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Organometallic–Polypeptide Block Copolymers: Synthesis and Self-Assembly of Poly(ferrocenyldimethylsilane)-b-Poly(ε-benzyloxycarbonyl-L-Lysine)

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Abstract: A new type of metallopolymer-polypeptide block copolymer poly(ferrocenyldimethylsilane)-*b*-poly(ε-benzyloxycarbonyl-L-lysine) was synthesized by ring-opening polymerization of ε-benzyloxycarbonyl-L-lysine N-carboxyanhydride initiated by using a primary amino-terminated poly(ferrocenyldimethylsilane). Studies on the self-organization behavior of this polypeptide block copolymer in both the bulk state and in solution were performed. In the bulk state, a cylindrical-in-lamellar structure was observed in a compositionally asymmetric sample. Rod-like micelles with a polyferrocenylsilane core formed in a polypeptide-selective solvent alone or in the presence of a common solvent. Significantly, an additional small quantity of the common solvent assisted the formation of longer micelles and micelles with better shape-regularity. This is attributed to a decrease in the number of nucleation events and PFS core reorganization effects.

Keywords: block copolymers · micelles · polyferrocenylsilane · polypeptides · rod-coil

Introduction

Self-assembly of block copolymers occurs in the bulk state or in a selective solvent, driven by the immiscibility of the constituent segments.[1] This approach is a powerful way to obtain nanostructured materials with well-defined shapes and functions.[2] Polypeptide hybrid-block copolymers have attracted considerable attention as interesting building blocks for novel supramolecular materials. Molecular design by combining the structural and functional control of polypeptides with the versatility of synthetic polymers has given access to materials with applications in areas as diverse as nanotechnology, drug delivery, tissue engineering, biomineralization and bioanalysis.[3] The incorporation of metallopolymer segments into block copolymer structures results in materials with novel chemical and physical characteristics.[4] For example, block copolymers with a polyferrocenylsilane (PFS) block have shown interesting redox, preceramic, etch-resistant, and catalytic properties.[5]

Research on the bulk state behavior of polypeptide block polymers has been focused mainly on rod-coil type copolymers with a rod-like rigid polypeptide segment such as poly(γ-benzyl-L-glutamate) (PBLG) or poly(ε-benzyloxycarbonyl-L-lysine) (PZLys).[6] The self-assembly of coil–coil block copolymers is controlled primarily by two parameters, the volume fraction Φ of each block and the Flory–Huggins interaction parameter χN.[1b] The behavior of rod-coil block copolymers is complicated by the liquid crystalline ordering of the rod blocks and the topological disparity between the rod and the coil blocks. To describe their influence on self-assembly, two additional parameters have been introduced, the Maier–Saupe parameter μN expressing the rod-rod aligning interactions, and a geometrical parameter ν that characterizes the relative block size.[7]

The self-assembly of block copolymers in solution generally results in three basic types of structures whose shapes are, in order of decreasing curvature, spherical micelles, cylindrical micelles, and vesicles/lamellar platelets.[8] The size and shape of the micelles is normally determined by the

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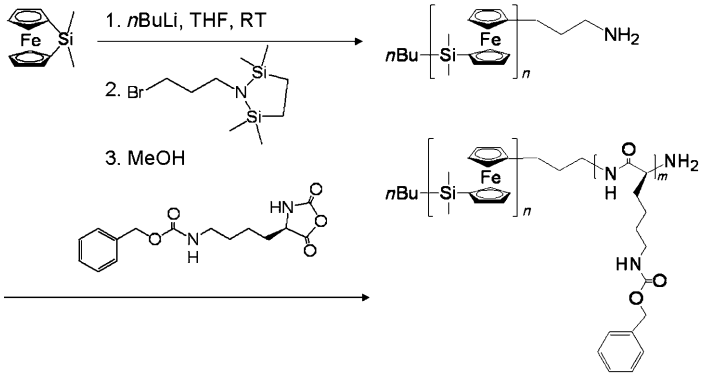
volume fractions of the constituent blocks and environmental factors such as the solvent and ionic strength.[9] More complex superstructures can form when specific factors, such as chirality and secondary structure effects,[10] as well as the crystallization of the core-forming block,[11,12] are involved. In most of cases, block copolymers with soluble, corona-forming polypeptide blocks form spherical micelles or vesicles.[10b] Non-spherical aggregates generated from polystyrene-*b*-poly(L-lysine) copolymers were reported by Klok and coworkers based on light scattering and small-angle neutron scattering data.[10c] Recently, Savin reported elongated aggregates from polybutadiene-*b*-poly(L-lysine) block copolymers.[10d]

