Synthesis and Self-Assembly of the Organic−Organometallic Diblock Copolymer Poly(isoprene-*b*-ferrocenylphenylphosphine): Shell Cross-Linking and Coordination Chemistry of Nanospheres with a Polyferrocene Core

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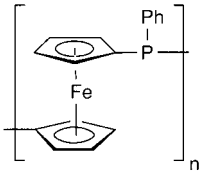
ABSTRACT: Narrow polydispersity samples of the organic-organometallic diblock copolymer, poly(isoprene-*b*-ferrocenylphenylphosphine) (PI-*b*-PFP), have been synthesized by sequential living anionic polymerizations in tetrahydrofuran. These block copolymers form "starlike" spherical micelles in hexane with a dense PFP core surrounded by a swollen corona of PI chains as characterized by transmission electron microscopy (TEM) and dynamic light scattering (DLS) measurements. Although the TEM results indicated a very narrow micelle core size distribution, DLS studies indicated a monomodal, but relatively broad distribution of the overall hydrodynamic size of the micelles in solution. The hydrodynamic size of the micelles and the broad size distribution in solution suggest that DLS measurements might be detecting aggregates of individual micelles. The PI corona chains were found to undergo a cross-linking reaction under UV irradiation in the presence of the radical initiator AIBN. The micelle solution concentration and UV irradiation time affect this cross-linking reaction. Furthermore, the phosphorus sites in the block copolymers could be coordinated to a transition metal, such as Au. The resulting Au-containing block copolymers still form spherical micelles, but with a different size and size distribution.

Introduction

In block-selective solvents, diblock copolymers form micellar aggregates with the insoluble block as the core and the soluble block as the corona.[1,2] Although the most common morphology for block copolymer micelles is spheres, other structures, such as cylinders or vesicles, have also been observed.[3,4] The structure of block copolymer micelles can be made permanent by cross-linking the core[5] or the corona.[6] Core or shell cross-linked spherical micelles are of considerable interest as nanospheres as they possess superior stability.[7]

Living anionic ring-opening polymerization (ROP) of silicon-bridged [1]ferrocenophanes allows access to block copolymers with transition metal atoms in the main chain.[8,9] Such block copolymers self-assemble in the solid state and in block-selective solvents to form redox-active nanoscale organometallic domains or micellar aggregates, respectively.[10,11] For example, the self-assembly of the prototypical polyferrocene block copolymer, poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) (PFS-*b*-PDMS), with a block ratio of 1:6, yielded cylinders of PFS in a PDMS matrix in the solid state and in hexane solution formed wormlike micelles with a cylindrical PFS core surrounded by a swollen corona of PDMS chains.[12] In this case, the unexpected formation of cylindrical structures in solution rather than spherical micelles has been attributed to the crystalline nature of the PFS block.[13] These cylindrical PFS-*b*-PDMS micelles have recently been shown to function as precursors to lithographically defined ceramic nanolines following a plasma etching procedure.[14]

Poly(ferrocenylphenylphosphine) (PFP), **1**, was first prepared by a condensation route[15] and subsequently by thermal ring-opening polymerization.[16] The recent successful synthesis of PFP homopolymer by the living anionic polymerization of phosphorus-bridged [1]ferrocenophane **2** has allowed access to a range of novel block copolymers containing amorphous polyferrocene blocks.[17−19] In a preliminary report,[20] we described the synthesis of poly(isoprene-*b*-ferrocenylphenylphosphine) (PI-*b*-PFP) by anionic ring-opening polymerization of monomer **2** initiated by living polyisoprene prepared in tetrahydrofuran (THF). In hexane, which is a good solvent for the PI block and a precipitant for the amorphous PFP block, this PI-*b*-PFP copolymer would be expected to form micellar aggregates with a PFP core. The micellization behavior is of interest because the phosphine groups should permit the introduction of additional metal atoms into the micelle core. Such self-assembled metal-containing micelles offer intriguing possible applications in catalysis, as redox-active encapsulants, or as precursors to magnetic nanostructures.[14,21] Since the corona region consists of polyisoprene synthesized in THF, its high pendant vinyl content provides the possibility to generate shell cross-linked micelles with advantageous stability for nanostructure applications. In this paper, we report our studies of the micellization of poly(isoprene-*b*-ferrocenylphenylphosphine) and our attempts to cross-link the shell of these micelles. In addition, we describe the coordination of Au moieties to the PFP block of PI-*b*-PFP and our studies of the micelles formed by the resulting block copolymer.



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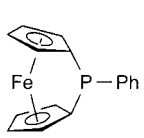

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Experimental Section

Materials and Equipment. Phosphorus-bridged [1]ferrocenophane monomer **2** was synthesized according to the

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procedures reported previously.[22,23] It was purified by repeated crystallization from hexane to ensure purity. Isoprene was purified by distillation from CaH_2 and a second distillation from *n*-butyllithium. Tetrahydrofuran was distilled from Na/benzophenone immediately before the reaction. Chlorocarbonyl gold(I) (Au(CO)Cl) was purchased from Strem Chemicals and used as received. All the other chemicals were obtained from Aldrich and also used as received.

The 200 MHz ^{1}H NMR spectra were recorded on a Varian Gemini 200 spectrometer with deuterated chloroform as the solvent. The 121.5 MHz ^{31}P NMR spectra were recorded on a Varian Gemini 300 spectrometer with deuterated chloroform as the solvent. Molecular weights of the polymer were estimated by size exclusion chromatography (SEC) using a Waters Associates 2690 separations module equipped with a column heater, Ultrastyragel columns with pore sizes of 10^3-10^5 Å, an in-line degasser, and a differential refractometer. A flow rate of 1.0 mL/min was used, and the eluent was THF. Polystyrene standards purchased from American Polymer Standards were used for calibration purposes.

