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New Amphiphilic Poly[bis(2,2,2-trifluoroethoxy)phosphazene]/Poly(propylene glycol) Triblock Copolymers: Synthesis and Micellar Characteristics

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ABSTRACT: Amphiphilic triblock copolymers were synthesized with two hydrophobic poly[bis(2,2,2-trifluoroethoxy)phosphazene] blocks linked to a central poly(propylene glycol) block. These were synthesized via the cationic polymerization of chlorophosphoranimines and coupling of these blocks to a diamine functionalized poly(propylene glycol) followed by macromolecular substitution. The micellar characteristics of these amphiphilic triblock copolymers were examined using fluorescence techniques, dynamic light scattering, and transmission electron microscopy. The critical micelle concentrations (cmcs) of PN−PPG−PN polymeric micelles determined by a fluorescence technique were in the range 9.5−12.4 mg/L. The mean diameters of the micelles of the PN−PPG−PN polymeric micelles, measured by dynamic light scattering, were between 197 and 364 nm.

Introduction

The amphiphilic character of a block copolymer can lead to self-assembly behavior similar to that of low molecular weight ionic surfactants, and this opens numerous avenues for the generation of new properties and uses.[1] Typical micelles have a core comprised of a hydrophobic polymer block and a corona of a hydrophilic polymer block. The simplest material to form this shape is a diblock copolymer with one hydrophobic and one hydrophilic component. More complex and less common micelles utilize triblock copolymers with a single hydrophobic block and two flanking hydrophilic blocks, or vice versa. The micellar characteristics of amphiphilic triblock copolymers depend on the nature of each hydrophilic and hydrophobic block. In principle, the surface properties of self-organized micelles should be highly dependent on the structure of the hydrophilic block. For example, a poly(propylene glycol) (PPG) block would provide more hydrophobicity for micellar aggregates than a poly(ethylene glycol) (PEG) block. On the other hand, the micellar core characteristics would be determined by the structure of the hydrophobic blocks.[2−4]

Polyphosphazenes possess an inorganic backbone with two organic groups connected to each phosphorus. These macromolecules generate many different chemical and physical properties depending on the structure of the side groups. In particular, polyphosphazenes that bear bioinert or biodegradable side groups have attracted much attention as potential biomaterials.[5] An ambient-temperature condensation route for the synthesis of polyphosphazenes via the controlled cationic polymerization of phosphoranimines has been reported.[6−8] This PCl_5-induced polymerization allows the production of a variety of polymeric phosphazene architectures with controlled molecular weights and architectures, including block copolymers.[8] The formation of block copolymers allows fine-tuning of the physical properties through the side-group systems.

This present study was focused on a triblock copolymer system with a central organic amphiphilic block of poly(propylene glycol) flanked by two outer organic/inorganic blocks of hydrophobic polyphosphazenes. The objective was to examine the feasibility that such a polymer might form micelles. PPG was chosen over PEO because of its more amphiphilic characteristics.[9] This work demonstrates that micelles can indeed be formed from such a system and that the micelles vary in size according to the length of the hydrophobic block. These materials are excellent candidates for nanoscale carrier applications such as for hydrophobic dye or pigment incorporation into water-based inks or surface coatings.

Experimental Section

Materials. Poly(propylene glycol)bis(2-aminopropyl ether) ($CH_3CH(NH_2)CH_2-PPG-NH_2$, $M_n = 4000$) (Aldrich) was used after drying under vacuum. Lithium bis(trimethylsilyl)amide (Aldrich) was used without further purification. Phosphorus pentachloride (Aldrich) was purified by sublimation under vacuum before use. 2,2,2-Trifluoroethanol was dried over calcium hydride and was distilled before use. Tetrahydrofuran and *n*-hexane (Aldrich) were distilled into the reaction flask from sodium benzophenone ketyl under an atmosphere of dry argon. Dichloromethane (Aldrich) was dried by passage through an alumina column. All glassware was flame-dried under vacuum before use. The reactions were performed under an atmosphere of dry argon or nitrogen.

