Supporting Online Material for

Cylindrical Block Copolymer Micelles and Co-Micelles of Controlled Length and Architecture

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Published 3 August 2007, Science 317, 644 (2007)
DOI: 10.1126/science.1141382

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FORMATION OF CYLINDRICAL BLOCK COPOLYMER MICELLES AND CO- 
MICELLES OF CONTROLLED LENGTH AND ARCHITECTURE

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SUPPORTING INFORMATION

GLOSSARY

In the following text, several acronyms will be used instead of the polymer and solvent names. 
The definition of these acronyms is given below:

PI Polyisoprene
PFS Polyferrocenyltrimethylsilane
PMVS Polymethylvinylsiloxane
PDMS Polydimethylsiloxane
PFMES Polyferrocenylmethylsiloxane
THF Tetrahydrofuran

EXPERIMENTAL METHODS

Polymer synthesis and characterization. Polyferrocenylsilane block copolymers were 
synthesized by anionic polymerization in THF solution and characterized as described previously 
(S1-S234). In the synthesis of PFS-PI copolymers, the PI block was synthesized first. Then the 
PI anion was used to initiate polymerization of dimethyl[1]silafurocophane. In the synthesis 
of PFS-PDMS, PFS-PMVS, and PFMES-PMVS copolymers, the [1]silafurocophane was 
polymerized first, followed by the ring-opening polymerization of the corresponding 
cyclotrisiloxane. After each synthesis, the polymer was purified by passage through a preparative 
gel permeation chromatography (GPC) column. This process removes any residual first-block 
homopolymer and also results in some narrowing of the molar mass distribution. Molar mass and 
the overall molar mass distribution were determined by GPC, using a Waters 2690 Separations 
Module chromatograph connected to a Viscotek Triple Detector Array or a Viscotek GPC MAX 
chromatograph equipped with a Viscotek Triple Detector Array. The final molecular 
characteristics of the copolymers were determined by combining $M_n$ of the first block from GPC
measurements and block ratios from $^1$H NMR analysis. The characteristics of the polymers used in this study are listed in Table S1.

**Micelle preparation.** Micelles of PFS$_{53}$-PI$_{320}$ were prepared by adding a known quantity of polymer (e.g., 10 mg) to ca. 10 mL of hexane or decane. The solution was warmed to 60 °C (hexane) or 70 °C (decane) for 30 min to 1 h, and then allowed to cool to room temperature and aged at room temperature for times ranging from two days to two months. During this time the samples were monitored by right-angle dynamic light scattering and by TEM to establish times in which the micelle size became constant. Once the size had stabilized (typically several days for hexane, and several weeks for decane), no further evolution of size was observed. The length of the micelles varied with solvent (hexane vs. decane) and with the polymer concentration at which the sample was prepared. The sample prepared in hexane at 1.0 mg/mL exhibited an apparent hydrodynamic radius $R_{h}^{\text{app}}$ of 63 nm in a DLS measurement at 90°, and a mean length of ca. 400 nm by TEM.

For light scattering experiments in decane, an initial solution was prepared by adding 1.2 mg polymer to 7.8 mL decane (0.15 mg/mL) and heating the solution for 80 min at 70 °C and then allowing the solution to cool to room temperature. This particular solution was then allowed to age in the dark at room temperature for 60 days.

Sonication experiments were carried out by immersing a sealed tube containing the sample into the water-containing chamber of a 70 watt ultrasonic cleaning bath at ca. 23 to 25 °C, typically for 40 min, in 10 min intervals, checking the sample by DLS after each interval. A TEM image of the sample obtained by sonication of a solution of PFS$_{53}$-PI$_{320}$ micelles in hexane (0.5 mg/mL) used for micelle extension experiments is shown in Fig. 1A of the text. These micelles are characterized by a mean length of 250 nm. The sample obtained by sonication of a solution of PFS$_{48}$-PI$_{264}$ micelles in decane used for the micelle growth experiments described in Fig. 2 of the text, was characterized by static and dynamic multi-angle light scattering to yield the fitting parameters (see below) collected in Table S2.