Transmission electron microscopy (TEM) measurements were carried out on a Hitachi model 600 electron microscope. The samples were prepared as follows. Thin carbon films (ca. 5 Å) were grown on mica as a support. Then 25 μL of a block copolymer micelle solution was sprayed onto the carbon film. Each carbon film was floated off the mica support in water and deposited onto a 300 mesh Gilder copper grid. The sample was air-dried before introduction into the electron microscope. Staining of the sample was unnecessary as the presence of iron in the PFP block led to sufficient contrast for imaging. Samples were also prepared using the negative staining method.[24] Dodecatungstophosphoric acid ($H_3PO_4 \cdot 12WO_3 \cdot xH_2O$) was dissolved in distilled water to make a 0.3 wt % solution, and then it was neutralized by potassium hydroxide to pH = 6.5. A drop of this staining solution (~10 μL) was added onto the same copper grid imaged without any staining. After 30 s, the excess staining solution was removed from the copper grid by a piece of filter paper. The copper grid was then air-dried before the TEM measurements. All TEM image analysis was performed using "image tool" computer software, which was developed at The University of Texas Health Science Center in San Antonio.

Dynamic light scattering (DLS) experiments were carried out on a variable angle laser light scattering photometer from Brookhaven Instruments Corporation. A 5 mW vertically polarized He−Ne laser from Spectra Physics was the light source. The micelle solution was filtered through disposable 0.5 μm PTFE filters from Millipore into glass scattering cells. The cells were placed into the BI-200SM goniometer and sat in a vat of thermostated toluene which matched the index of refraction of the glass cells. The angular range of the goniometer was 7−162°. The scattered light was detected by a photomultiplier interfaced to the BI-2030AT digital correlator with 136 channels and measured the correlation function in real time. Dynamic light scattering data were analyzed following the method of cumulants.[25] The logarithm of the normalized intensity autocorrelation function, $g^{(1)}(\tau)$, can be fitted into a power series in terms of the delay time τ,

$$\ln g^{(1)}(\tau) = -\Gamma_1\tau + (\Gamma_2/2!)\tau^2 - (\Gamma_3/3!)\tau^3 + ... \qquad (1)$$

where Γ_1 is the first cumulant, Γ_2 the second cumulant, and so forth. Once Γ_1 is determined, the concentration and angular dependence can be expressed as

$$\Gamma_1/q^2 = D_z(1 + k_D c + ...)(1 + CR_g{}^2q^2 + ...) \qquad (2)$$

where D_z is the *z*-average diffusion coefficient, C is a parameter that is characteristic of the molecular architecture, k_D is the effective interaction parameter, and q is the scattering vector, with its magnitude given by

$$q = 4\pi n_0 \sin(\theta/2)/\lambda_0 \qquad (3)$$

where θ is the scattering angle, n_0 is the refractive index of solvent, and λ_0 is the wavelength of the laser beam. From the diffusion coefficient, the *z*-average hydrodynamic radius, R_h, can be calculated from the Stokes−Einstein relation

$$R_h = kT/(6\pi\eta D_z) \qquad (4)$$

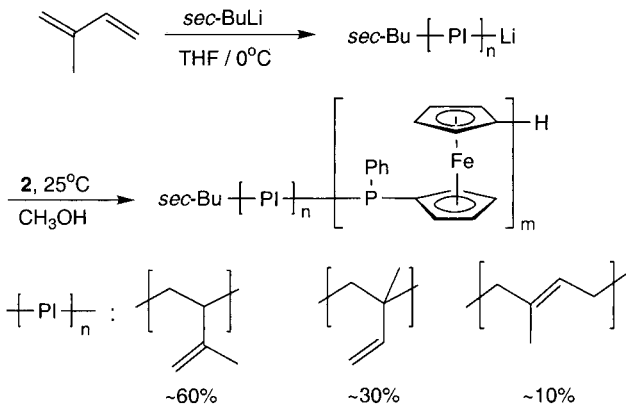
where η is the solvent viscosity. For the determination of the *z*-average diffusion coefficient for each sample, five different scattering angles were used. Dynamic light scattering data were also analyzed using the CONTIN method[26] to determine the distribution of hydrodynamic size.

Synthesis of Block Copolymers. The block copolymers used in the current study, poly(isoprene-*b*-ferrocenylphenylphosphine), were synthesized by living anionic polymerization through sequential monomer addition. The polymerization was carried out under a nitrogen atmosphere in a flamed and vacuum-dried glass reactor equipped with a three-way stopcock and a rubber septum. Monomer, initiator, and solvent were transferred into the polymerization reactor via a stainless steel cannula or a glass syringe. A representative experimental procedure is shown as follows. Isoprene (0.5 g) was polymerized first in THF at 0 °C using *sec*-butyllithium (0.05 mmol) as the initiator. Upon the completion of the synthesis of polyisoprene block (2 h), an aliquot of the polymerization solution was drawn from the reaction flask for the analysis of that block. Then phosphorus-bridged [1]ferrocenophane **2** (0.35 g) was added as a solution in THF. The reaction mixture was warmed to room temperature, and the polymerization was allowed to continue for another 30 min before it was quenched by adding a few drops of degassed methanol. The crude product was obtained by precipitation into methanol, filtered, and dried under vacuum. Then, it was extracted with hexane to remove polyisoprene homopolymers. Finally, the yellow gumlike pure block copolymer was recovered and dried under vacuum for 24 h. Yield: 0.5 g, 59%. This block copolymer was designated as PI_{140}-*b*-PFP_{82}. The subscripts indicate the degree of polymerization for that block, in which the PI block was calculated from the result of size exclusion chromatography and PFP block was calculated on the basis of the degree of polymerization of PI block and the ^{1}H NMR integration ratio of PI to PFP. However, the expected composition for this block copolymer, based on the reaction stoichiometry, was PI_{147}-*b*-PFP_{24}. The significant deviation from the theoretical value for PFP block length is mainly due to the termination of a fraction of living polyisoprene chains in the second stage of the anionic polymerization. Two other block copolymers were synthesized in the same way. For PI_{113}-*b*-PFP_{18}, 1.1 g of isoprene, 0.45 g of monomer **2**, and 0.12 mmol of *sec*-butyllithium were used. Yield: 1.1 g, 71%. For PI_{226}-*b*-PFP_9, 1.8 g of isoprene, 0.3 g of monomer **2**, and 0.18 mmol of *sec*-butyllithium were used. Yield: 1.6 g, 76%. The following data were found for all three samples. ^{1}H NMR ($CDCl_3$): δ = 7.2−7.6 (br, Ph), 5.5−5.9 (br, vinyl), 4.5−5.2 (br, vinyl), 3.7−4.4 (br, Cp), 0.9−2.2 (br, alkyl) ppm. ^{31}P NMR ($CDCl_3$): δ = −28.9 (s, −fc*P*Phfc−) ppm.