The micellization of asymmetric block copolymers with a core-forming PFS block as the minority component have been studied by our group and also by other researchers.[12] For example, well-defined rod-like micelles have been obtained with various PFS block copolymers and we have inferred that the crystallization of the core-forming PFS block can act as the driving force for their formation. We have also shown that the formation of rod-like micelles behaves as a living supramolecular polymerization allowed micelle length control and the formation of block co-micelle architectures.[12g,h] With this background in mind, we anticipated that PFS-*b*-polypeptide copolymers could couple the ability of PFS block copolymer to form well-defined rod-like micelles and the advantageous features of polypeptides, such as secondary structure formation, diverse functionality and biocompatibility. Previously, our group reported the synthesis and self-assembly of a PFS-*b*-PBLG diblock copolymer.[13] Spherical micelles in water were prepared from the deprotected polymer, PFS-b-poly(L-glutamic acid). In this paper we present the synthesis and characterization of PFS-*b*-PZLys diblock copolymers, as well as an examination of the self-assembly of these materials in bulk and in solvents selective for the PZLys block.

Results and Discussion

Synthesis of PFS-*b*-PZLys block copolymers: The block copolymers were synthesized in a two-step reaction as shown in Scheme 1. The first step involved the synthesis of PFS terminated with a primary amine group by using a method similar to that reported by Kim et al.[13] Dimethyl[1]silaferrocenophane was polymerized anionically at room temperature in THF using *n*-butyllithium as an initiator.[14] An aliquot of the solution was removed 40 minutes after the initiation and quenched with degassed methanol to obtain an H-terminated PFS sample for GPC analysis. Subsequently, the living anionic PFS chains were quenched with 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane at low temperature. The primary amino groups were deprotected by simply precipitating the reaction solution into methanol. The tetramethyl-1-aza-2,5-disilacyclopentane protective group is very labile toward methanol; thus complete deprotection was achieved during this precipitation step. The primary amino-terminated PFS homopolymer was successfully separated from unfunctionalized PFS using flash silica column chromatography in a 50–60% yield. Aliquots of H-terminated polymer were analyzed by GPC and yielded values of $M_n = 11\,000$, corresponding to 45 repeat units. The molecular weight distribution of the PFS homopolymer was very narrow, with a polydispersity index (PDI) of 1.03.



Scheme 1. Synthesis of PFS-*b*-PZLys block copolymers.

The quenching of a living anionic polymer with an alkyl halide is often accompanied with a side reaction that involves polymer dimerization, resulting from a Wurtz-type coupling reaction between two living polymer chains.[15,16] Formation of dimers in our system was confirmed by GPC as shown previously by Kim et al,[13] which may account for the relatively low yield here. The susceptibility of an alkyl halide toward the Wurtz-type reaction is in the order RI > RBr > RCl. To avoid Wurtz-type coupling, other researchers have used 1-(3-chloropropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclo-pentane as a quencher for anionic chains to prepare primary amino-terminated polystyrene,[15,17] polyisoprene[18] and polybutadiene.[10d,19] Therefore, we also tested the suitability of this alkyl chloride as a quencher of anionic PFS. The quenching processes were carried out at $T = -78$, 0, 25, and 50 °C, respectively. Unfortunately, the yield of the amino functionality on the PFS was always lower than 10%. We assume that this low yield was caused by the relatively low nucleophilicity of the PFS carbanion. The conditions described above using the 3-bromopropyl derivative at −78 °C represent our optimum coupling conditions.

In the second synthetic step, the primary amino-terminated PFS homopolymer was used as macroinitiator to initiate the ring-opening polymerization (ROP) of ε-benzyloxycarbonyl-L-lysine N-carboxyanhydride (Z-Lys NCA) in order to obtain diblock copolymers. This ROP of Z-Lys NCA was carried out in a THF/DMF mixed solvent, because the PFS macroinitiators we used here are insoluble in DMF, which is generally used as the solvent for the ROP of N-carboxyanhydrides. The reaction was allowed to proceed over 5 days under a purified nitrogen atmosphere in a dry box, after which the resulting viscous amber solution was precipitated into methanol. After vacuum-drying, the amber block copolymers were obtained as glassy solids. All block copolymers were easily soluble in common organic solvents such

as THF, CH_2Cl_2, and chloroform. The block copolymers were separated from any macroinitiator residues by repeated precipitations of CH_2Cl_2 solutions of block copolymers into warm cyclohexane until PFS homopolymer was not detectable with a UV-vis detector ($\lambda = 450$ nm) on GPC analysis. Figure 1 shows the GPC profiles of PFS-*b*-PZLys **1**