Equipment. ^1H and ^{31}P spectra were recorded on a Bruker WM-360 NMR spectrometer operated at 360 and 90.27 MHz, respectively. ^1H NMR spectra were referenced to solvent signals while ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as an external reference, with positive shift values downfield from the reference. Molecular weights were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector, American Polymer Standards AM gel 10 mm and AM gel 10 mm 104 Å column, and calibrated vs polystyrene standards (Polysciences). The samples were eluted at 40 °C with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate (Aldrich) in THF (OmniSolv).

Synthesis of Bromophosphoranimine 1. A hexane (700 mL) solution of $LiN(SiMe_3)_2$ (36.55 g, 0.22 mol) was cooled to 0 °C, and PCl_3 (30.00 g, 0.22 mol) was added slowly over 30 min. The reaction mixture was stirred at 0 °C for 1 h and allowed to warm to room temperature followed by stirring for 2 h. Then, a stock solution prepared from $NaOCH_2CF_3$ (0.44 mol; 43.62 g of $HOCH_2CF_3$ and 10.02 g of Na metal) was transferred to the reaction mixture

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at room temperature. Following addition of the salt, the reaction mixture was stirred at room temperature for 12 h. After completion of the reaction, the mixture was centrifuged for 30 min to remove sodium chloride. The solution was transferred to a round-bottom flask, and the solvent was removed at reduced pressure by rotary evaporation. The remaining solution was vacuum distilled to produce a colorless liquid. The product was dissolved in benzene (200 mL) and cooled to 10 °C. To this solution was added bromine (29.61 g) in benzene (50 mL), and the mixture was stirred at 10 °C for 2 h and allowed to warm to room temperature. The solvent was removed at reduced pressure, and the crude product was vacuum distilled at least twice to remove unreacted bromine and produce a colorless liquid (34.86 g, yield 40%). ^{1}H NMR ($CDCl_3$): δ 0 (s, 9H), 4.23 (q, 4H). ^{31}P NMR ($CDCl_3$): δ −33.93.

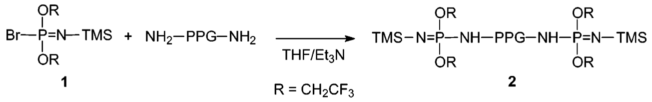
Synthesis of Trifluoroethoxyphosphoranimine 3. To a solution of bromophosphoranimine **1** (11.63 g, 29.36 mmol) in THF (50 mL) was added a solution of sodium trifluoroethoxide (32.30 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h and allowed to warm to room temperature. After completion of the reaction, the reaction mixture was passed through a pad of Celite to remove precipitated sodium chloride. The filtrate was collected, and the solvent and excess trifluoroethanol were removed at reduced pressure. The crude product was purified by vacuum distillation (at 40 °C) to yield a colorless liquid (6.10 g, yield 50%). ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 9H), 4.23 (q, 6H). ^{31}P NMR ($CDCl_3$): δ −11.90.

Synthesis of Chlorophosphoranimine 4.[10] A solution of $LiN(SiMe_3)_2$ (53.53 g, 0.32 mol) in 700 mL of diethyl ether was cooled to 0 °C, and PCl_3 (43.95 g, 0.32 mol) was added dropwise over 30 min. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. Sulfuryl chloride (43.19 g, 0.32 mol) was added slowly, and the reaction mixture was stirred at 0 °C for 3 h. After completion of the reaction, the salt was removed by filtration. The crude product was purified by vacuum distillation (30 °C, 0.3 mmHg) to yield a colorless liquid (25.15 g, yield 35%). ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 9H). ^{31}P NMR ($CDCl_3$): δ −54.10.