Micelle Formation. All the micelle solutions were prepared as follows. The block copolymer (5 mg) was dissolved in THF (2 mL) first. Hexane (18 mL in total) was added dropwise into this solution with stirring to reach a final volume ratio of hexane:THF = 9:1 and a polymer concentration of 0.25 mg/mL. The micelle solution was stirred overnight and then dialyzed against pure hexane over 2 days to remove THF. The micelle solution was finally filtered through a 0.5 μm PTFE filter before the TEM and DLS experiments.

Metal Coordination. The reaction of poly(isoprene-*b*-ferrocenylphenylphosphine) with Au(CO)Cl was carried out at room temperature in a M-Braun glovebox under an atmosphere of purified N_2. The block copolymer PI_{113}-*b*-PFP_{18} (20 mg, 0.034 mmol of P sites), dried under vacuum overnight before the reaction, was dissolved in freshly distilled and deoxygenated THF. A slight excess of white crystalline Au(CO)Cl (~10 mg, 0.038 mmol) relative to phosphorus sites was added to this block copolymer solution with stirring. After 30 min, the reaction mixture was taken out of the glovebox, and

Scheme 1. Synthesis of Poly(isoprene-*b*-ferrocenylphenylphosphine)



the THF was removed under vacuum. The crude product was redissolved in THF in air, and the resulting solution was found to be turbid. Following centrifugation, the clear supernatant was separated from some solids and dried under vacuum prior to any characterization of the product. Yield: 20 mg, 72%. ^{31}P NMR ($CDCl_3$): δ = 23.4 (s, −fc*P*(AuCl)Phfc−) ppm.

Shell Cross-Linking of Micelles. Cross-linking of the shell of the micelles was carried out in a 21 W Rayonet photochemical reactor with a UV wavelength of 300 nm. 2,2′-Azobis(isobutyronitrile) (AIBN) was used as a radical initiator. Each time, 2 mL of micelle solution (either 0.25 or 0.02 mg/mL) was used. After the addition of AIBN (∼1 mg), it was left for 12 h to allow complete mixing before the UV irradiation.

Results and Discussion

Block Copolymer Synthesis. Poly(isoprene-*b*-ferrocenylphenylphosphine) was synthesized by the addition of phosphorus-bridged [1]ferrocenophane **2** to a solution of living polyisoprene in THF (Scheme 1). The reaction was terminated by the addition of degassed methanol. Because of limitations in our ability to purify **2**, some living polyisoprene chains were terminated upon the addition of the ferrocenophane monomer. These polyisoprene homopolymers present in the crude product were then removed by extraction with hexane. This resulted in a relatively low yield of the final block copolymer and a deviation of the molecular weight from that expected on the basis of the reaction stoichiometry. The pure block copolymers were characterized by size exclusion chromatography and ^{1}H NMR.

It has been previously noted that PFP homopolymers do not elute from a Styragel size exclusion chromatography column when using THF as the solvent.[15,16] However, when the polymer is derivatized with S_8 to yield the corresponding poly(ferrocenylphenylphosphine sulfide), analysis by SEC using THF as the eluent becomes possible. To facilitate analysis of our block copolymers, the samples of PI-*b*-PFP were sulfurized in this way prior to the SEC measurements.[16,18] The SEC results for the PI block and for the sulfurized block copolymers are listed in Table 1, along with the ^{1}H NMR analysis results. These data show that both the polyisoprene block and the PI-*b*-PFP block copolymer samples have narrow molecular weight distributions. It is also apparent that the molar block ratio of PI to PFP inferred from SEC measurements is consistently higher by roughly a factor of 2 than that determined from ^{1}H NMR integration. This difference is a consequence of the fact that the polystyrene standards used for SEC calibration have a different hydrodynamic volume than PI or sulfurized PFP of a comparable molecular weight. As a consequence, all the molecular weights are apparent values. Previous work has shown that SEC analysis generally underestimates the molecular weight of a polyferrocene homopolymer by a factor of 2 when compared with the static light scattering results.[27] That observation is consistent with the results obtained here. Thus, the degree of polymerization of PFP block was calculated on the basis of the degree of polymerization of PI block from the SEC result and the ^{1}H NMR integration ratio of PI to PFP. Because all the PI blocks were synthesized under the same reaction conditions and have similar molecular weights, this calculation should give us relatively consistent results for all three block copolymers. The ^{1}H NMR results indicated that the microstructure of the PI block consists of roughly 60% 3,4-, 30% 1,2-, and 10% trans 1,4-units, expected from the solvent used for the polymerization.[28] In the following text, different block copolymers will be denoted by PI_n-*b*-PFP_m, where *n* and *m* represent the number-average degree of polymerization of the PI block and the PFP block determined from SEC measurements and ^{1}H NMR integration, respectively.