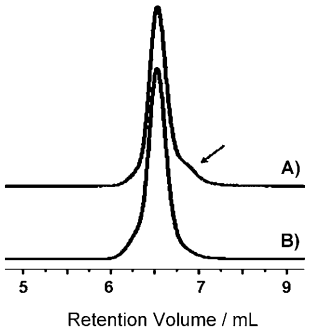


Figure 1. Gel permeation chromatograms (UV-vis detector, $\lambda = 450$ nm) of PFS-*b*-PZLys **1** in THF (0.003 M tetrabutylammonium bromide) at 25 °C (A) before and (B) after purification. The shoulder (arrow) in profile A is due to the PFS macroinitiator residue.

before and after purification. The GPC traces showed narrow molecular weight distributions for the block polymers with PDI values of 1.1 to 1.3. The ^{1}H NMR spectrum of PFS-*b*-PZLys **2** recorded in CD_2Cl_2 with the peak assignments is shown in Figure 2. The block ratios for the block copolymers were deduced from the integration of the signals from PFS and PZLys. The molecular characteristics of the PFS-*b*-PZLys samples are summarized in Table 1.

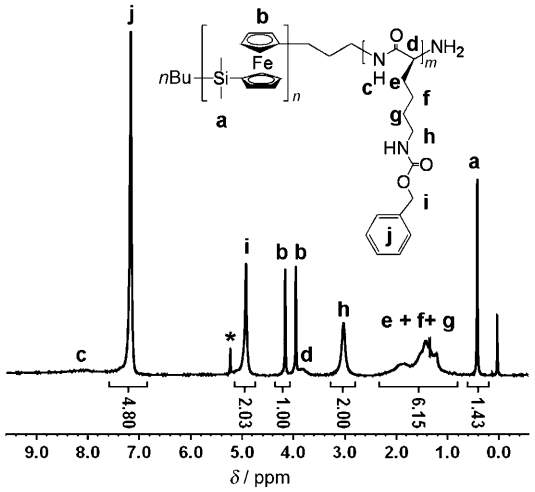


Figure 2. ^{1}H NMR spectrum of PFS-*b*-PZLys **2** in CD_2Cl_2 at 25 °C. ($\star$ solvent residue)

Self-assembly in the bulk state: PFS-*b*-PZLys block copolymer films were cast from THF solution onto glass slides. The films were annealed in a vacuum oven first at 50 °C for one hour, then at 160 °C for 3 days, before they were rapidly removed from the oven and quenched in liquid nitrogen to suppress PFS crystallization.

Table 1. Molecular characteristics of PFS macroinitiator and PFS-*b*-PZLys block copolymers.

polymer	DP_n (PFS)[a]	DP_n (PZLys)[b]	M_n[c]	PDI (M_w/M_n)
PFS macroinitiator	45	–	11 000	1.03[d]
PFS-*b*-PZLys **1**	45	75	30 500	1.25[e]
PFS-*b*-PZLys **2**	45	180	58 800	1.16[e]

[a] Degree of polymerization of PFS obtained by gel permeation chromatography (GPC) with a triple detector and THF as the eluant. [b] Degree of polymerization of PZLys obtained by ^{1}H NMR. [c] Number average molecular weight obtained by calculation based on the degree of polymerization. [d] Polydispersity index (PDI) of the PFS macroinitiator obtained by GPC with a triple detector and THF as eluant. [e] PDI of PFS-*b*-PZLys obtained by GPC with a triple detector and THF (0.003 M tetrabutyl ammonium bromide) as the eluant.

The films were microtomed at room temperature to obtain block copolymer sections with a thickness of ≈70 nm for TEM measurements. Because of the presence of iron and silicon as heavy atoms in the PFS domains, no staining was needed to obtain sufficient contrast in the TEM images. TEM studies of PFS-*b*-PZLys **1** revealed a lamellar structure (see Figure S1 in the Supporting Information). Babin et al. observed that the α-helix to β-sheet transition temperature for PZLys blocks in polyisoprene-*b*-PZLys block copolymers increases with increasing the degree of polymerization (DP) of PZLys blocks.[18] The transition temperature for a PZLys block with a DP_n of 75 is ≈155 °C,[18] which is close to the temperature (160 °C) at which we annealed our PFS-*b*-PZLys block copolymer samples. Therefore, our study was focused on block copolymer PFS-*b*-PZLys **2**, in which the DP_n of PZLys block is 180, corresponding to a transition temperature higher than 200 °C.[18]