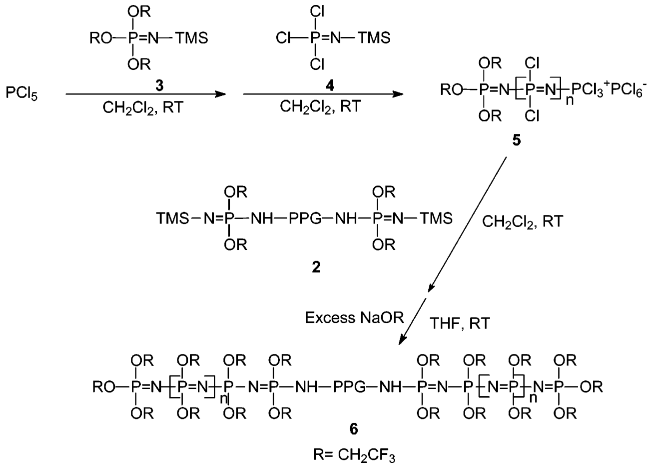
Synthesis of Triblock Copolymers 6. A mixture of $NH_2{-}PPG{-}NH_2$ (2.10 g, 0.53 mmol) and triethylamine (0.10 g) in THF (100 mL) was cooled to 0 °C. To this solution was added dropwise $(CF_3CH_2O)_2BrP{=}NSiMe_3$ (0.42 g, 1.05 mmol) over a 30 min period. The reaction mixture was stirred for 12 h at room temperature. All volatiles and solvent were removed under reduced pressure to produce a yellow viscous liquid. This end-functionalized product was dissolved in CH_2Cl_2 for further reaction. In a separate reaction vessel, PCl_5 (0.44 g, 2.10 mmol) was dissolved in 50 mL of distilled CH_2Cl_2 at room temperature. The end-capper reagent $(CF_3CH_2O)_3P{=}NSiMe_3$ (0.44 g, 14.70 mmol) was added to the solution, which was stirred for 1 h at room temperature. The monomer, $Cl_3P{=}NSiMe_3$ (3.30 g, 9.62 mmol), was then added to the reaction mixture which was stirred for 2 h to generate "living" poly(dichlorophosphazene) chains. The solution of PPG−phosphoranimine in CH_2Cl_2 was then added to the polyphosphazene solution, and the mixture was stirred for 10 h at room temperature to terminate the polymerization. The CH_2Cl_2 was removed from the reaction mixture under reduced pressure, and the polymer was redissolved in 25 mL of freshly distilled THF. An excess of $NaOCH_2CF_3$ (34.65 mmol) in THF was added to the polymer solution to replace the labile chlorine atoms in the phosphazene blocks. The reaction mixture was stirred at room temperature until ^{31}P NMR spectroscopy indicated complete replacement of the chlorine atoms. The reaction solution was then concentrated and precipitated repeatedly from THF into deionized water and into hexanes. The polymer was purified again by dialysis against EtOH/H_2O (4/1 vol/vol), followed by drying under reduced pressure to give a viscous yellowish liquid.

Sample Preparation. To prepare micellar solutions, Nanopure water with a conductivity of 18.2 MΩ/cm (10 mL) was added dropwise to a stirred THF solution of the triblock copolymer (10 mL). The THF was removed on a rotary evaporator at 30 °C for 2 h. The micellar solution was diluted with Nanopure water to obtain a concentration range from 5×10^{-4} to 1×10^{-4} g/L. For the measurement of fluorescence spectra, a pyrene solution in THF (1.2×10^{-3} M) was added to Nanopure water to give a pyrene concentration of 12×10^{-7} M, and THF was removed using a rotary evaporator at 30 °C for 2 h. The pyrene solution was mixed with the triblock copolymer solutions to obtain copolymer concentrations from 2.5×10^{-4} to 1.25×10^{-4} g/L. The pyrene concentration of the samples was 6.0×10^{-7} M. All the samples were sonicated for 15 min and were allowed to stand for 2 days before fluorescence measurements.

Scheme 1



Scheme 2



Fluorescence Measurements. The fluorescence spectra were obtained using a Perkin-Elmer LS 55 spectrofluorometer. For the measurement of pyrene excitation spectra, emission and excitation bandwidths were set at 5 nm each, and the emission wavelength was set at 393 nm.

Sizes and Size Distributions. The sizes and size distributions of the triblock copolymer micelles were evaluated by dynamic light scattering (DLS) using a particle size analyzer (BI-90Plus, Brookhaven Instruments Corp., Holtsville, NY) with a scattering angle of 90°. Samples were filtered through a 0.45 μm syringe filter before measurement of particle size for each sample. Measurements were conducted at room temperature (25 °C).

