

# Synthesis and Characterization of Amphiphilic PMTFPS-*b*-PEO Diblock Copolymers

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**ABSTRACT:** A series of new amphiphilic poly [methyl(3,3,3-trifluoropropyl) siloxane]-*b*-poly(ethyleneoxide) (PMTFPS-*b*-PEO) diblock copolymers with different ratio of hydrophobic segment to hydrophilic segment were prepared by coupling reactions of end-functional PMTFPS and PEO homopolymers. PMTFPS-*b*-PEO diblock copolymers synthesized were shown to be well defined and narrow molecular weight distributed by characterizations such as NMR, GPC, and FTIR. Additionally, the solution properties of these diblock copolymers were investigated

using tensiometry and transmission electron microscopy. Interestingly, the critical micellization concentration increases with increasing length of hydrophobic chain. Transmission electron microscopy studies showed that PMTFPS-*b*-PEO diblock copolymers in water preferentially aggregated into vesicles. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3620–3626, 2012

**Key words:** block copolymers; polysiloxanes; fluoropolymers; synthesis; solution properties

## INTRODUCTION

Amphiphilic copolymers, constructed by covalently combining two incompatible segments into one molecule, could self-assemble in selective solvent into aggregates of various morphologies such as spheres, rods, vesicles, lamellae, large compound micelles, large compound vesicles, and several others.<sup>1–7</sup> This special property of amphiphilic copolymers has attracted lots of research interest in past decades from areas like biology, colloid science, drug and gene delivery, advanced materials formation, etc.<sup>8–11</sup> Superior to ordinary surfactants, the self-assembling properties of amphiphilic copolymers could be easily controlled by a change of the chemical structure, chain length, and the proportion of hydrophobic and hydrophilic segments.<sup>12–14</sup>

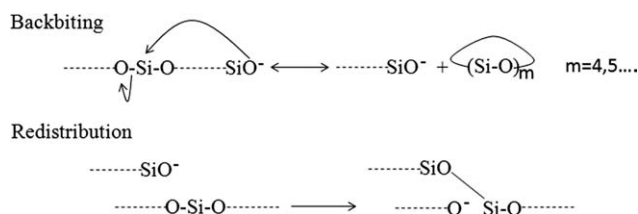
Polysiloxane-based copolymers, as we know, exhibit unique properties such as high hydrophobicity and flexibility, optical transparency, biocompatibility, etc. These characteristics make polysiloxanes interesting as blocks for the preparation of amphiphilic copolymers with properties different from

those of many other purely organic polymers. A special example of amphiphilic copolymers based on polysiloxane is the so-called “superspreaders” consisting of trisiloxanes and polyethers.<sup>15,16</sup> The remarkable surface-active properties of the “superspreaders” have received much attention. Polydimethylsiloxane is the most studied one among all the siloxanes. Copolymers based on polydimethylsiloxane have already been used in various applications such as foam stabilizers, antifoams, coating additives, and emulsion stabilizers.<sup>17–19</sup> And, copolymers comprising polydimethylsiloxane and polyether generally rank as some of the most effective lacquer additives. Several researchers<sup>20–24</sup> also carried out detailed investigation into the solution properties of copolymers comprising polydimethylsiloxane and polyether. Their potential to aggregate in aqueous solutions was shown by these studies, and spontaneous vesicle formations were reported for amphiphilic block copolymers comprising polydimethylsiloxane and polyethyleneoxide.

On the other hand, polymers containing fluorinated alkyl side chains have also attracted great attention because of their amazing properties,<sup>25–27</sup> such as high chemical and thermal stability, outstanding antiadhesive and oil-repellent properties, low refractive index, and low dielectric constant. Incorporation of fluorinated alkyl group into polysiloxane chain will result in polysiloxanes with many properties even superior to polydimethylsiloxanes.

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**Scheme 1** Side reactions occurring in the ring-opening polymerization of  $F_3$ .