Table 1. Characterization Data for PI-*b*-PFP

	PI block[a]		PI_n-*b*-PFP_m[a]					
sample	M_n (g/mol)	PDI	M_n (g/mol)	PDI	n[b]	m[c]	n:m[d]	n:m[e]
PI_{140}-*b*-PFP_{82}	9500	1.11	22 300	1.16	140	82	1.7:1	3.5:1
PI_{113}-*b*-PFP_{18}	7700	1.04	10 600	1.05	113	18	6.3:1	15:1
PI_{226}-*b*-PFP_9	15400	1.07	16 700	1.08	226	9	25:1	57:1

[a] Apparent values based on SEC measurements using polystyrene standards. Values for the block copolymer are after sulfurization of the PFP block. [b] Calculated from SEC results. [c] Calculated from n and ^{1}H NMR integration ratios. [d] Calculated from ^{1}H NMR integration. [e] Calculated from M_n of SEC results.

PI-*b*-PFP Micelles. The block copolymer micelle solutions were prepared by adding hexane slowly (roughly one drop per second) to a solution of the block copolymer in THF with stirring. Hexane is a solvent for the PI block and a precipitant for the PFP block. Under these conditions, the resulting micelles are expected to consist of a collapsed or mildly solvent-swollen PFP core surrounded by a corona of PI blocks. The onset of micellization, as indicated by the slight turbidity of the solution and strong scattering intensity from DLS measurements, can be observed at a THF:hexane volume ratio of about 1:1, for both PI_{140}-*b*-PFP_{82} and PI_{113}-*b*-PFP_{18}. No visible turbidity was observed for PI_{226}-*b*-PFP_9, presumably due to the relatively short PFP block length. Hexane was added continuously beyond this point to reach a predominant hexane volume fraction (90%). The THF was then removed by dialysis against hexane.

Figure 1a shows a representative transmission electron micrograph of the micelles prepared from PI_{140}-*b*-PFP_{82}. Because the micelles have an iron-rich PFP core, no staining was necessary to visualize their morphology. The TEM image shows that micelles with a spherical shape are present. Because of the low contrast between the supporting carbon film and the PI corona, the spheres on the TEM image were expected to only represent the PFP core region. To verify this, the TEM sample was stained by a negative staining method using dodecatungstophosphoric acid. A representative transmission electron micrograph of the PI_{140}-*b*-PFP_{82} micelles after negative staining is shown in Figure 1b. Since the block copolymer is very hydrophobic, the reagent for negative staining will only stain the carbon

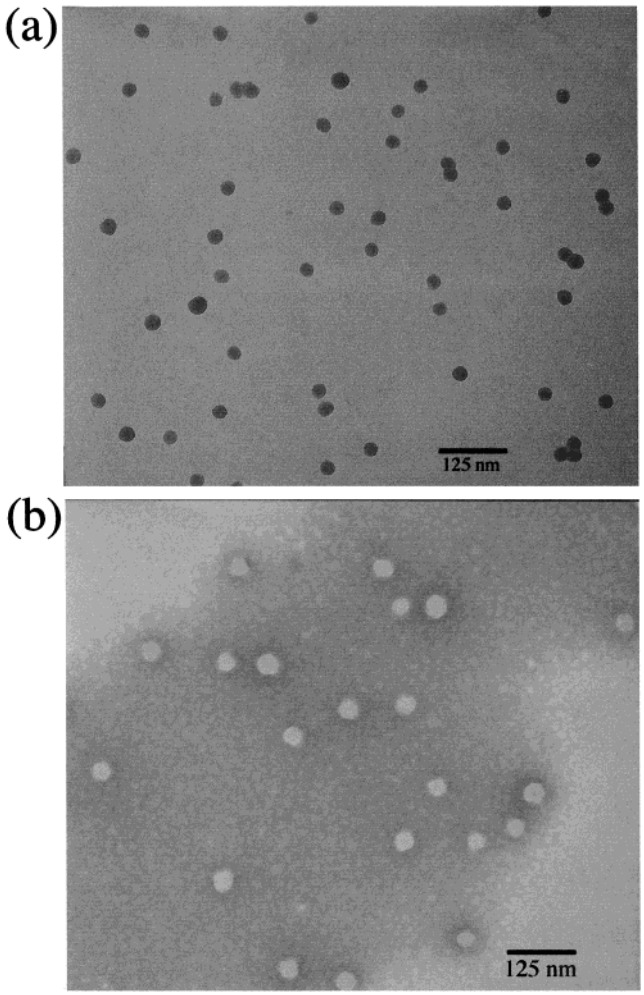


Figure 1. Representative TEM image of PI_{140}-*b*-PFP_{82} micelles (a) without staining and (b) with negative staining.