Results and Discussion

A series of new ABA triblock copolymers of a polyphosphazene and poly(propylene glycol) were prepared by the synthetic procedure illustrated in Schemes 1 and 2. Phosphoranimines such as $(CF_3CH_2O)_2BrP{=}NSiMe_3$ (**1**) readily undergo bromine replacement reactions in the presence of amines to produce phosphoranimines such as $RNH(CF_3CH_2O)_2P{=}NSiMe_3$.[6,7] These species can then be utilized as initiators and/or terminators in the cationic living polymerization of $Cl_3P{=}NSiMe_3$. Stoichiometric amounts of amine-terminated poly(propylene glycol), such as $H_2N{-}PPG{-}NH_2$ were allowed to react with **1** in THF in the presence of triethylamine (Scheme 1). This process produced the phosphoranimine-terminated poly(propylene glycol), $Me_3SiN{=}P(OCH_2CF_3)_2NH{-}PPG{-}NH(CF_3CH_2O)_2P{=}NSiMe_3$ (**2**).

Living polyphosphazene **5** can be terminated with triorganophosphoranimines, which allows the controlled introduction of two functional units at the termini of the polyphosphazene chain.[11,12] Thus, compound **2** was employed as a PPG macromolecular terminator for the living polymerization of polyphosphazenes. As illustrated in Scheme 2, triblock copolymers were prepared by the addition of **2** to **5**. Following termination, the

Table 1. Properties of the Triblock Copolymers

		block ratio (PN/PPO/PN)			
triblock copolymer[a]	M_n (^{1}H NMR)	feed	found[b]	wt % of hydrophobic block[d]	M_n (M_w/M_n)[c]
$PN_{0.2}-PPG_{1.0}-PN_{0.2}$	7 600	0.2:1:0.2	0.1:1:0.1	0.09	26 000 (1.32)
$PN_{0.4}-PPG_{1.0}-PN_{0.4}$	12 000	0.4:1:0.4	0.3:1:0.3	0.55	38 000 (1.33)
$PN_{0.5}-PPG_{1.0}-PN_{0.5}$	18 000	0.5:1:0.5	0.4:1:0.4	0.74	34 000 (1.35)
$PN_{0.7}-PPG_{1.0}-PN_{0.7}$	27 000	0.7:1:0.7	0.7:1:0.7	0.89	55 000 (1.25)

[a] All the samples were prepared by using PPG with M_n of 4000 as specified by Aldrich. [b] Calculated from ^{1}H NMR spectra, by comparison of peaks at 4.55 ppm ($-OCH_2CF_3$) to peaks at 1.13 ppm ($-OCH_2CH(CH_3)-$). [c] Measured by GPC. [d] Weight percentage of the hydrophobic PN block in the triblock copolymer.

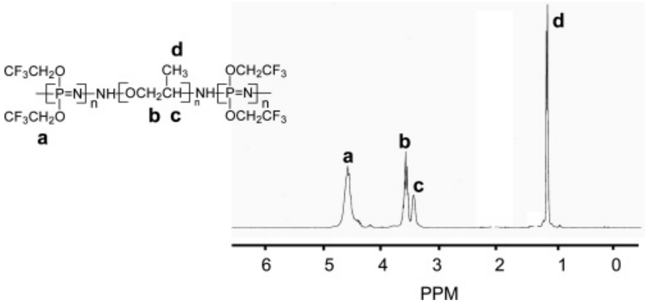


Figure 1. ^{1}H NMR spectrum of $PN_{0.5}-PPG_{1.0}-PN_{0.5}$.

chlorine atoms were replaced by reaction with $NaOCH_2CF_3$ to give PN−PPG−PN triblock copolymer **6**. The molar composition ratios of the repeating units of PPG to polyphosphazene block (x:y:z) in **6** were 0.2:1:0.2 for $PN_{0.2}-PPG_{1.0}-PN_{0.2}$, 0.4:1:0.4 for $PN_{0.4}-PPG_{1.0}-PN_{0.4}$, 0.5:1:0.5 for $PN_{0.5}-PPG_{1.0}-PN_{0.5}$, and 0.7:1:0.7 for $PN_{0.7}-PPG_{1.0}-PN_{0.7}$. The number-average molecular weights of copolymers **6** were estimated by comparing the ^{1}H NMR peak integration ratio of the trifluoroethoxy protons at 4.55 ppm and the methyl protons of PPG at 1.13 ppm (Table 1). The difference between the conclusions from the GPC and ^{1}H NMR estimates can probably be attributed to the inherent approximations in the GPC analysis.