Better performances, hence, could be anticipated for amphiphilic copolymers based on fluorinated polysiloxane instead of polydimethylsiloxane. Higher incompatibility between hydrophobic and hydrophilic segments would also bring about differences in solution behaviors and is worthy of investigation. However, fluorinated polysiloxane-based amphiphilic copolymers were rarely reported.<sup>28</sup> This may be caused by the difficulty to achieve narrow molecular weight distributed fluorinated polysiloxanes. Severe “backbiting” and redistribution side reactions take place in the ring-opening polymerization of fluoro-containing cyclosiloxane resulting in very limited poly(fluorinated)siloxane homopolymers (10–20%) with broad molecular weight distribution (MWD) when equilibrated (Scheme 1).<sup>28–32</sup>

Only by careful selection of polymerization method and reaction conditions, we could prepare poly(fluorinated)siloxane homopolymers with narrow MWD, which is critical to achieve amphiphilic copolymers with narrow MWD.

In our work, we prepared a series of amphiphilic diblock copolymers comprising poly[methyl(3,3,3-trifluoropropyl)siloxane] (PMTFPS) and poly(ethylene oxide) (PEO) with different ratio of hydrophobic segment to hydrophilic segment. To achieve copolymers with narrow MWD, the synthesis and purification technique were carefully determined. Termination before equilibrium with proper reaction conditions give PMTFPS homopolymers with MWD lower than 1.17. And, by combined use of anionic ring-opening polymerization and condensation polymerization methods, we successfully prepared a series of well-defined PMTFPS-*b*-PEO diblock copolymers with MWD ranging from 1.07 to 1.30. Additionally, the solution properties of these prepared copolymers were investigated by tensiometry and transmission electron microscopy.

## EXPERIMENTAL

### Materials

1,3,5-Trimethyl-1,3,5-tris(3,3,3-trifluoropropyl) cyclo-trisiloxane ( $F_3$ ) (Shanghai 3F Co.; 99.9%) was first dried over 3A molecular sieves, then refluxed in

$\text{CaH}_2$  for hours, and finally vacuum distilled into ampoules. *n*-Butyllithium (*n*-BuLi) in hexane (2 mol/L) was purchased from Aldrich and titrated before use.<sup>33</sup> Tetrahydrofuran (THF) (Sinopharm Chemical Reagent Co.; 99%) was refluxed in sodium for hours until it turned blue with the addition of diphenyl ketone. Dimethylchlorosilane (98%) was purchased from Aldrich and distilled before use. Speier’s catalyst was prepared dissolving  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (Sinopharm Chemical Reagent Co.; A.R.) in isopropanol to form 0.01M solution. Toluene (Sinopharm Chemical Reagent Co.; 99.5%) was distilled from sodium. Methanol (Sinopharm Chemical Reagent, 99%) was used as received for precipitation. Allyl-terminated polyethylene oxide (PEO) was kindly provided by Clariant Corporation and characterized by GPC before use. Other solvents used in the experiments were purified according to standard methods.

### Synthesis of Si–H functional PMTFPS homopolymers

High-vacuum technique was used to maintain a “pure” reaction environment ( $10^{-3}$  Pa) before Ar was filled to protect the reaction system. *n*-BuLi was first transferred to the reactor under the protection of Ar.  $F_3$  was dissolved in THF to form a clear solution, and subsequently, the solution was added into the reactor to start the reaction. The addition of the THF solution of  $F_3$  was divided into two steps. Step 1, a certain amount of the solution was added (1.2 mol  $F_3$ /mol *n*-BuLi) and stirred for 1 h at 0°C. Step 2, the residual solution was added and stirred for another 2 h at 0°C. In both steps, monomer concentration was kept above 1.3 mol/L to yield narrow MWD homopolymers according to our previous work.<sup>28</sup> Dimethylchlorosilane was added to terminate the reaction and the solution was stirred for another 12 h at room temperature. The resultant mixture was centrifuged for 10 min and separated. The organic phase was vacuum distilled to remove remaining solvent.

<sup>1</sup>H-NMR (500 MHz,  $\text{CDCl}_3$ , ppm): 0.00–0.22 [m,  $\text{OSi}(\text{CH}_3)_2\text{O}$ ], 0.58–0.65 [t,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ], 0.70–0.81 [t,  $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}$ ], 0.85–0.95 [t,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ], 1.25–1.40 [m,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ], 1.90–2.15 [t,  $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}$ ], 4.73–4.75 [s, SiH].