**Light scattering experiments.** Multi-angle static (SLS) and dynamic (DLS) light scattering experiments were carried out at 21 °C with an instrument from ALV that has been described previously (S5). Data were collected over scattering angles of 20° to 150° in 5° intervals. Values of $dn/dc$ of PFS$_{48}$-PI$_{264}$ in decane (0.157 L/mg) were calculated using the Dale-Gladstone relation: $dn/dc \approx (n_p - n_s)/\rho_p$, where $n_p$ is the refractive index of the polymer constituting block, $n_s$ is the refractive index of the solvent, and $\rho_p$ is the density of the polymer. The error in the approximation of $(dn/dc)_{\text{block}}$ has been estimated to be lower than 5% (S6). Considering a density of 1.26 g/cm$^3$ and a refractive index of 1.68 for the PFS block and a density of 0.92 g/cm$^3$ and a refractive index of 1.52 for the PI block, the calculated block refractive increment in decane is $(dn/dc)_{\text{PFS}} \approx 0.214$ L/mg for the PFS block and $(dn/dc)_{\text{PI}} \approx 0.120$ L/mg for the PI block. From those values, we deduced the overall copolymer $(dn/dc)_{\text{tot}}$ using the weighted sum of the $dn/dc$ values of the polymer blocks:

$$\left(\frac{dn}{dc}\right)_{\text{tot}} = w_{\text{PFS}} \left(\frac{dn}{dc}\right)_{\text{PFS}} + w_{\text{PI}} \left(\frac{dn}{dc}\right)_{\text{PI}}$$  \hspace{1cm} (S1)

where $w_{\text{PFS}}$ and $w_{\text{PI}}$ are respectively the weight fractions of the PFS and PI blocks. From the calculated values of the refractive increment of each block of the copolymer in $n$-decane and
their weight fraction in the copolymer ($w_{\text{PFS}} = 0.393$ and $w_{\text{PI}} = 0.607$), we evaluated $(dn/dc)_{\text{tot}}$ to be $0.157 \text{ L/mg}$ for PFS48-PI264 in $n$-decane.

For samples diluted to concentrations below 0.1 mg/mL, the fitting parameters to the scattering data were independent of concentration. For sonicated samples of relatively low aspect ratio, the SLS data were fitted to a traditional Zimm plot. For all elongated structures, the data were fitted to the equations described below. DLS data were examined by a CONTIN analysis as well as by a second-order cumulant analysis.

For all static light scattering experiments, the data were examined in terms of a Casassa-Holtzer analysis (S7,S8) where $q R_0/\pi M_0 Kc$ is plotted as a function of $q$, which in the high $q$ limit (for light scattering) approaches a plateau whose value is related to the mass per unit length of the rod-like objects. Here $M_w$ is the weight average molecular weight of the micelle and $M_0$ is that of diblock copolymer. The linear aggregation number ($N_{\text{ag,L}}$, polymer molecules per nm) can be calculated from the expression

$$N_{\text{ag,L}} = \lim_{q \to \infty} q P(q) M_w / M_0 \pi$$

(S2)

To calculate the length of the rod-like micelles, we used the form factor $P(q)$ for long, thin rigid rods, monodisperse in length:

$$P(q)_{\text{long}} = \frac{2}{qL} \int_0^L \sin(qL) d(qL) - \left( \frac{2}{qL} \sin \left( \frac{qL}{2} \right) \right)^2$$

(S3)

To accommodate polydispersity in the fit, we considered a system of rods, polydisperse in length, with a weight average Zimm-Schulz distribution.

$$w(L) = \frac{b^{z+1}}{z!} L^z e^{-bl}$$

(S4)

Here $b = (z+1)/L_w$, and $z$ is the dispersion parameter ($z = 1/[(L_w/L_0)-1]$). For micelles, monodisperse in length, $z$ is infinite, while $z$ decreases when the polydispersity increases (S9).