The bright field TEM images of PFS-*b*-PZLys **2** in Figure 3 revealed a lamellar structure. The dark domains correspond to the electron-rich PFS phase, and the brighter domains represent the PZLys domains. This assignment was confirmed by EDX, as shown in Figure 3C. The small angle X-ray scattering (SAXS) pattern in Figure 4A shows peaks at approximate q ratios of 1:2:3:4, indicating a lamellar structure. The spacing calculated from the SAXS pattern (≈36 nm) is consistent with that estimated from TEM (30–45 nm). The peaks in the SAXS pattern are quite broad. The reason for the observation of broad SAXS peaks in polypeptide block copolymers has been discussed by Schlaad et al.[20] It is caused by fluctuations in the thickness of polypeptide layers, as a consequence of the packing of helices with different lengths. A fluctuation in the thickness of PZLys layers can be seen in Figure 3B and Figure 3C.

Figure 4B shows the wide angle X-ray scattering (WAXS) pattern of a PFS-*b*-PZLys **2** film. The pattern displays a set of three Bragg peaks at $q = 0.46$, 0.79 and 0.92 Å^{-1} and in a ratio of 1:3$^1/_2$:2, corresponding to hexagonal packing of PZLys α-helices with a spacing of 13.7 Å. The spacing can be assigned to the distance between neighboring PZLys chains.[21] The bulk state morphology of a series of polypeptide-*b*-polyvinyl rod-coil diblock copolymers have been stud-

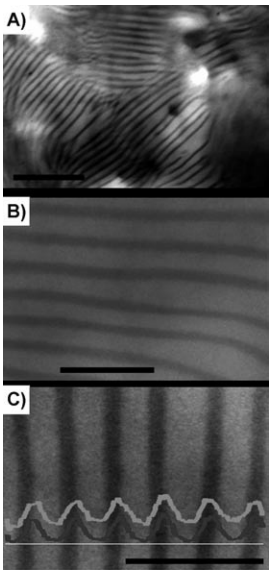


Figure 3. Bright field TEM images of PFS-*b*-PZLys **2** section. A) Under low magnification; Scale bar: 300 nm. The bright spots correspond to very thin areas or holes in the section. B) Under high magnification; Scale bar: 100 nm. C) Under high magnification with EDX analysis profiles (top: iron; bottom: silicon); Scale bar: 100 nm.

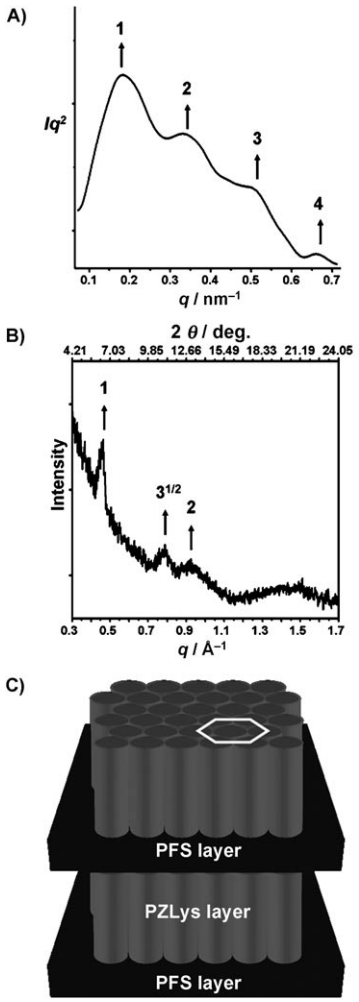


Figure 4. A) SAXS and B) WAXS Patterns for a PFS-*b*-PZLys **2** film. C) A schematic representation of HL morphology for PFS-*b*-PZLys **2** (not to scale). Helices are presented as rods.

ied by other researchers.[6] For most of the block copolymer samples studied, regardless of the volume fraction of the two components, only a lamellar morphology was observed. This organization has been termed a hexagonal-in-lamellar (HL) morphology, referring to the local hexagonal packing of the α-helical polypeptide chains within phase-segregated lamellas. The lack of more complex phases for rod-coil block copolymers originates from the anisotropic liquid crystalline behavior of the rod blocks.[7] Therefore, it is not surprising that PFS-*b*-PZLys **2** presents a lamellar structure, although the volume fraction of PFS is as low as 0.19, calculated using a PFS density of 1.26 g mL^{-1}[22] and a PZLys density of 1.26 g mL^{-1}.[23] A schematic representation of HL morphology for PFS-*b*-PZLys **2** is given in Figure 4C.