### Preparation of PMTFPS-*b*-PEO block copolymers

A solution of Si–H-terminated PMTFPS homopolymer and allyl-terminated PEO homopolymer was stirred aggressively at room temperature under nitrogen atmosphere. The polymers were coupled by hydrosilation reaction applying  $10^{-4}$  mol/mol double bond speier’s catalyst. The solution was heated to 80°C and stirred for 24 h. After the completion of

hydrosilation reaction, the solvent toluene was vacuum distilled. Products were purified by precipitation in methanol.

$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ , ppm): 0.00–0.22 [m,  $\text{OSi}(\text{CH}_3)_2\text{O}$ ], 0.58–0.65 [t,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ], 0.70–0.81 [t,  $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}$ ], 0.85–0.95 [t,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ], 1.25–1.40 [m,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ], 1.90–2.15 [t,  $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}$ ], 3.38–3.42 [ $\text{CH}_3\text{O}(\text{CH}_2)_2\text{O}$ ], 3.50–3.80 [ $\text{O}(\text{CH}_2)_2\text{O}$ ].

### Preparation of self-assembled aggregates

PMTFPS-*b*-PEO diblock copolymer was dissolved directly in water and stirred for several days before the TEM samples were prepared. A drop of the sample solution was placed on carbon film-coated standard 200-mesh TEM copper grid and air dried at room temperature for at least 2 days before observation.

### Characterization methods

Gel permeation chromatography (GPC) analysis was performed on a Waters 1525/2414 GPC system consisting of a Waters 1525 binary high-performance liquid chromatography pump, a Waters 717 plus autosampler, three Waters Styragel columns (Styragel HR2, HR3, and HR4), and a Waters 2414 refractive-index detector, and THF was used as the eluent at a flow rate of 1.0 mL/min at 40°C. The calibration curve was made with PS standards (Waters Corp.).

$^1\text{H-NMR}$  analysis was conducted with a Bruker 500-MHz nuclear magnetic resonance spectrometer (Advance DMX500) and was carried out with a 5 wt % solution in  $\text{CDCl}_3$  at room temperature.

Infrared spectra of the polymers were recorded on a Nicolet 5700 Fourier transform infrared (FTIR) instrument. The polymer films were casted onto KBr disks to be analyzed.

TEM images were obtained on a JEM-1230 instrument operated at an accelerating voltage of 80 kV. The high electron density of PMTFPS, when compared with PEO, gives sufficient contrast for TEM observation without the need of special staining techniques.

Equilibrium surface tension was measured with a CAM200 tensiometer (KSV). All tensiometry measurements were carried out at 20°C. For the PMTFPS-*b*-PEO copolymers investigated, the variation of the surface tension,  $\gamma$ , with the surfactant concentration,  $c$ , was determined. The CMC value of correspondent copolymer was determined by the sharp break in the curve (surface tension versus log concentration), which marked the onset of the aggregation. According to Gibbs' law applied to equilibrium systems, we know that the adsorption of the surfactant at the gas/liquid interface leads to a reduction of the

surface tension of the solution. The surface excess concentration,  $\Gamma$ , and the surface area per surfactant,  $A_s$ , have been calculated using following equations,

$$\Gamma = - \left[ \frac{1}{2.303RT} \right] \frac{d\gamma}{d \log c}$$

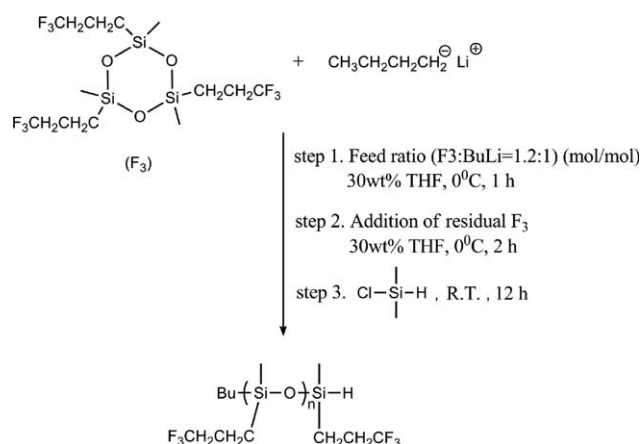
$$A_s = \frac{1}{L\Gamma_\infty}$$

where  $R$  is the gas constant,  $T$  is the absolute temperature, and  $L$  is the Avogadro constant number.