We also considered the influence of semiflexibility on the form factor (S10,S11). In every case reported, structures are best described as rigid rods.

For samples in which a value of the radius of gyration $R_g$ could be obtained from a fit of the data to a Zimm plot, a value of the rod diameter could be estimated from the expression (S12)

$$R_g / R_h = 1/3^{0.5} \left( \ln(L/d) + 0.38 \right)$$

(S5)

**Micelle growth experiments.** Micelle growth experiments in hexane were carried out by adding 0.1 mL aliquots of PFS53-PI320 in THF containing 0.5 mg; 1 mg; and 2 mg polymer to 1.0 mL solutions of PFS53-PI320 micelles in hexane (0.5 mg/mL). After swirling to mix the solutions, they were allowed to age at room temperature. They were monitored from time to time by DLS and aging was continued (several days) until the $R_h^{\text{app}}$ values became constant. The results of these experiments are shown in the text in Fig. 1.

Micelle growth experiments in decane were carried out by adding different amounts (0.01, 0.04, 0.07, 0.12 mL) of a solution of PFS48-PI264 in THF (2.316 mg/mL) to ca. 1 mL aliquots of the sonicated PFS48-PI264 micelles (0.051 mg/mL) in decane (see Table S3). As a control experiment, another sample was prepared by adding 0.03 mL of pure THF to the decane solution.
of sonicated PFS\(_{48}\)-PI\(_{264}\) micelles. The vials were weighed before and after addition of the THF solutions. After swirling to mix the solutions, the vials were covered with aluminum foil to prevent dust from entering but also to allow the THF to evaporate over the 7 days that the samples were allowed to age at room temperature. Just prior to the light scattering experiments, the vials were reweighed and the concentrations were recalculated. We chose THF as the common good solvent because of its volatility and because its refractive index is close to that of decane (1.407 versus 1.411), so that the value of \(dn/dc\) was not affected significantly by traces of THF remaining in the solution.

**Long-term aging experiments for samples in decane.** After the samples described in the preceding paragraph (sonicated micelles, samples A – F) were examined by SLS and DLS measurements, they were carefully sealed and stored in the dark at room temperature for 5 months (20 weeks). Aliquots of each sample were taken for transmission electron microscopy (TEM) measurements. Then the light scattering experiments were repeated.

Samples for electron microscopy (EM) were prepared at room temperature by placing a drop of each solution onto a pre-coated copper grid. Excess fluid was then removed with a clean piece of filter paper. Bright field TEM micrographs were obtained with a Hitachi model 600 instrument operating at 75 kV, whereas dark field TEM micrographs were obtained with a Hitachi model STEM HD2000 electron microscope working at 200 kV. Due to the poor contrast obtained in the transmission mode for contour length distribution studies, these images were taken in the dark field mode. In this mode, electron rich objects appear bright, while electron poor objects remain dark, increasing the contrast effects. Contour length distributions were evaluated by image analysis. For each sample, the contours of 400 to 450 micelles were traced by hand using the software Image PRO Express and analyzed to obtain the parameters described below and in the text. Contour length distributions (CLD) were fitted to the frequency Zimm Schulz distribution function given by:

\[
F(L) = \frac{z^z L^{z-1} e^{-\frac{L}{L_n}}}{L_n^z z!}
\]  

(S6a)

where \(L_n\) is the number average length deduced from TEM measurements. For \(z = 2\) equation S6a can be rewritten as:

\[
F(L) = L \exp(-2L/L_n).
\]  

(S6b)

This is also the expression developed by Israelachvili for spontaneous self assembly of one-dimensional micelles (S13).