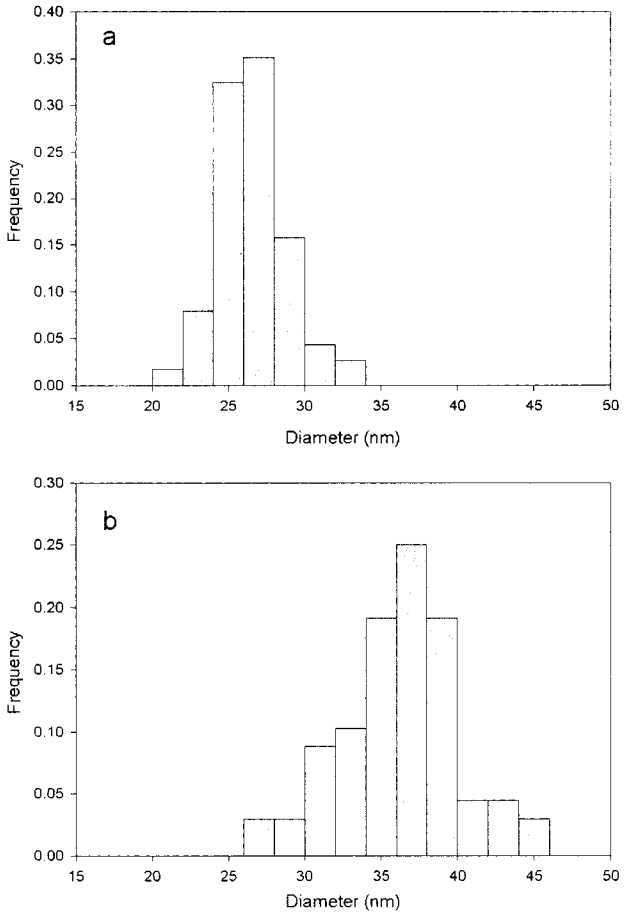


Figure 2. Histograms of size distribution determined from TEM image analysis for PI_{140}-*b*-PFP_{82} micelles (a) without any staining and (b) with negative staining.

film surface where no micelles are present. Because of the high electron density of the tungsten atoms in the staining reagent, the area covered by the thin layer of staining reagent on the carbon surface will appear darker. In this case, the regions with circular bright spots in Figure 1b represent the surface area covered by the block copolymer micelles. The spheres in Figure 1b have a larger average diameter than those in Figure 1a.

Computerized image analysis provides further details about the average size and size distribution of the micelles. Figure 2a,b shows the histograms of the size distribution obtained from the image analysis. Roughly 100 particles were analyzed in each case on the basis of several different TEM images taken at different areas on the same copper grid. For the spheres imaged without any staining, the diameters range mainly from 20 to 34 nm with an average of 27 nm and a standard deviation of 3 nm. The spheres imaged after negative staining have diameters ranging mainly from 26 to 46 nm with an average of 36 nm and a standard deviation of 4 nm. The distribution is monomodal in both cases. We see that the average diameter increases from 27 ± 3 nm for a nonstained sample to 36 ± 4 nm for a negatively stained sample. If we assume that the dark circles in Figure 1a represent the PFP core region, on the basis of its average diameter (27 nm), we can calculate that a whole collapsed micelle on a carbon film will have a diameter of 32 nm. This calculation was carried out by taking the PFP density as 1.4 g/cm^3, the PI density as 0.91 g/cm^3, and the molar block ratio of the block copolymer from ^{1}H NMR (PI:PFP = 1.7:1). Although this calculated value is smaller than the average of 36 nm from TEM of negative stained sample, it can still be considered reasonable, since the PI corona could be flattened on the carbon surface. We expect the PFP core to maintain its spherical structure due to its much higher glass transition temperature (126 °C).[18] Therefore, the actual diameter of an individual collapsed micelle on the carbon would be larger than the value calculated on the basis of a collapsed sphere. Because we see a significant increase in diameter after negative staining, this experiment establishes that the spheres visualized without staining only represent the PFP core. In the following discussion, the diameter determined from TEM without staining will be considered as the diameter of the PFP core.

The polymers PI_{113}-*b*-PFP_{18} and PI_{226}-*b*-PFP_9 also yielded spherical micelles in hexane, but with a smaller PFP core. For the micelles formed by both polymers, image analysis showed monomodal core size distributions. The average diameters (D_{core}) and their standard deviations (SD_{core}) for both samples are listed in Table 2, along with those obtained for PI_{140}-*b*-PFP_{82} for comparison. It is clear that the micelle core diameters decrease as the poly(ferrocenylphenylphosphine) block length decreases.

The core radii polydispersity index (RPI)[29] can be calculated from eq 5, assuming a Gaussian distribution of the particle diameters

Table 2. Summary of Characterization Data for PI-*b*-PFP Micelles from TEM and DLS

sample	D_{core}[a] (nm)	SD_{core}[b] (nm)	RPI[c]	R_h[d] (nm)	L[e] (nm)	Γ_2/Γ_1^2 [f]
PI_{140}-*b*-PFP_{82}	27	3	1.01	36	23	0.25
PI_{113}-*b*-PFP_{18}	11	1	1.01	59	54	0.16
PI_{226}-*b*-PFP_9	8	1	1.02	50	46	0.23

[a] Average diameter of the PFP core from TEM image analysis. [b] Standard deviation of the core diameter from image analysis. [c] $RPI = (SD_{core}/D_{core})^2 + 1$. [d] Hydrodynamic radius from DLS using cumulant analysis. [e] Corona brush length $L = R_h - (D_{core}/2)$. [f] See eq 1 for definitions.