## RESULTS AND DISCUSSION

### Ring-opening polymerization of $\text{F}_3$

A series of PMTFPS homopolymers were prepared using *n*-BuLi as shown in Scheme 2. *n*-BuLi in hexane was first injected into a reactor protected by Ar. Subsequently, the THF solution of  $\text{F}_3$  was added to start the reaction. Yellowish color of *n*-BuLi in hexane vanished immediately on the addition of THF solution of  $\text{F}_3$  indicating a very fast initiation process. Dimethylchlorosilane addition resulted in immediate white lithium chloride salt and a colorless solution. Table I gives a summarization of molecular weight and MWD of homopolymers prepared. As we know, for lots of ROP processes, if monomer conversion is greater than 85%, backbiting reactions are no longer neglectable.<sup>34</sup> To minimize backbiting reactions, reaction process was followed and our conversions were limited to 80%. The influences of polymerization conditions on the homopolymer have been carefully studied in our previous work using polystyrenelithium (PSLi) as the initiator.<sup>28</sup> High monomer concentration was shown to effectively inhibit backbiting and redistribution side reactions. Therefore, the monomer concentration was kept above 1.3 mol/L for our anionic ROPs of  $\text{F}_3$  to



**Scheme 2** Anionic ring-opening polymerization of  $\text{F}_3$  initiated by *n*-BuLi.

**TABLE I**  
Properties of Si-H Functional PMTFPS Homopolymers Prepared by Anionic Ring-Opening Polymerization

Homopolymer	$M_n^a$	$M_n^b$	$M_n^c$	$M_w/M_n^c$
PMTFPS-3	584	646	928	1.14
PMTFPS-6	1,052	1,114	1,417	1.11
PMTFPS-9	1,520	1,738	2,092	1.15
PMTFPS-12	1,988	2,050	2,327	1.17
PMTFPS-21	3,392	3,298	3,717	1.10

<sup>a</sup> Calculated by  $M_n = \frac{n_{F_3}}{n_{BuLi}} \times C_{\text{conversion}} \times 3 \times 156 + 116$ .

<sup>b</sup> Determined via  $^1\text{H-NMR}$  spectroscopy using the resonances of trifluoropropyl groups between 1.9 and 2.15 ppm in comparison to the methylene group bonded to silicon found between 0.58 and 0.65 ppm.

<sup>c</sup> GPC conditions: THF, 40°C, DRI detector.

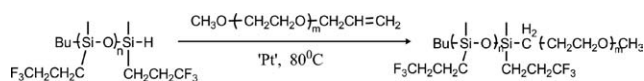
optimize the preparation of well-defined PMTFPS homopolymers with narrow MWD.

From Table I, Si-H functional PMTFPS homopolymers with MWD ranging from 1.10 to 1.17 were synthesized. Discrepancies between molecular weight from GPC analysis and that from  $^1\text{H-NMR}$  analysis were attributed to the fact that the GPC molecular weight was made in comparison to polystyrene standards. As we know, absolute molecular weight was impossible to obtain for PMTFPS by GPC calibrated with polystyrene standards. The purity of PMTFPS homopolymers was proved by GPC analysis. No monomer residues were detected after the purification procedure in these homopolymers.

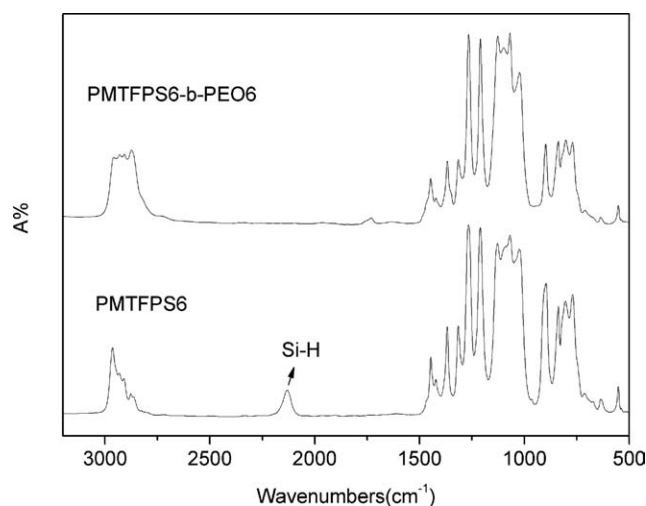
### Preparation of PMTFPS-*b*-PEO diblock copolymers