**SUPPORTING RESULTS**

**Initial micelle growth experiments.**

In initial micelle growth experiments, solutions of PFS\(_{53}\)-PI\(_{320}\) in THF were added to 1.0 mL aliquots of as-prepared PFS\(_{53}\)-PI\(_{320}\) micelles in hexane (ca. 1 mg/mL) and examined by TEM. After aging for several days, the structures seen in the TEM had grown from a mean length of ca. 1 \(\mu\)m to longer objects whose size varied with the amount of polymer added. An example is
shown in Fig. S1. The PFS core width as seen in the TEM images did not change. Because it was difficult to quantify the lengths of the structures, we began micelle growth experiments with shorter structures obtained by sonication.

**Light scattering data: micelle growth experiments**

The solution of sonicated PFS<sub>48</sub>-PI<sub>264</sub> micelles in decane gave a good fit to a traditional Zimm plot as shown in Fig. S2. When the data were fitted to eqs S3 and S4, an acceptable fit was obtained with a distribution centered at L = 98 nm with z = 2, implying that $M_w/M_n = 1.5$. The fitting parameters from SLS and DLS experiments, and the value of the rod diameter calculated from eq. S5 are collected in Table S3. The fitting parameters remained essentially unchanged after adding THF (0.3 mL) to 1.0 mL of this solution and allowing the solution to age for 7 days, during which the THF largely evaporated (see above).

The sonicated micelles in decane and samples A – F were examined by static and dynamic light scattering after aging for 7 days at room temperature. The samples were allowed to age for an additional 20 weeks (5 months) in the dark and then re-examined by SLS and DLS. At the same time, these 5-month samples were examined by dark field TEM to determine contour length distributions.

In Fig. S3A we show that $R_{\text{h}}^{\text{app}}$ values determined from 90° DLS measurements show little change except for a small increase for sample F. In Fig. S3B we plot values of $R_{\text{h}}^{\text{app}}$ vs $q$. The upturn at low $q$ is expected for elongated structures. Values of the linear aggregation number $N_{\text{ag}}/L$ (Fig. S3C) show only small variations from sample to sample and little change with extended aging. Fig. S3D shows that the sonicated micelles themselves give identical Holtzer-Casassa plots after aging for 7 days and 5 months.

In Table S3, we compare fitting parameters obtained by static light scattering measurements for the sonicated micelles and for samples A – F. The mean length of the micelles increases with the amount of polymer added in the micelle growth experiment. Few differences can be seen for the samples aged for 7 days and 5 months. The mean lengths of samples E and F appear to have increased by ca. 15%.

The results obtained from the image analysis are summarized in Table S4 and compared to the data obtained by SLS measurements on the same samples (5 months aging).

Unlike the other samples, sample F showed the presence of a significant number of small objects. An example is shown in the TEM image in Fig. S5. These objects are responsible for the sharp spike in the CLD for this sample seen in Fig. S4F. Their origin is unclear; they may arise from sample handling effects.

**Triblock co-micelle formation experiments.**

To prepare M<sub>(PFS<sub>48</sub>-PMVS<sub>300</sub>)</sub>-b-M<sub>(PFS<sub>53</sub>-PI<sub>320</sub>)</sub>-b-M<sub>(PFS<sub>48</sub>-PMVS<sub>300</sub>)</sub>, we first prepared sonicated PFS<sub>53</sub>-PI<sub>320</sub> micelles in decane (0.5 mg/mL) as seeds. As shown in Fig. 3A of the text, we obtained rod-like micelles with a length of ca. 200 nm. To a 1.0 mL aliquot of this solution, we added 0.1 mL of THF containing 1.0 mg of a different diblock copolymer, PFS<sub>50</sub>-PMVS<sub>300</sub>, and
monitored the solution by right-angle DLS. After about 2 days, the value of $R_{\text{h,app}}$ had leveled off, and a TEM image of the structures generated is shown in Fig. 3B of the text.

