1/2) stretch out from both the inner and outer surfaces of the wall and are solvated to stabilize the aggregates. The changes of the spectra with MR are very similar to that of PS-*b*-P4VP during cross-linking the P4VP block.[24]

In addition, the mixture solution at the MR of 2/1 was measured by $^1$H NMR as well. The spectrum at the MR of 2/1 is almost the same as spectrum D (data not shown). What is unexpected is that no signal associated with PFOA (pure PFOA in deuterated chloroform will give a widened signal of the H atoms in the carboxyl groups in the range 10−13 ppm) was found although the PFOA is two times the stoichiometric amount. This means that these free PFOA molecules (unconnected with pyridine rings) are mainly in the aggregated state rather than molecularly dispersed in solution. It is quite possible that these free PFOA molecules are encapsulated inside the aggregates and consequently decrease the value of $\langle R_g\rangle/\langle R_h\rangle$. This assumption agrees with the results obtained by DLS, SLS, and SEM measurements and is further supported by our study using DSC.

Figure 3 presents our DSC results. Although the signals were recorded between −10 and 52 °C, only those from 20 to 52 °C are shown for clarity. No signal can be found in the DSC traces of both pure PFOA solution (20 mg/mL) and the pure block copolymer solution (40 mg/mL) from −10 to 52 °C, since they are molecularly dispersed in their respective solutions at such concentrations. However, the DSC traces of the mixture solutions at MR values of 1/5, 1/1, and 2/1 show clearly the signals of typical first-order phase transitions. As the DLS measurements of the aggregate solutions proved that no dissociation of the aggregates (as well as the H-bonding, otherwise the aggregates may dissociate) occurred at temperatures ranging from 20 to 52 °C and both the PS and P4VP blocks cannot show any first-order transition, it is reasonable to think that PFOA is responsible for the transition; that is, the melting of PFOA crystallites within the aggregates gives the signals.

When the MR is 1/5, all the PFOA molecules are bound with pyridine rings and crystallized in the aggregates, giving a single peak (44.6 °C, peak 1a). In this case, the PFOA crystallites are certainly imperfect due to the existence of many unbound pyridine rings, leading to the lower melting temperature. In both cases of MR of 1/1 and 2/1, there are two transitions. The lower ones (peak 2a at 46.6 °C and peak 3a at 46.5 °C) are associated with the crystallites of PFOA bound to the P4VP block chains, and the melting temperatures are higher than that for the MR of 1/5, reflecting that the imperfectness of the crystallites is becoming less. The transitions at higher temperature (peak 2b at 49.6 °C and peak 3b at 51.0 °C) are probably associated with the crystallites formed by the free PFOA. Without the interference of the P4VP chains, the crystallites seem more perfect, showing even higher melting points. It is noticed that the peak area of 2b is very small relative to that of 2a, while the area of peak 3b is almost the same as that of peak 3a. This result is obviously understandable, as it implies that most of the PFOA is bound to P4VP block chains when the MR is 1/1 while the bound and the unbound amounts are comparable when the MR is 2/1. Furthermore, there is a little difference between the melting temperature of peak 3b and that of peak 2b, and both the melting temperatures are lower than that of the bulk PFOA crystal (56 °C). A similar phenomenon was reported for the melting temperature of PCL crystallites in the core of micelles.[26]

## 4. Conclusions

In summary, the complexation between PFOA and PS-*b*-P4VP takes place in chloroform, as demonstrated by a low field shift of the $^{13}$C NMR signal of the carbon atoms in the carboxyl groups of PFOA when mixed with pyridine. Different from the cases of the complexes of PS-*b*-P4VP with other surfactants, the high-polarity of the bound pyridine units cannot be shielded by PFOA tails in chloroform, possibly due to their rigidity;[27,28] the complexes of PFOA/PS-*b*-P4VP at MR greater than or equal to 1/5 and less than or equal to 1/1 self-assemble into vesicles. In addition, when the MR is 2/1, the unbound PFOA molecules are encapsulated inside the formed aggregates instead of being solubilized in chloroform. In all the cases, both the bound and the unbound PFOA molecules are crystallized, and the polystyrene blocks are solvated to stabilize the aggregates. These conclusions are supported by the DLS, SLS, SEM, $^1$H NMR, and DSC measurements.

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