Amphiphilic PMTFPS-*b*-PEO diblock copolymers were prepared applying speier's catalyst to a solution of purified Si-H functional PMTFPS and allyl-terminated PEO homopolymers (Scheme 3). Figure 1 shows the comparison of FTIR spectra of PMTFPS homopolymer and PMTFPS-*b*-PEO diblock copolymer. From Figure 1, Si-H group of PMTFPS homopolymer was no longer detectable in PMTFPS-*b*-PEO diblock copolymer after the purification process. Peaks assigned to methylene groups located around 2850 and 2930  $\text{cm}^{-1}$  greatly increased after the reaction, which qualitatively indicated successful introduction of PEO segment.

$^1\text{H-NMR}$  spectra of before and after the coupling reaction were shown in Figure 2. As could be seen, Si-H group resonance located around 4.7 ppm disappeared completely after the coupling reaction,



**Scheme 3** Synthesis of PMTFPS-*b*-PEO diblock copolymer.

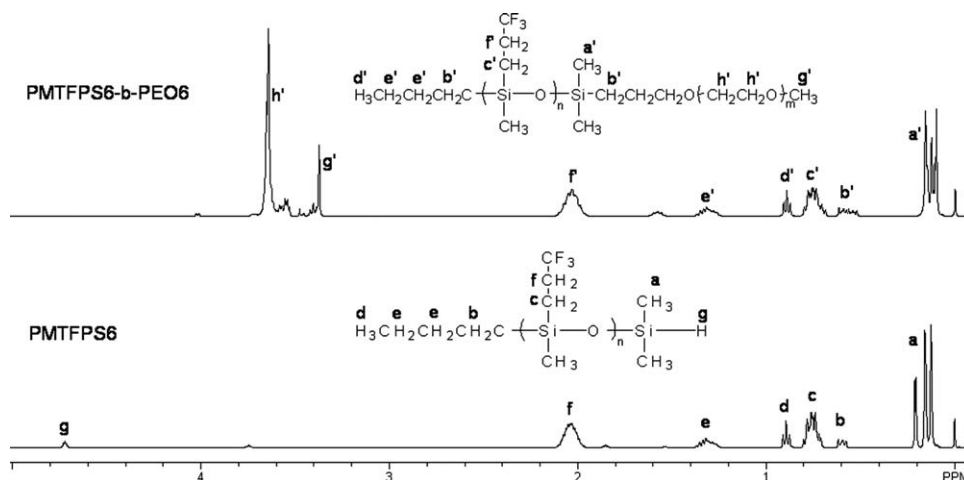


**Figure 1** Comparison of FTIR spectra of Si-H functional PMTFPS homopolymer and PMTFPS-*b*-PEO diblock copolymer.

which suggested the completeness of the hydrosilylation reaction. And also, the peaks located around 0.6 ppm assigned to methylene group bonded to silicon nearly doubled after the coupling reaction, which showed another support for the successful preparation of PMTFPS-*b*-PEO diblock copolymers. Newly formed peaks corresponded to hydrogen on PEO chain.

Figure 3 shows GPC traces of Si-H functional PMTFPS homopolymer and PMTFPS-*b*-PEO diblock copolymer. With the introduction of trifluoropropyl groups, the refractive index of PMTFPS homopolymer and PMTFPS-*b*-PEO diblock copolymer become lower than THF, which is GPC solvent used. Therefore, some negative peaks were obtained. From Figure 3, no homopolymer residues were detected in PMTFPS-*b*-PEO diblock copolymer, which proved the purity of PMTFPS-*b*-PEO diblock copolymers after the purification procedure. Monomodal GPC traces of PMTFPS homopolymer and PMTFPS-*b*-PEO diblock copolymer both indicated properties of narrow MWD.