To prepare $M_4$(PFS40-PDMS330)-b-$M_4$(PFS53-PI320)-b-$M_4$(PFS40-PDMS330) triblock co-micelles, we carried out a similar experiment in which we added 0.1 mL of THF containing 1.0 mg of PFS40-PDMS330 to a 1.0 mL aliquot of a sonicated PFS53-PI320 micelle solution in hexane (0.5 mg/mL). After aging 3 days at room temperature, the TEM image seen in Fig. 3C of the text was obtained. A sample of this solution was subjected to Pt(0)-catalyzed hydrosilylation by treatment with tetramethyldisiloxane and Karstedt’s catalyst as described previously (S3,S14) to cross-link the PI corona of the middle block. The solvent was allowed to evaporate from a portion of this solution, and the dried product was redissolved in 1.0 mL THF. A drop of this solution, placed on a carbon-coated TEM grid yielded the image seen in Fig. 3D of the text.

To test whether co-micellization is possible if the polyferrocenylsilane block of the added block copolymer cannot crystallize, we carried out an analogous experiment with a PFMES diblock copolymer. To a solution of sonicated PFS53-PI320 micelles in hexane (0.5 mg in 1.0 mL), we added PFMES45-PMVS765 (0.5 mg) in THF (0.1 mL) under conditions similar to those described above. The solution was monitored by DLS and showed no change $R_{\text{h,app}}$ over 3 days. TEM images (e.g., Fig. S6) showed a mixture of cylindrical micelles, similar to those seen for PFS53-PI320 itself, and small spherical objects, assumed to be the spherical micelles formed by PFMES45-PMVS765. The mixed morphology indicates that PFMES-PMVS is unable to integrate into PFS53-PI320 cylinders because of its inability to crystallize.
Supporting Figures

Fig. S1. Micelles formed by addition of 2 mg PFS$_{53}$-PI$_{320}$ in 0.1 mL THF to 1.0 mL of non-sonicated PFS$_{53}$-PI$_{320}$ micelles (1 mg/mL) in hexane. The red, blue and green spots mark the ends of individual extended micelles.

Fig. S2: Plot of the Rayleigh ratio vs $q^2$ for sonicated PFS$_{48}$-PI$_{264}$ micelles in decane after dilution to 0.051 g/mL. This plot gave $M_w = 9.1 \times 10^6$, $R_g^{app} = 38.3$ nm, and an overall aggregation number $N_{ag} = 310$ polymer chains per micelle.
Fig. S3: (A). Values of the apparent hydrodynamic radii $R_{h}^{app}$ from DLS measurements at 90° for samples A – F plotted against the polymer concentration when the samples were prepared, comparing measurements made after aging the samples for 7 days and 5 months.

(B). The $q$-dependence of the apparent hydrodynamic radii $R_{h}^{app}$ from DLS measurements on samples A – F following aging for 5 months.

(C) Comparison of fitted values of the linear aggregation number $N_{ag}$ from SLS measurements on samples A – F comparing measurements made after aging the samples for 7 days and 5 months. The sample at “c = 0” refers to data for the sonicated micelles to which no THF was added.

(D) Holtzer-Casassa plots for the sample of sonicated PFS$_{48}$-Pl$_{264}$ micelles in decane shown in Fig. S2 after aging for 7 days and for 5 months (20 weeks) at room temperature.
Fig. S4. Calculated distribution of contour lengths of PFS$_{48}$-Pl$_{264}$ micelles in n-decane for samples A - F after aging at 21 °C for 5 months. The CLDs were determined from analysis of multiple dark field TEM images for each sample, in which 400 to 450 micelles were evaluated using ImagePro Express. The red curves used to describe each distribution were calculated from eq. S6 using the $L_{ni}$ values obtained from the image analysis.
**Fig. S5.** A dark field TEM image of sample F. The presence of some short objects is highlighted by dashed yellow circles.