Poly(ferrocenyldimethylsilane) is a semicrystalline polymer with a melting point of ≈130–145 °C.[24] The WAXS pattern of the as-cast PFS-*b*-PZLys **2** film indicated the presence of PFS crystallites. The purpose of thermal annealing was to eliminate the influence of crystallization of PFS on the self-assembly of the block copolymer. The necessity for a thermal annealing step makes it difficult to study this block copolymer systematically. Future work will involve more detailed and systematic studies on PFS-*b*-PZLys block copolymers, in which the PFS block is amorphous such as poly(ferrocenylethylmethylsilane) or poly(ferrocenylmethylphenyl-silane).[25]

Self-assembly in solution: We attempted to prepare PFS-*b*-PZLys block copolymer micelles by two methods. In the first method, the block copolymer was dissolved directly in DMF at room temperature with stirring. DMF is a good solvent only for the PZLys block. Therefore, the formation of micelles with a PFS core and a PZLys corona was expected. Micelles were prepared from PFS-*b*-PZLys **1** in this way. Two days after the preparation, a micelle sample was collected on a carbon-coated grid for TEM imaging. Figure 5A and Figure 5B are TEM images showing the presence of rod-like micelles. Owing to the high electron density of the PFS core, the PZLys corona is invisible in the images. The lengths of the micelles ranged from 40 to 300 nm and the widths of the PFS core varied from 10 to 20 nm. The micelles have somewhat irregular shapes, characterized by the rough surface profiles of the PFS cores.

By TEM, the morphology of the micelles exhibited no obvious change after a two-week aging period at room temperature in DMF. The micelle solution was then divided into two portions. To one portion a small amount of THF was added. THF is a good solvent for both the PFS and the PZLys blocks. Figure 5C and Figure 5D show the TEM images of micelles after aging in the DMF/THF mixed solvent for 2 weeks. The shape of micelles became more uniform. Most of the micelles have a smooth surface. The mor-

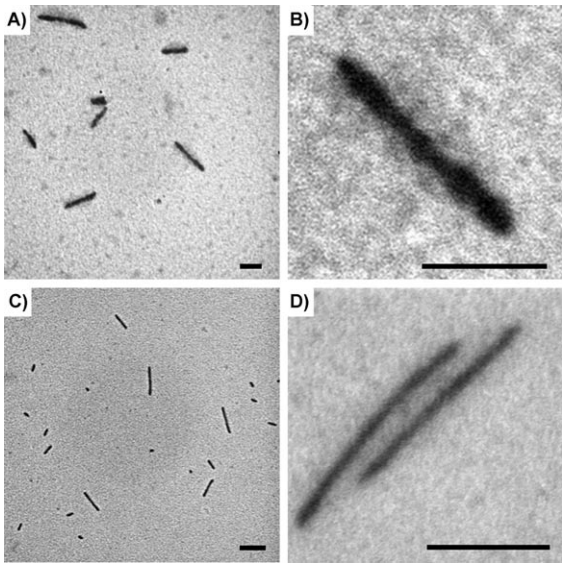


Figure 5. Bright field TEM images at low (A,C) and higher magnification (B,D) of the micelles prepared from PFS-*b*-PZLys **1** by method 1. A) and B) 2 days after preparation; C) and D) after aging 2 weeks in DMF and another 2 weeks in DMF/THF (9/1 by volume); Scale bar: 100 nm.

phology of the micelles in the other portion, without the presence of THF, showed no apparent change.

In the second method, a sample of PFS-*b*-PZLys block copolymer was first dissolved in THF. Then DMF was added dropwise to reach a 90% volume fraction of DMF. In this way, longer micelles with a well-defined rod-like shape were obtained. Figure 6 shows the evolution of micelle morphology over time. The micelles were prepared from PFS-*b*-PZLys **1**. Irregular elongated structures with a core diameter of 25 to 40 nm were observed 3 days after sample preparation. A small portion of the micelles appear to possess thin filaments at the ends. After 7 days, longer micelles with one or two thin filaments at the ends formed. After 9 days, all the micelles evolved into well-defined rod-like objects with lengths up to 1 μm. The widths of the micelle cores are quite uniform and are estimated to be 12–14 nm, significantly smaller than the irregular structures formed initially and more similar to the values for the filament structures apparent in Figure 6A,B.[26]

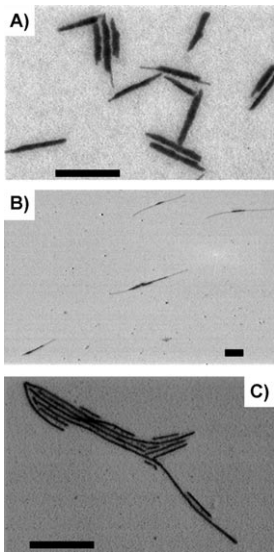


Figure 6. Bright field TEM images of micelles prepared from PFS-*b*-PZLys **1** by method 2. A) 3 days, B) 7 days, C) 9 days after preparation; Scale bar: 300 nm.