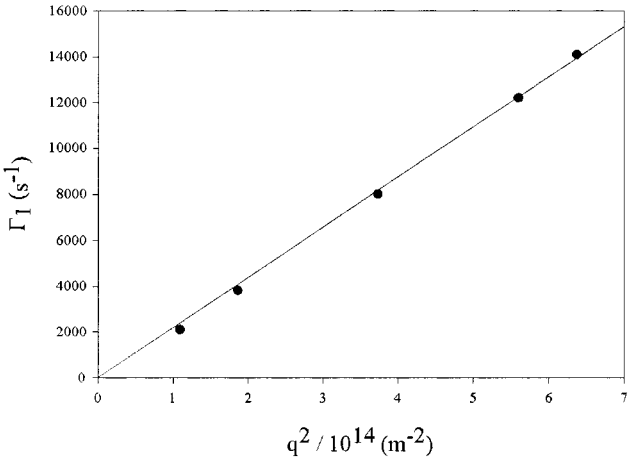


Figure 3. Plot of Γ_1 vs q^2 for PI_{140}-*b*-PFP_{82} micelles in hexane solution with a concentration of 0.25 mg/mL. Γ_1 and q are defined in eqs 1 and 3.

$$RPI = (SD_{core}/D_{core})^2 + 1 \quad (5)$$

From the results listed in Table 2, it is clear that the core diameters of the micelles have a very narrow size distribution ($RPI \ll 1.1$).

Dynamic light scattering measurements gave further information about the overall micelle structure in hexane solution. The hydrodynamic diameters of the micelles were determined at five different scattering angles and analyzed using the cumulant method by extrapolation to 0° scattering angle. A typical Γ_1 vs q^2 plot for the PI_{140}-*b*-PFP_{82} micelle solution of 0.25 mg/mL is shown in Figure 3. It gives a linear correlation with $r^2 = 0.998$, indicating that only translational diffusion occurs. From the plot of Γ_1/q^2 vs q^2, the intercept will give an apparent z-average diffusion coefficient D_z at this concentration. Since D_z is normally concentration dependent, a plot of D_z as a function of concentration will yield the magnitude of k_D, the diffusion second virial coefficient. The measurements of D_z for different concentrations of PI_{140}-*b*-PFP_{82} micelles show that the magnitude of k_D is negligible for polymer concentrations between 0.05 and 0.25 mg/mL. Thus, the concentration dependence of D_z can be neglected for this concentration range. Very small values of k_D were also found for PI_{113}-*b*-PFP_{18} and PI_{226}-*b*-PFP_9. Thus, D_z for all three block copolymers micelles were, for simplicity, determined at the same concentration, 0.25 mg/mL. Finally, the hydrodynamic radii R_h was calculated from the Stokes−Einstein relation. The R_h values for these block copolymer micelles are also summarized in Table 2.

The ratio Γ_2/Γ_1^2 is a useful measure of size polydispersity for the micelles in solution. For "starlike" spherical micelles of narrow size distribution, Γ_2/Γ_1^2 has typical values of 0.04−0.07.[30] The values we obtained

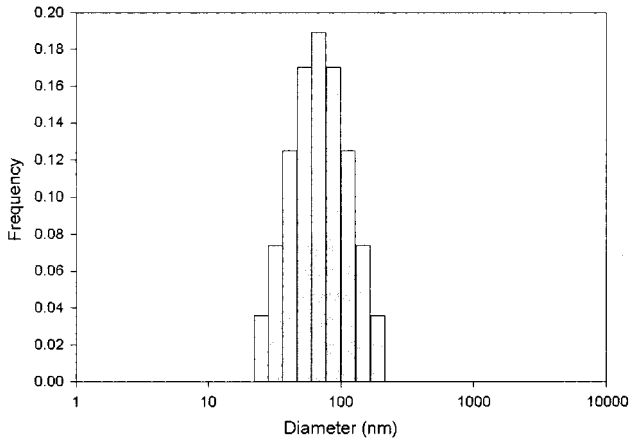


Figure 4. Histogram of micelle hydrodynamic diameter in hexane for PI_{140}-*b*-PFP_{82} from CONTIN analysis of intensity autocorrelation function, determined at 90° scattering angle. The *x*-axis is plotted using a log scale.

for all the micelle solutions are much higher, indicating a relatively broad overall micelle size distribution in hexane solution, even though we deduced from TEM measurements that the micelle core had a very narrow size distribution. A CONTIN analysis of the intensity autocorrelation function at 90° scattering angle is shown in Figure 4 for PI_{140}-*b*-PFP_{82} micelles. The distribution is monomodal but relatively broad. This result is consistent with the relatively large Γ_2/Γ_1^2 value we obtained for these micelles. Monomodal size distributions were also observed for PI_{113}-*b*-PFP_{18} and PI_{226}-*b*-PFP_9 micelles in hexane by dynamic light scattering.

We observed that the PI-*b*-PFP block copolymer tends to oxidize over time in air when it is dissolved in a good solvent, such as THF or chloroform. In contrast, in the solid state, the material is very stable in air. The micelle solutions in 1/1 (v/v) THF/hexane were found to undergo a continuous growth in size. These solutions eventually turned a brownish color, and the polymers precipitated out, while the micelle solutions in hexane or hexane/THF (90/10, v/v) are very stable over long periods of time. From this result, we believe that the PFP micelle core is densely packed in solutions with a high volume fraction of hexane. Dynamic light scattering experiments on PI_{140}-*b*-PFP_{82} micelles in hexane/THF (90/10, v/v) showed that the mean hydrodynamic radius did not change over a period of 3 weeks for a solution exposed to air. Furthermore, the color of the micelle solution does not change over time, whereas the oxidized polymer exhibits a typical brownish color. This result was further confirmed by UV−vis spectra of the micelle solution, in which no change was found over time. These results indicate that the micelles are very stable with a PFP core in a dense, collapsed state. The same stability was also observed for micelle solutions of PI_{113}-*b*-PFP_{18} and PI_{226}-*b*-PFP_9.