**Fig. S6.** TEM image for a sample prepared by adding a solution of PFMES$_{40}$-PMVS$_{250}$ (0.5 mg) in THF (0.1 mL) to a solution of sonicated PFS$_{53}$-PI$_{320}$ micelles (0.5 mg) in hexane (1.0 mL), and allowing the solution to age 3 days at room temperature.
Supporting Tables

**Table S1:** Composition and characteristics of the polyferrocenylsilane diblock copolymers used in this study

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n^a$ (First block) (g/mol)</th>
<th>Block Ratio$^b$</th>
<th>$M_n^c$ (Diblock) (g/mol)</th>
<th>PDI$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFS$<em>{53}$-PI$</em>{1320}$</td>
<td>22,000$^d$</td>
<td>1:6</td>
<td>34,800</td>
<td>1.05</td>
</tr>
<tr>
<td>PFS$<em>{48}$-PI$</em>{264}$</td>
<td>18,000$^d$</td>
<td>1:5.5</td>
<td>29,600</td>
<td>1.08</td>
</tr>
<tr>
<td>PFS$<em>{48}$-PMVS$</em>{300}$</td>
<td>11,700$^c$</td>
<td>1:6</td>
<td>37,500</td>
<td>1.10</td>
</tr>
<tr>
<td>PFS$<em>{40}$-PDMS$</em>{330}$</td>
<td>9,700$^c$</td>
<td>1:8.3</td>
<td>34,200</td>
<td>1.09</td>
</tr>
<tr>
<td>PFMES$<em>{45}$-PMVS$</em>{765}$</td>
<td>11,400$^f$</td>
<td>1:17</td>
<td>83,500</td>
<td>1.10</td>
</tr>
</tbody>
</table>

a. Determined by GPC analysis versus polystyrene standards using THF as the eluent.
b. Determined by $^1$H NMR measurements.
c. Determined by combining $M_n$ of the first block (GPC) and the block ratio ($^1$H NMR).
d. $M_n$ of PI.
e. $M_n$ of PFS
f. $M_n$ of PFMES

**Table S2:** Preparation of PFS$_{48}$-PI$_{264}$ micelle samples in decane for light scattering studies

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>sonicated micelles (mg)</td>
<td>0.052</td>
<td>0.054</td>
<td>0.062</td>
<td>0.059</td>
<td>0.057</td>
<td>0.050</td>
</tr>
<tr>
<td>decane (mL)</td>
<td>1.0</td>
<td>1.1</td>
<td>1.2</td>
<td>1.2</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>THF added (mL)</td>
<td>0.03</td>
<td>0.01</td>
<td>0.02</td>
<td>0.04</td>
<td>0.07</td>
<td>0.12</td>
</tr>
<tr>
<td>weight of free chains</td>
<td>0</td>
<td>0.02</td>
<td>0.04</td>
<td>0.1</td>
<td>0.17</td>
<td>0.28</td>
</tr>
<tr>
<td>added (mg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>final polymer</td>
<td>0.05</td>
<td>0.08</td>
<td>0.09</td>
<td>0.13</td>
<td>0.20</td>
<td>0.34</td>
</tr>
<tr>
<td>concentration$^a$</td>
<td>mg/mL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. after aging for 7 days accompanied by the evaporation of the THF and re-determination of the overall polymer concentration.
Table S3: Main characteristics determined by SLS for the micelle samples aged for 7 days and for 5 months.