Micelles of PFS-*b*-PZLys **2** were prepared by method 2. The TEM image in Figure 7A shows the presence of rod-like micelles with lengths up to a few μm. The widths of the micelle cores are similar to those of PFS-*b*-PZLys **1** micelles. An AFM image of the micelles in Figure 7B reveals a uniform height of ≈11 nm and an apparent width of ≈60 nm. The latter distance presumably reflects the width of both the core and corona of the micelle.

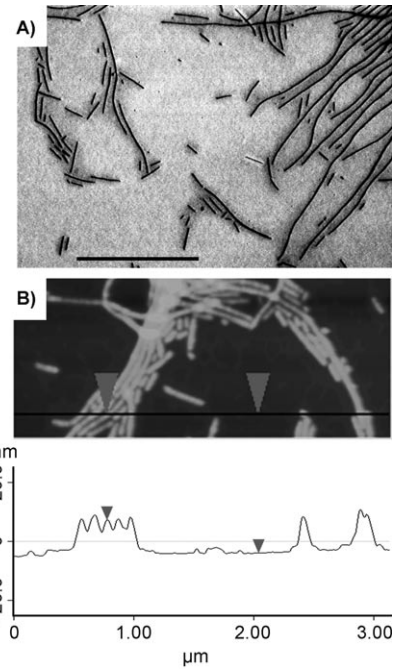


Figure 7. Morphology of PFS-*b*-PZLys **2** micelles 2 weeks after preparation. A) Bright field TEM image; Scale bar: 1000 nm. B) AFM image in height mode and line profile.

Micelle films for WAXS measurements were cast from PFS-*b*-PZLys **2** micelle solutions 5 and 14 days after the micelle preparation. The presence of rod-like micelles in the micelle solution 5 days after the preparation was confirmed by TEM (see Figure S3). Both WAXS patterns in Figure 8 show a strong peak at $2\theta = 13.7°$ corresponding to a lattice spacing of 6.4 Å, which can be assigned to the distance between adjacent planes containing planar zigzag PFS chains.[24a,b] The WAXS pattern of the film cast 5 days after the micelle preparation also shows a set of three Bragg peaks with q ratio of $1:3^{1}/_{2}:2$, characterizing the hexagonal packing of PZLys α-helices. This may originate from the presence of free PFS-*b*-PZLys polymer chains in the micelle solution. The self-assembly of the free chains upon casting

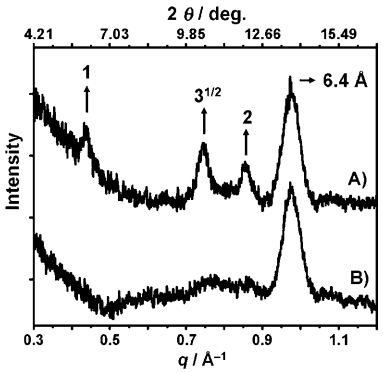


Figure 8. WAXS patterns of PFS-*b*-PZLys **2** micelle films cast A) 5 and B) 14 days after the preparation of micelle solution.

may then have induced the hexagonal packing of PZLys α-helices. By comparing the WAXS pattern of the film cast 14 days after the micelle preparation to that of the film cast 5 days after the micelle preparation, a decrease in the intensity at angles associated with the hexagonal packing of PZLys α-helices relative to that at 13.7° can be observed. This is due to the decrease of free polymer in the micelle solution upon aging.[27] Similar WAXS results were obtained from PFS-*b*-PZLys **1**. (see Figure S5 in the Supporting Information)

The crystallization of PFS appears to be the dominating factor for the formation of long rod-like micelles from most asymmetric PFS block copolymers.[12a,b] In this context, we assume the effect of THF on the shape regularity and length of the PFS-*b*-PZLys micelles is related to its ability to increase the block copolymer solubility and to influence the crystallization of PFS. The crystallization process consists of two major events: nucleation and crystal growth. In the nucleation stage, some of the PFS chains gather and arrange themselves to form nuclei. In the crystal growth stage, more PFS chains add to the nuclei and then to the growing crystal, which results in the formation of larger/longer micelles.