If we assume that the actual micelle core diameter in hexane equals that determined from the TEM images, we are able to calculate the PI corona brush length L on the basis of the values of R_h and D_{core} (Table 2). However, the corona length obtained in this way is much longer than one would expect from a hexane-swollen PI chain of the same molecular weight tethered to a spherical surface. In addition, it is curious that the micelles show a broad size distribution in hexane, from both cumulant and CONTIN analysis of the DLS data, while the TEM results clearly show that the micelle core

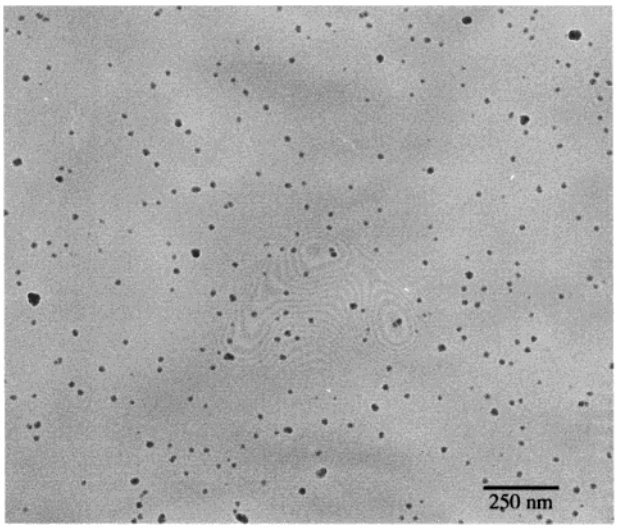


Figure 5. Representative TEM image of PI_{113}-*b*-PFP_{18} micelles with coordinated Au.

size has a narrow distribution. All of these results suggest that the DLS results are dominated by the presence of aggregated micelles in solution.[31] Even if the number fraction of these aggregates were relatively small, their large size might make a dominant contribution to the DLS signal.

Metal Coordination to the PFP Block of PI-*b*-PFP. To investigate the metal coordination behavior of poly(isoprene-*b*-ferrocenylphenylphosphine), PI_{113}-*b*-PFP_{18} was reacted with Au(CO)Cl. The ^{31}P NMR for the block copolymer before and after the reaction showed a shift of more than 50 ppm from −28.9 ppm to a single peak at 23.4 ppm, a chemical shift typical of metal-coordinated phosphorus atoms. From the single peak in the ^{31}P NMR spectrum of the product, we infer that a gold atom became coordinated to each phosphorus site in the polymer backbone. The resulting polymer is very soluble in solvents such as THF and chloroform and forms clear solutions, indicating that potential cross-linking of the polymers due to the coordination of Au to more than one phosphorus site is not significant. Another feature of the block copolymer formed after reaction with the Au(CO)Cl is that the material eluted from the Styragel SEC column using THF as the solvent, unlike the block copolymer precursor. The SEC result showed that the block copolymer with coordinated Au has a M_n of 9000 g/mol and a PDI of 1.09. The molecular weight value is close to that of the sulfurized analogue, but the PDI is slightly broader. This result provides further evidence that the Au atoms are coordinated to the phosphorus sites in the block copolymer. The block copolymer with coordinated Au is very stable in solution over time when exposed to air, which is also a strong indication that metal coordination reduces the reactivity of the phosphorus sites.

Micelle solutions of this block copolymer with coordinated Au atoms were prepared in the same way as for the PI-*b*-PFP polymers. A representative TEM image of the resulting micelles is shown in Figure 5. Spherical micelles were observed, and image analysis was used to determine the average core size and size distribution. From this analysis, a monomodal size distribution with an average diameter of 20 nm and a standard deviation of 4 nm were obtained. The RPI value in this case can be calculated as 1.04. The micelles of the original block copolymer have an average diameter of 11 nm and RPI of 1.01. It is clear that the core size increased significantly, and its size distribution broadened. Dynamic light scattering measurement indicated that these micelles in hexane solution have a mean hydrodynamic radius of 71 nm and a Γ_2/Γ_1^2 value of 0.31. Both values are larger than those of the original PI-*b*-PFP block copolymer (R_h = 59 nm, Γ_2/Γ_1^2 = 0.16). This result indicates that the coordinated Au atom in the PFP repeat unit does not affect the global micelle morphology, but it does affect the micelle size and size distribution.

Shell Cross-Linking of Micelles. The last topic we describe involves our attempts to cross-link the shell of the PI-*b*-PFP micelles in hexane. Because the PI block of the copolymer was synthesized in THF, it contains a high pendant vinyl content. We conceived that in the presence of a radical initiator, such as AIBN, the shell of PI-*b*-PFP micelle might be cross-linked under UV irradiation.[32] To explore this reaction, a PI_{140}-*b*-PFP_{82} micelle solution in hexane (0.25 mg/mL) was used. For comparison, three identical micelle solutions were subject to the following tests. The first solution was left untreated. The second micelle solution without the addition of AIBN was irradiated for 30 min with UV light of wavelength 300 nm. The third micelle solution was subject to UV irradiation for 30 min in the presence of AIBN. The solvent, hexane, for the first micelle solution was evaporated, and then THF was added. The DLS measurement of the resulting solution showed negligible scattering intensity, indicating the absence of aggregates. We inferred that the block copolymer molecules redissolved in THF. The hexane of the second micelle solution was evaporated after the UV irradiation and THF was added. The DLS measurement also showed no evidence for the presence of aggregates. Here, too, there was no indication of covalent bonds formed between polymer molecules. When the hexane of the third micelle solution was removed after the UV irradiation, and THF was added, the resulting solution showed a slight turbidity, visible to the eye. The DLS experiment of the filtered THF solution indicated the presence of objects with a hydrodynamic diameter of 49 nm, a strong indication that a reaction had occurred to cross-link the PI corona chains in the micelles. However, when we examined the nature of the aggregates by TEM, we found that the unfiltered samples showed large aggregates, while in the images obtained from the filtered solution, few micelles were observed. This suggests that there might be intermicellar cross-linking reactions, which occur in addition to the shell cross-linking.