Properties of amphiphilic PMTFPS-*b*-PEO diblock copolymers were summarized in Table II. The  $M_n$  values of homopolymers and copolymers calibrated with polystyrene standards qualitatively proved the successful preparation of PMTFPS-*b*-PEO diblock copolymers. It is worth mentioning that for some copolymers, the refractive index is quite the same with THF, which is solvent used in GPC characterization. That would to some extent influence the calculation of  $M_n$  values, and we thought it to be the reason why the values of some copolymers deviate quite a bit from the sum of two respective constituting blocks. PMTFPS-*b*-PEO diblock copolymers with MWDs ranging from 1.07 to 1.30 were synthesized.



**Figure 2** Comparison of  $^1\text{H}$ -NMR spectra of Si-H functional PMTFPS homopolymer and PMTFPS-*b*-PEO diblock copolymer.

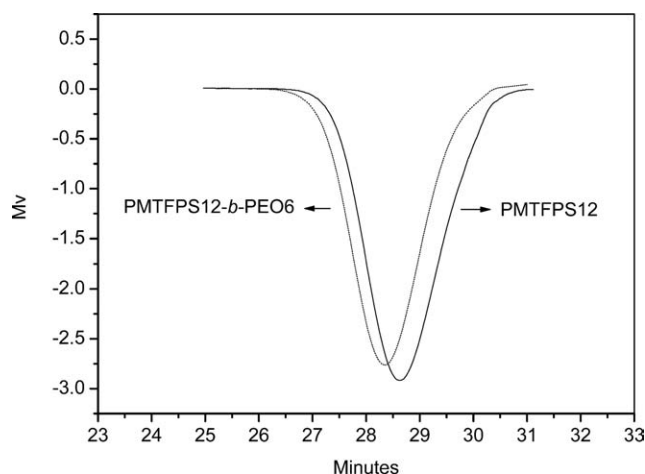
### Equilibrium surface tension

For the investigated copolymers, the variation of the surface tension with the surfactant concentration was determined. The obtained values of the critical micelle concentration (CMC), the maximum surface excess concentration,  $\Gamma_{\text{max}}$ , and the surface area per surfactant,  $A_s$ , of the copolymers are summarized in Table III. Figure 4 shows the equilibrium surface tension,  $\gamma$ , as a function of copolymer concentration of aqueous solutions,  $c$ , at 20°C.

The surface area per surfactant,  $A_s$ , was determined from the slope of the surface tension plots. The results obtained are listed in Table III. As could be seen, the value of  $A_s$  increases with the increasing size of hydrophobic and hydrophilic segments. And the variance of  $A_s$  value is much more sensitive to the change of hydrophobic segment than that of

hydrophilic one. This seems to indicate that the  $A_s$  at the air-water interface is mainly governed by the hydrophobic PMTFPS segment, in other words, PMTFPS segment has a larger area demand than PEO segment. However, as we know, normal alcohol ethoxylates with 12 oxyethylene units in the polar headgroup typically have values for the surface area per molecule of 70–80 Å<sup>2</sup>. The values for our investigated copolymers seem unrealistic low. This, we think, could be caused by the extreme hydrophobicity of PMTFPS segment that induces extreme tight packing of the hydrophobic segment, and in turn forces the PEO segment to become much more extended than normal.

As for the CMC values of investigated copolymers, from Table III, we see that along with the increase of hydrophobic chain length, the value of CMC increased unexpectedly. The usual trend for surfactants is that the aggregation, which is usually micelle formation, starts at a lower concentration the longer the hydrophobic tail. But in our work, the investigated copolymers showed the opposite