<table>
<thead>
<tr>
<th>Sample&lt;sup&gt;a&lt;/sup&gt;</th>
<th>sonicated</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aged for 7 days</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$L_w$ (nm)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>98</td>
<td>100</td>
<td>185</td>
<td>245</td>
<td>360</td>
<td>460</td>
<td>600</td>
</tr>
<tr>
<td>$N_{ag/L}$&lt;sup&gt;c&lt;/sup&gt; (molecules/nm)</td>
<td>3.1</td>
<td>2.9</td>
<td>2.7</td>
<td>2.8</td>
<td>3.0</td>
<td>3.1</td>
<td>3.3</td>
</tr>
<tr>
<td>$N_{ag}$&lt;sup&gt;c&lt;/sup&gt; (molecules/micelle)</td>
<td>310</td>
<td>290</td>
<td>510</td>
<td>680</td>
<td>1090</td>
<td>1420</td>
<td>1980</td>
</tr>
<tr>
<td>$(z+1)/z$ (polydispersity index, SLS)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>2.0</td>
<td>1.5</td>
<td>monodisperse</td>
</tr>
<tr>
<td><strong>Aged for 5 months</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$L_w$ (nm)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>98</td>
<td>100</td>
<td>165</td>
<td>220</td>
<td>340</td>
<td>490</td>
<td>730</td>
</tr>
<tr>
<td>$N_{ag/L}$&lt;sup&gt;c&lt;/sup&gt; (molecules/nm)</td>
<td>3.1</td>
<td>3.0</td>
<td>2.9</td>
<td>3.1</td>
<td>3.0</td>
<td>3.3</td>
<td>3.7</td>
</tr>
<tr>
<td>$N_{ag}$&lt;sup&gt;c&lt;/sup&gt; (molecules/micelle)</td>
<td>310</td>
<td>300</td>
<td>480</td>
<td>690</td>
<td>1030</td>
<td>1620</td>
<td>2680</td>
</tr>
<tr>
<td>$(z+1)/z$ (polydispersity index, SLS)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>1.2</td>
<td>monodisperse</td>
</tr>
</tbody>
</table>

a. the sample labeled “sonicated” is the freshly sonicated micelle sample prior to addition of any solvent or additional block copolymer.
b. deduced from the fit of $Kc/R_0$ using eqs S1, S3 and S4
c. calculated as $N_{ag/L} \times L_w$
Table S4: Comparison of data obtained from TEM image analysis and SLS experiments for samples aged 5 months.

<table>
<thead>
<tr>
<th>Concentration (mg/mL)(^a)</th>
<th>Sonicated(^b)</th>
<th>A(^c)</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
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<tr>
<td></td>
<td>0.051</td>
<td>0.052</td>
<td>0.076</td>
<td>0.090</td>
<td>0.133</td>
<td>0.202</td>
<td>0.342</td>
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<tr>
<td>(L_n) (nm) (TEM)</td>
<td>96</td>
<td>106</td>
<td>112</td>
<td>120</td>
<td>242</td>
<td>510</td>
<td>830</td>
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<tr>
<td>(L_w) (nm) (TEM)</td>
<td>143</td>
<td>148</td>
<td>196</td>
<td>282</td>
<td>479</td>
<td>815</td>
<td>1148</td>
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<tr>
<td>(L_w/L_n) (TEM)</td>
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<td>1.7</td>
<td>2.3</td>
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<td>1.6</td>
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<td>(L_n) (nm) (SLS)</td>
<td>65</td>
<td>66</td>
<td>85</td>
<td>110</td>
<td>170</td>
<td>410</td>
<td>730</td>
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<tr>
<td>(L_w) (nm) (SLS)</td>
<td>98</td>
<td>100</td>
<td>165</td>
<td>220</td>
<td>340</td>
<td>490</td>
<td>730</td>
</tr>
<tr>
<td>(L_w/L_n) (SLS)</td>
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<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>1.2</td>
<td>1.0</td>
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</table>

\(a\). concentration refers to the total block copolymer concentration at the time of sample preparation: after addition to the sonicated micelles of 0.03 mL of pure THF (A) and after addition of 0.01 (B), 0.02 (C), 0.04 (D), 0.07 (E) and 0.12 (F) mL of PFS\(_{48}\)-PI\(_{264}\) in THF (2.316 mg) followed by THF evaporation.

\(b\). the sample labeled “sonicated” is the freshly sonicated micelle sample prior to addition of any solvent or block copolymer solution.
REFERENCES AND NOTES:

S1  L. Cao, I. Manners, M.A. Winnik, Macromolecules 35, 8258 (2002).