We observed that the common solvent THF can improve the shape regularity of the micelles when we tried to prepare micelles using method 1. Using this method, short micelles with an irregular shape formed upon dissolving the PFS-*b*-PZLys block copolymer directly in DMF. The irregular shape of the micelles may be caused by kinetic factors that leave defects in the semi-crystalline PFS core. The PFS chains at the defect points would be less stable thermodynamically than in crystalline domains of the PFS core, but they might be "frozen" because of the low mobility of the PFS. The addition of THF may plasticize regions of the core and increase the mobility of PFS chains at the defect point. The PFS-*b*-PZLys chains could then reorganize to eliminate many of the defects, and yield micelles with a more uniform shape.

If the micelles were prepared by the second method, THF was introduced into the system before the formation of micelles and longer micelles formed. We believe that fewer PFS nuclei formed in the mixed solvent, as the PFS block is more soluble, leading to the formation of longer micelles. Again, the irregular shape of the micelles shown in Figure 6A may be caused by kinetic factors in the early stage of micellization. Further growth of the micelles was less kinetically controlled. Therefore, the addition of more PFS chains to the micelles resulted in the thin filaments with uniform width as shown in Figure 6B. The growth of the micelles accompanied with the removal of some defects formed in the early stages eventually led to micelles with uniform shape as shown in Figure 6C.

Figure 9 summarizes the micellizaton process for PFS-*b*-PZLys block copolymer in DMF alone or in the presence of a small amount of the common solvent THF. A detailed light scattering study of the kinetic process of micellization would be useful to probe the exact role of THF in this system.

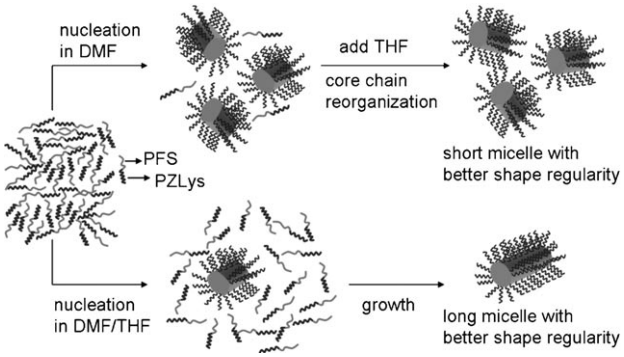


Figure 9. A mechanism for the self-assembly of PFS-*b*-PZLys diblock copolymer in a selective solvent DMF alone or in the presence of common solvent THF. The shape of the micelles is shown as cylindrical for simplification.

Summary

A new type of metallopolymer-polypeptide block copolymer poly(ferrocenyldimethylsilane)-*b*-poly(ε-benzyloxycarbonyl-L-lysine) was synthesized by ring-opening polymerization of ε-benzyloxycarbonyl-L-lysine N-carboxyanhydride initiated with primary amino-terminated poly(ferrocenyldimethylsilane). Studies on the self-organization behavior of this polypeptide block copolymer in both the bulk state and in solution were carried out. In the bulk state, a cylindrical-in-lamellar structure was observed in a compositionally asymmetric sample. Micelles with a rod-like shape were obtained in a selective solvent alone or in the presence of a common solvent. The presence of a small amount of the common solvent resulted in the formation of longer micelles or micelles with improved structural uniformity. We suggest that this is a result of a decrease in the number of nucleation events and the facilitation of PFS core chain reorganization.

Experimental Section

Materials and instrumentation: All reagents were purchased from Aldrich. THF was distilled over Na/benzophenone and redistilled over *n*-butyllithium under vacuum. DMF was vacuum distilled over CaH_2. 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane was vacuum distilled over CaH_2. Distilled reagents were used immediately. [1]Dimethylsilaferrocenophane,[14] 1-(3-chloropropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane[15] and ε-benzyloxycarbonyl-L-lysine N-carboxyanhydride (Z-Lys NCA)[28] were synthesized according to the methods reported in the literature.