**Figure 3** Comparison of GPC traces of Si-H functional PMTFPS homopolymer and PMTFPS-*b*-PEO diblock copolymer.

**TABLE II**  
Properties of PMTFPS-*b*-PEO Diblock Copolymers

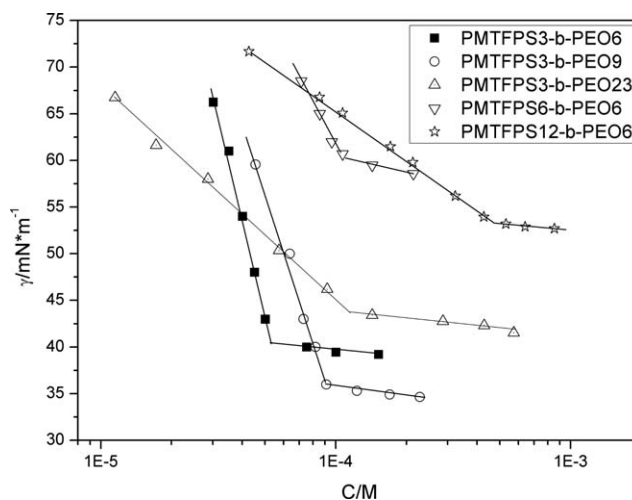
Sample	$M_n^a$ (PMTFPS)	$M_n^a$ (PEO)	$M_n^a$ (diblock)	$M_w/M_n^a$ (diblock)
PMTFPS3- <i>b</i> -PEO6	928	350	1,295	1.19
PMTFPS3- <i>b</i> -PEO9	928	450	1,429	1.16
PMTFPS3- <i>b</i> -PEO23	928	1,100	2,079	1.24
PMTFPS6- <i>b</i> -PEO6	1,417	350	1,770	1.15
PMTFPS6- <i>b</i> -PEO9	1,417	450	2,239	1.16
PMTFPS6- <i>b</i> -PEO23	1,417	1,100	2,579	1.18
PMTFPS9- <i>b</i> -PEO6	2,092	350	2,363	1.30
PMTFPS9- <i>b</i> -PEO9	2,092	450	2,751	1.10
PMTFPS9- <i>b</i> -PEO23	2,092	1,100	3,518	1.07

<sup>a</sup> GPC conditions: THF, 40°C, DRI detector.

**TABLE III**  
Critical Micelle Concentration of PMTFPS-*b*-PEO in Aqueous Solution and Other Parameters Derived from the Gibbs Plot at 20°C

Copolymer	CMC (mol/L)	$\Gamma_{\max}$ (mol/m <sup>2</sup> )	Area per molecule (Å <sup>2</sup> )
PMTFPS3- <i>b</i> -PEO6	5.30E-5	1.96E-5	8.479
PMTFPS3- <i>b</i> -PEO9	9.12E-5	1.40E-5	11.892
PMTFPS3- <i>b</i> -PEO23	1.14E-4	4.05E-6	40.962
PMTFPS6- <i>b</i> -PEO6	1.07E-4	7.85E-6	21.147
PMTFPS12- <i>b</i> -PEO6	4.65E-4	3.08E-6	53.929

trend. The factor that governs the CMC values of amphiphilic block copolymers may not only be restricted to the hydrophobicity, which in fact is the governing factor for ordinary surfactants.<sup>22</sup> Geometry of amphiphilic block copolymers also has to be taken into consideration. For aggregates of different morphologies, the order of CMC value against the change of block length could be different. For our investigated copolymers, the preferential formation of aggregates was shown to be vesicle (see the Discussion in the next section). As we know, micelle-forming surfactants have a relatively large headgroup compared with the tail. If the hydrophilic headgroup becomes small compared with the hydrophobic tail, micelles will not form; instead, there may be a direct transition from a very dilute solution of surfactant unimers into a vesicular phase. One example of such behavior is tri(ethylene glycol) monododecyl ether, commonly abbreviated C12E3.<sup>35</sup> The hydrophobic tails of PMTFPS-*b*-PEO are bulky, rendering micelle formation unfavorable, and favoring formation of a lamellar phase, just as with C12E3. The reverse order of CMC values found in our works most likely reflects the ease with which these block copolymers pack into lamellar aggregates.