The ^{1}H NMR spectrum of $PN_{0.5}-PPG_{1.0}-PN_{0.5}$ in Figure 1, as a representative example, shows the characteristic resonance peaks of a PN−PPG−PN triblock copolymer. The PN−PPG−PN triblock copolymers were soluble in THF, acetone, methanol, and DMF but were insoluble in chloroform and n-hexane.

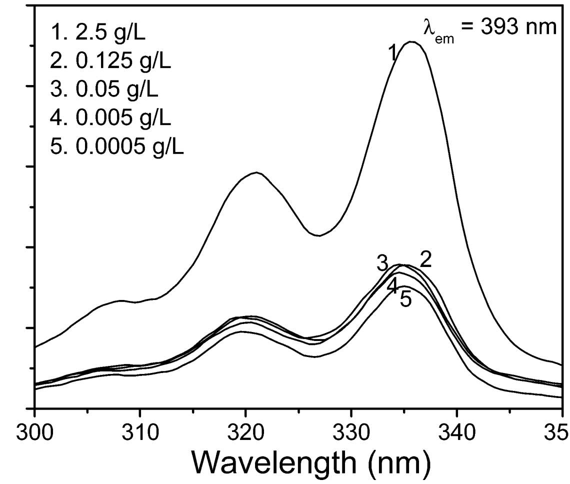


Figure 2. Excitation spectra of pyrene as a function of $PN_{0.4}-PPG_{1.0}-PN_{0.4}$ concentration in water. The spectrum of pyrene in pure water is identical to those of the low concentration samples in the figure.

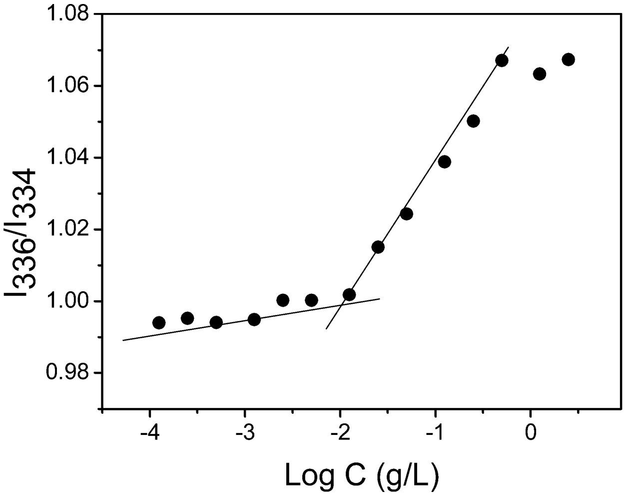


Figure 3. Plot of I_{336}/I_{334} (from pyrene excitation spectra) vs log C for $PN_{0.4}-PPG_{1.0}-PN_{0.4}$.

Table 2. Properties of PN−PPG−PN Micelles

triblock copolymer	cmc[a] (mg/L)	d^b (nm)	$\mu_2/\Gamma^{2\,c}$	K_v ($\times 10^{-5}$)
$PN_{0.2}-PPG_{1.0}-PN_{0.2}$	12.4	364	0.26	0.3
$PN_{0.4}-PPG_{1.0}-PN_{0.4}$	10.8	197	0.47	1.5
$PN_{0.5}-PPG_{1.0}-PN_{0.5}$	9.8	395	0.11	1.5
$PN_{0.7}-PPG_{1.0}-PN_{0.7}$	9.5	314	0.15	3.3

[a] Measured at 25 °C. [b] Mean diameters by dynamic light scattering at 25 °C. [c] Polydispersity factor.