All of the polymerizations were carried out in an M-Braun dry box under a purified N_2 atmosphere. ^{1}H NMR spectra were obtained by using a Varian 400 spectrometer with CD_2Cl_2 as solvent. Molecular weights of the polymers were measured by using a Viscotek GPC max system (VE 2001 GPC solvent/sample module and TriSEC Model 302 triple detector array) or a Viscotek GPC max liquid system equipped with a UV-Vis detector (model 2501) with THF or THF (0.003 M tetrabutylammonium bromide) as the eluant. Small angle X-ray scattering (SAXS) measurement was performed by using a Nanostar SAXS system (CuK_α radiation, $\lambda =$ 1.54 Å) from Bruker AXS GmbH. The sample-to-detector distance was set to 0.6 m. The SAXS pattern was smoothed in order to obtain a better resolution of the peaks. Wide angle X-ray scattering (WAXS) measurements were performed in the reflection mode by means of a Bruker AXS D8 Discovery Diffraction System (CuK_α radiation, $\lambda = 1.54$ Å). TEM measurements were made by using a Hitachi H-600 instrument at an acceleration voltage of 75 kV or a Hitachi S-5200 instrument equipped with an Oxford Instruments Inca EDX system at an accelerating voltage of 30 kV. EDX measurements were performed in the line-scan mode. Diblock copolymer thin sections were prepared by microtoming the block copolymer film by using a Leica UCT ultramicrotome. TEM specimens were prepared on a 200 mesh carbon-coated copper grid. AFM imaging was carried out in air using the tapping mode feature of a Nanoscope IIIa Dimension 5000 microscope (Veeco Digital Instruments). The silicon probe cantilevers (MikroMasch, resonance frequencies in the range of 135–190 kHz, free amplitude: 20–25 nm) were used with nominal spring constants of between 3.5 and 12.5 Nm^{-1}. In the AFM experiments, micelles were deposited onto a freshly cleaved mica surface.

Synthesis of amino-terminated PFS macroinitiator: Dimethyl[1]silaferrocenophane (1.0 g) was dissolved in THF (10 mL) followed by the addition of *n*BuLi (63 μL, 1.6 M in hexanes). The polymerization was allowed to proceed for 40 min at room temperature. The polymer solution was then cooled to −78 °C with a dry ice acetone bath. An aliquot of the solution was removed and quenched with degassed methanol to obtain an H-terminated PFS sample for GPC analysis. In the polymerization reaction, the living chains end were quenched with a 5-fold excess of 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane (150 mg). After stirring for 1 hour at −78 °C, the solution was allowed to warm slowly to room temperature by removing the dry ice acetone bath, and the reaction was stirred for another 2 h. Then, the solution was precipitated into methanol to release the amino functionality. The amino-terminated PFS was successfully separated from unfunctionalized PFS using flash column chromatography over silica (30 g). First the column was eluted with CH_2Cl_2 to separate unfunctionalized PFS. Then the eluant was changed to THF, and amino-terminated PFS was collected. Yield: 55% (0.55 g).

Synthesis of PFS-*b*-PZLys block copolymers (1–2): The procedure for the synthesis of various block copolymer samples was identical except for the molecular weight of the PFS macroinitiators and the feed ratio of α-NCA to PFS macroinitiator. A representative diblock copolymerization to form **2** is described here. ε-Benzyloxycarbonyl-L-lysine N-carboxyanhydride (Z-Lys NCA) (0.70 g) was dissolved in dry DMF (4.0 mL). To this solution was added at once a THF solution of PFS macroinitiator (0.12 g in 4.0 mL). The solution was stirred for 5 days at ambient temperature. The amber viscous solution was then precipitated into methanol. The amber precipitate was filtered, thoroughly washed with methanol, and then vacuum dried overnight. Yield: 80% for **1** (0.42 g), 87% for **2** (0.73 g). Each copolymer was purified by repeated precipitations of CH_2Cl_2 solutions (2 mL) of block copolymers into warm cyclohexane (50 mL) until PFS homopolymer was not detectable by a UV-vis detector (450 nm) by GPC. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 7.90$–8.40 (-NHCO-), 7.17–7.37 (Ph-), 5.02 (Ph-CH_2-), 4.24 (Cp), 4.03 (Cp), 3.81–3.98 (α-CH), 2.93–3.25 (α-CH-$(CH_2)_3$-CH_2-), 0.90–2.17 (α-CH-$(CH_2)_3$), 0.48 ppm (CH_3-Si).

Preparation of PFS-*b*-PZLys films: The films were cast from THF solution of diblock copolymer samples (≈20 mg/mL) onto a glass slide. The films were allowed to dry slowly in a half-sealed 200 mL vial loaded with 100 mL of THF. The films were annealed in a vacuum oven first at 50 °C for one hour, then at 160 °C for 3 days before they were rapidly removed from the oven and quenched in liquid nitrogen. The films were scratched off from the glass slide by a razor blade.

Preparation of PFS-*b*-PZLys micelles: Two methods were employed to prepare PFS-*b*-PZLys micelles. Method 1: a sample of block copolymer (1.0 mg) was dissolved directly in dry DMF (1.0 mL) with stirring. Method 2: a sample of block copolymer (1.0 mg) was dissolved first in THF (0.1 mL) with stirring, followed by the dropwise addition of dry DMF (0.9 mL).

Preparation of PFS-*b*-PZLys micelle films: Micelle films were prepared by casting micelle solutions onto glass slides. The films were dried in air at room temperature for 1 day and then dried under vacuum for 1 day.

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