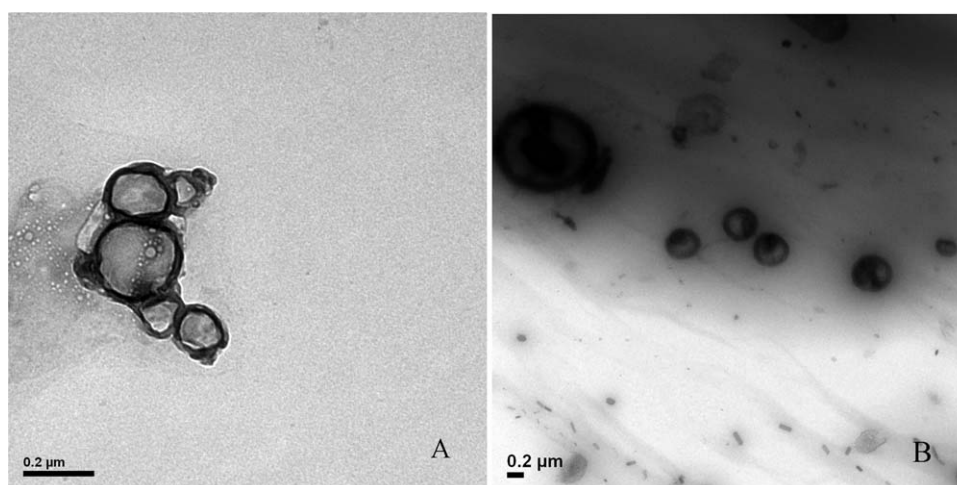


**Figure 4** Equilibrium surface tension,  $\gamma$ , as a function of copolymer concentration of aqueous solutions of PMTFPS3-*b*-PEO6, PMTFPS3-*b*-PEO9, PMTFPS3-*b*-PEO23, PMTFPS6-*b*-PEO6, and PMTFPS12-*b*-PEO6 at 20°C.

#### TEM analysis

Morphologies of the aggregates formed from dilute aqueous solutions of PMTFPS-*b*-PEO diblock copolymers were investigated by transmission electron microscopy. TEM samples were prepared at least 2 days ahead of observation. The high electron density of PMTFPS, when compared with PEO, gives sufficient contrast for TEM observation without the need of special staining techniques.

Spontaneous vesicle formation was observed as shown in Figure 5, which supported the hypothesis for unexpected CMC variation along with increasing length of hydrophobic chain. As we know, vesicles are normally formed from amphiphilic copolymers, which have relatively longer hydrophobic blocks than hydrophilic blocks.<sup>36,37</sup> However, for copolymers investigated here, extreme asymmetry in copolymer



**Figure 5** TEM of 0.02 wt % aqueous solution of PMTFPS9-*b*-PEO9 (A) and PMTFPS9-*b*-PEO6 (B).

structure does not seem to be a necessity. Spontaneous vesicle formation was also reported for aqueous solution of PDMS10-*b*-PEO12 diblock copolymer.<sup>21</sup> The reason is not clear but could be attributed to the steric hindrance for these hydrophobic chains to pack into micelles. Because of the hollow spherical morphology, vesicles can mainly be applied for encapsulation of various agents within the vesicle core and their further delivery in both synthetic and living systems. And additionally, vesicles have already been exploited as nano-reactors for controlled processes, which take place within their aqueous core.<sup>38</sup> The capability of spontaneous vesicle formation of PMTFPS-*b*-PEO diblock copolymers makes PMTFPS-*b*-PEO diblock copolymers new candidates for applications or potential applications in vesicle-based areas.

### CONCLUSIONS

In summary, we showed that amphiphilic block copolymers consisting of a PMTFPS hydrophobic block and a PEO hydrophilic block could be easily synthesized by coupling reactions of two separate end-functionalized segments. By proper selection of polymerization and purification techniques, PMTFPS homopolymers with MWD lower than 1.17 and PMTFPS-*b*-PEO diblock copolymers with MWD from 1.07 to 1.3 were successfully prepared. These copolymers showed a critical micellization concentration that unexpectedly increased with increasing length of hydrophobic chain. The origin for this behavior was discussed though still not fully understood. Steric constraints in the packing of the hydrophobic tails into closed aggregates may be responsible for this. TEM studies showed that the amphiphilic PMTFPS-*b*-PEO copolymers preferentially aggregated into vesicles. As for the detailed TEM investigation of aggregates formed from these copolymers in water and solvent mixture, works are under way and will be reported in the future.

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