To minimize this large amount of intermicellar cross-linking, the reaction was repeated with a diluted micelle solution of 0.02 mg/mL. Dynamic light scattering measurements indicated that dilution of the micelle solution with hexane did not change the micelle size. The cross-linking reaction of the diluted micelle solution was monitored as a function of irradiation time (between 5 and 30 min). In each instance, after irradiation, the hexane was evaporated, and the sample was dissolved in THF. Then an aliquot of the THF solution was used for the preparation of each TEM sample as described earlier. Figure 6a−c shows three representative TEM images for the cross-linked micelles, obtained after transfer to THF without filtering the micelle solution. The micelle solution irradiated for 30 min formed some

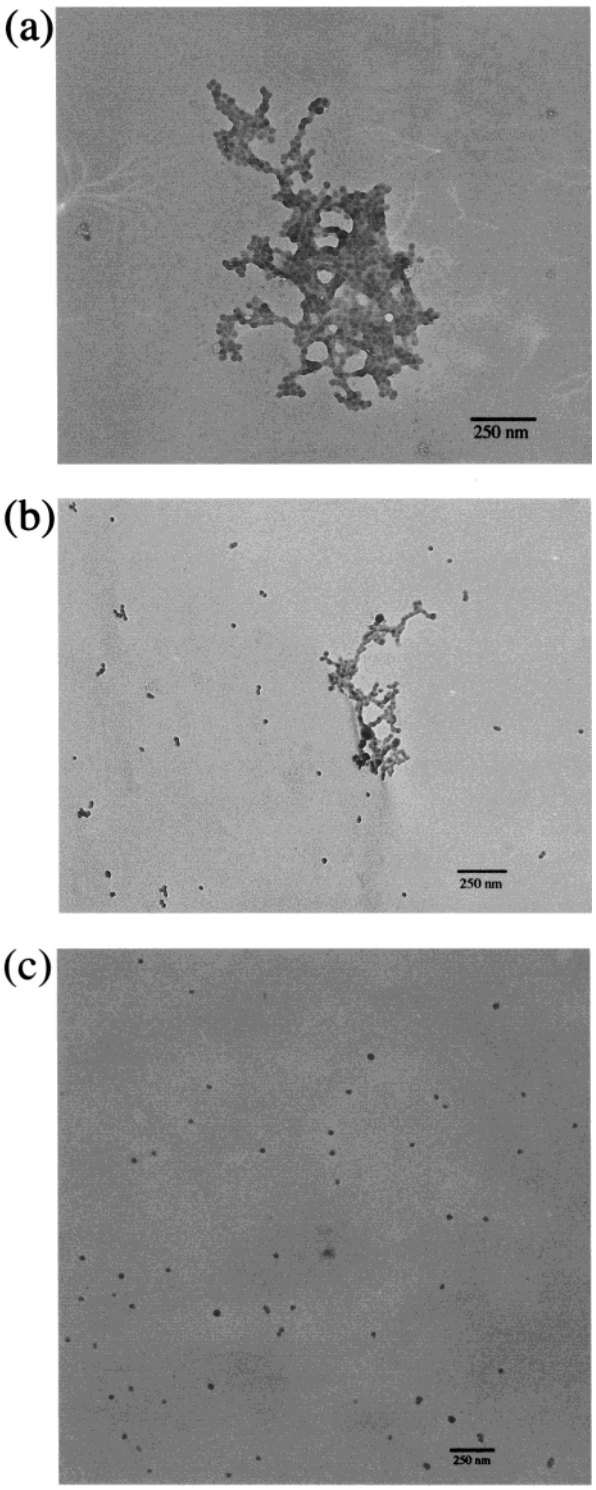


Figure 6. Representative TEM images of cross-linked PI_{140}-*b*-PFP_{82} micelles in THF with decreasing UV irradiation time: (a) 30, (b) 15, and (c) 5 min.

very large aggregates as shown in Figure 6a due to extensive intermicellar cross-linking. The micelle solution irradiated for 15 min also formed mainly aggregates, as indicated in Figure 6b. Finally, the micelle solution irradiated for only 5 min formed mostly individual cross-linked micelles, as shown in Figure 6c. It is clear that the possibility of intermicellar cross-linking, which results in the formation of large aggregates of micelles, increases with the irradiation time. With short irradiation times, a high fraction of individual cross-linked micelles can be obtained.

Summary

Micellization of poly(isoprene-*b*-ferrocenylphenylphosphine) with different block ratios in hexane was studied by transmission electron microscopy and dynamic light scattering measurements. The aggregates formed have the structure of "starlike" spherical micelles with a dense PFP core surrounded by a corona of PI chains, as expected for polyferrocene block copolymers with a short, amorphous insoluble organometallic block.[1,13] The micelle core has a monomodal size distribution, and the core radius increases as the length of the PFP blocks increases. Although the TEM results indicate a very narrow core size distribution, the DLS studies indicate a larger size and a relatively broad size distribution of the micelles in solution. The combination of TEM and DLS measurements suggests that PI-*b*-PFP micelles probably aggregate in hexane.

These micelles were found to undergo a cross-linking reaction of the PI component under UV irradiation in the presence of the radical initiator AIBN. By varying the micelle solution concentration and irradiation time, intermicellar cross-linking could be minimized. The phosphorus sites in the block copolymer backbone could be coordinated to a transition metal, such as Au. The resulting gold-modified block copolymers still formed spherical micelles, but with a larger size and a broader size distribution. Experiments aimed at improved control of the cross-linking reaction and at incorporating other transition metals into the micelle core are currently in progress, and we are also exploring applications of the micellar materials.[10,11,14]

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