Self-Association of Triblock Copolymers in an Aqueous Phase. The amphiphilic nature of the triblock copolymers, consisting of PPG flanked by hydrophobic fluoroalkoxyphosphazene blocks, provides an opportunity to form micelles in water. The characteristics of the triblock copolymer micelles in an aqueous phase were investigated by fluorescence techniques, dynamic light scattering, and TEM. The critical micelle concentrations (cmcs) of the triblock copolymers in an aqueous phase were determined by a fluorescence technique using pyrene as a probe.[13−17] In Figure 2, the excitation spectra of pyrene are shown at various concentrations of $PN_{0.4}-PPG_{1.0}-PN_{0.4}$. The characteristic feature of the pyrene excitation spectra, the symmetry-forbidden (0,0) band shift from 334 to 336 nm following pyrene partition into the micellar hydrophobic core, was utilized to determine the cmc values of PN−PPG−PN triblock copolymers. For the PN−PPG−PN triblock copolymers, a red shift of (0,0) band from 334 to 336 nm was detected and was utilized to determine the cmc values. Figure 3 shows the intensity ratios (I_{336}/I_{334}) of the pyrene excitation spectra vs the logarithm of $PN_{0.4}-PPG_{1.0}-PN_{0.4}$ triblock copolymer concentration. A negligible change of intensity ratios (I_{336}/I_{334}) was detected within a low concentration range, but at a certain concentration, the intensity ratios showed a substantial increase, reflecting the incorporation of pyrene into the hydrophobic core region of the micelles. Therefore, the cmc was determined from the crossover point at the low concentration range in Figure 3. The cmc values of the block copolymers were in the range of 9.5−12.4 mg/L depending on the block composition (Table 2). These values are much lower than those of low molecular weight surfactants (e.g., 2.3 g/L for sodium dodecyl sulfate) but

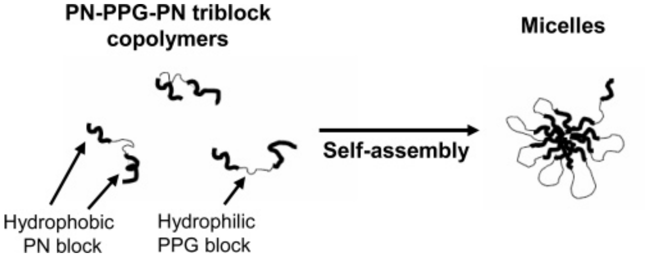


Figure 4. Schematic representation of micelles formed from PN−PPG−PN triblock copolymers.

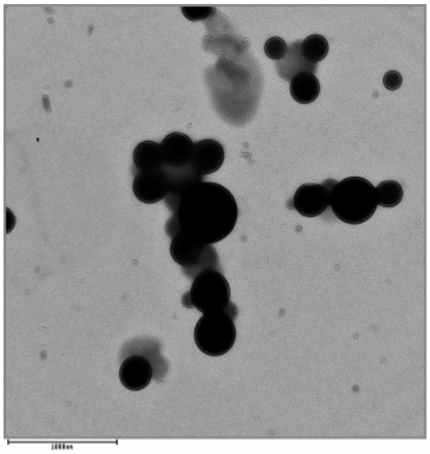


Figure 5. TEM micrograph of $PN_{0.5}$−$PPG_{1.0}$−$PN_{0.5}$ micelles. The bar indicates 1000 nm.

comparable with those of other polymeric amphiphiles.[14−16,18] As the proportion of the hydrophobic phosphazene component became higher, lower cmc values were generated. The mean diameters (*d*) of the block copolymer micelles, measured by dynamic light scattering, were in the range 197−364 nm (Table 2). The mean diameters of the micelles were not significantly affected by the change in the length of the hydrophobic PN block. Considering the block length in the PN−PPG−PN copolymers and the assumption of a folded triblock copolymer structure in the micelles, this system appears not to generate micelles with *d* values as large as 197−364 nm in an aqueous phase. Therefore, it is suggested that the micelles of PN−PPG−PN are folded in half to maintain the hydrophobic core and a hydrophilic corona (Figure 4). Larger structures are then formed by association of individual micelles rather than via an enlarged core−shell structure. The polydispersity factors (μ_2/Γ^2) of the micelles, estimated by the cumulant method, were fairly low (0.11−0.47), which suggests a narrow size distribution.[14,19,20]

The size and shape of the micelles formed from PN−PPG−PN triblock copolymers were examined by TEM. Figure 5 shows micelles formed from a 0.25 g/L solution of $PN_{0.5}$−$PPG_{1.0}$−$PN_{0.5}$. The micelles have a spherical shape, and the estimated diameters are in good agreement with the mean diameters measured using dynamic light scattering.

Partitioning of Pyrene in Micellar Solutions. The hydrophobicity of the hydrophobic micellar core was estimated by measuring the partition equilibrium constant K_v of pyrene, a hydrophobic probe, in the micellar solutions of the triblock copolymers PN−PPG−PNs. In this work, the equilibrium constant K_v was calculated following the method suggested by Wilhelm et al.[13] In this method, pyrene binding to the micelles is considered in terms of a simple equilibrium distribution between a micellar (PN) phase and the water phase. The ratio of the pyrene concentration in the micellar phase to the water phase ($[Py]_m/[Py]_w$) can be correlated to the ratio of volume of each phase as expressed in eq 1.

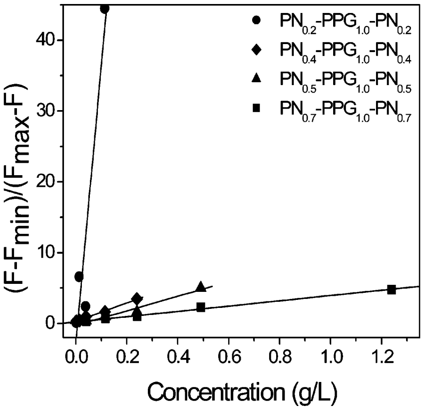


Figure 6. Plots of $(F - F_{min})/(F_{max} - F)$ vs concentration of $PN_{0.2}$−$PPG_{1.0}$−$PN_{0.2}$ (●), $PN_{0.4}$−$PPG_{1.0}$−$PN_{0.4}$ (◆), $PN_{0.5}$−$PPG_{1.0}$−$PN_{0.5}$ (▲), and $PN_{0.7}$−$PPG_{1.0}$−$PN_{0.7}$ (■) in water.

$$[Py]_m/[Py]_w = K_v V_m/V_w \qquad (1)$$

Equation 2 can be rewritten as

$$[Py]_m/[Py]_w = K_v x(c - \mathrm{cmc})/1000\rho \qquad (2)$$

where *x* is the weight fraction of PN blocks in the triblock copolymer, *c* is the concentration of the triblock copolymer, and ρ is the density of the PN core of micelles, which is assumed to be the bulk density of the polyphosphazene (1.10 g/mL). In the intermediate range of polymer concentrations with substantial increases of intensity ratios (I_{336}/I_{334}), $[Py]_m/[Py]_w$ can be written as

$$[Py]_m/[Py]_w = (F - F_{min})/(F_{max} - F) \qquad (3)$$

where F_{max} and F_{min} correspond to the average magnitude of I_{336}/I_{334} in the flat region of the high and low concentration ranges in Figure 3, and *F* is the intensity ratio (I_{336}/I_{334}) in the intermediate concentration range of the triblock copolymers. Combining eqs 2 and 3, K_v values of pyrene were determined by using a plot $(F - F_{min})/(F_{max} - F)$ vs PN−PPG−PN concentration, as shown in Figure 6.

The K_v values, as summarized in Table 2, were in the range from 3.0×10^4 to 3.3×10^5 for the PN−PPG−PN system. As the length of the hydrophobic blocks in the copolymers increases, the K_v value increases, suggesting that the hydrophobicities of the micelles also increase.[16] K_v values in the range 1.79×10^5−5.88×10^5 have been reported for poly(2-ethyl-2-oxazoline)−poly(ϵ-caprolactone) and poly(2-ethyl-2-oxazoline)−poly(L-lactide).[21]

Conclusions

Amphiphilic triblock copolymers based on a poly(propylene glycol) as the central block flanked by hydrophobic polyphosphazene blocks were synthesized via the controlled cationic-induced polymerization of $Cl_3N{=}PSiMe_3$ at ambient temperature. The block copolymers formed PN−PPG−PN polymeric micelles that self-organized in an aqueous phase. These were examined by using fluorescence techniques, dynamic light scattering, and transmission electron microscopy. The critical micelle concentrations (cmcs) of the PN−PPG−PN polymeric micelles depend on the length of the hydrophobic polyphosphazene block and were in the range 9.5−12.4 mg/L. From the

TEM and dynamic light scattering results, the PN−PPG−PN polymeric micelles were spherically shaped with sizes that ranged between 197 and 364 nm in diameter. The hydrophobicity of the micellar core was estimated by measurement of the partition equilibrium constant, K_v, of pyrene in the micellar solution of PN−PPG−PN, and the values were in the range from 3.0×10^4 to 3.3×10^5, which were similar to those of other reported polymeric micelles.

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