

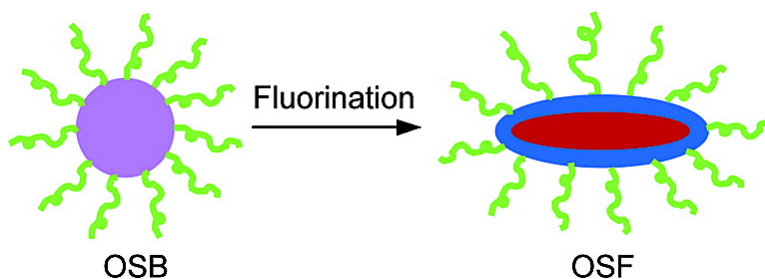
Communication

## Micellar Shape Change and Internal Segregation Induced by Chemical Modification of a Tryptych Block Copolymer Surfactant

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## Micellar Shape Change and Internal Segregation Induced by Chemical Modification of a Tryptych Block Copolymer Surfactant

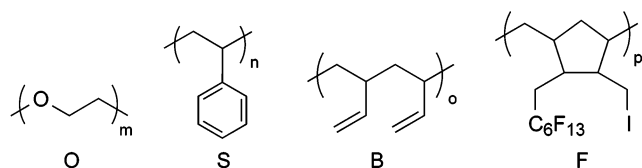
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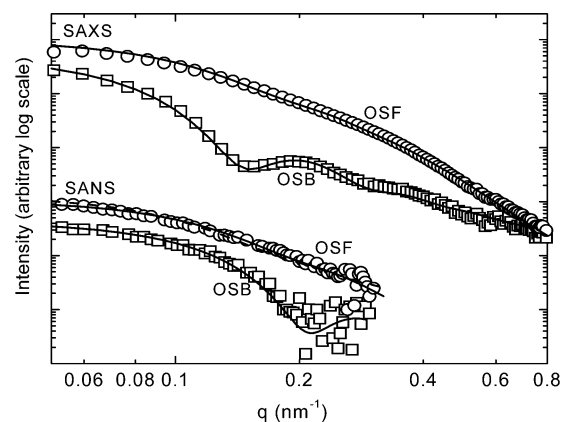
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The self-assembly of amphiphilic block copolymers in aqueous media is of fundamental interest and is important for dispersant technology,<sup>1</sup> nanomaterial synthesis,<sup>2</sup> and controlled release.<sup>3</sup> Whereas the micellar behavior of AB diblock and ABA triblock copolymers is relatively well understood,<sup>4–6</sup> the solution self-assembly of ABC triblocks is more complex. In particular, we are interested in the possibility of forming structured micelles,<sup>7</sup> that is, assemblies in which separate B and C core domains exist within a solvated A corona. Several recent studies<sup>8–15</sup> on amphiphilic ABC systems report the formation of multilayer (core/shell/corona) spherical micelles. In most cases,<sup>8–12,15</sup> the multilayer structure is induced by an external variable such as pH or temperature, and in all of these cases the micellization relies on ionic interactions. Incorporation of fluorinated segments into amphiphilic systems offers a nonionic route to structured micelles.<sup>16</sup>

In this Communication, we describe the detailed characterization of micelles formed by two nonionic, amphiphilic ABC triblock copolymers. In one of the copolymers, two hydrophobic blocks are mixed homogeneously within the core of a spherical micelle. Fluorination of one hydrocarbon block in the aforementioned material induces internal segregation into an inner core and an intermediate shell. Furthermore, the strong incompatibility that results from fluorination drives a shape change into an oblate ellipsoid. These micellar structures were confirmed by combined light, X-ray, and neutron scattering measurements, as well as TEM imaging. The combination of internal segregation and shape control in the self-assembly of amphiphilic ABC triblock copolymers is particularly important for the design of new self-assembled nanostructured materials.



A poly(ethylene oxide)-*b*-poly(styrene)-*b*-1,2-poly(butadiene) triblock copolymer (OSB) was synthesized by anionic polymerization<sup>17,18</sup> (Figure S1). The number average molecular weights of each block are  $M_n(O) = 13.2$  kg/mol,  $M_n(S) = 4.7$  kg/mol, and  $M_n(B) = 1.3$  kg/mol by <sup>1</sup>H NMR spectroscopy,<sup>19</sup> and the polydispersity index is 1.02 by SEC. Selective fluorination of the B block in OSB with *n*-perfluorohexyl iodide, following the procedure developed for SB diblocks,<sup>20</sup> gave poly(ethylene oxide)-*b*-poly(styrene)-*b*-1,2-poly(butadiene):C<sub>6</sub>F<sub>13</sub>I (OSF). No significant chain scission or coupling during fluorination was confirmed by the low polydispersity (1.03). OSF contained eight C<sub>6</sub>F<sub>13</sub>I groups per chain on average<sup>21</sup> (70% conversion of the double bonds).



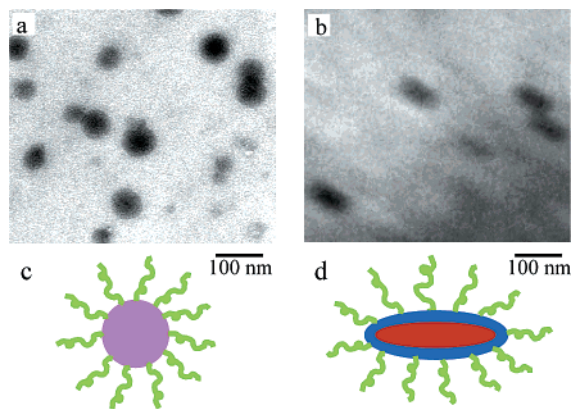
**Figure 1.** SANS and SAXS of 1 wt % OSB (□) and OSF (○) aqueous solutions at room temperature: SANS of OSB is fit by a uniform sphere model; SANS of OSF is fit by a simple ellipsoid (solid line) and a core shell ellipsoid (dashed line) model; SAXS of OSB is fit by a Pederson model; SAXS of OSF is fit by a simple ellipsoid model.

Both OSB and OSF could be directly dissolved in water, and the aqueous solutions (1 wt %) were examined by dynamic light scattering (DLS). The intensity autocorrelation functions at several scattering angles were well described by single exponentials (Figure S2), indicating a single predominant micellar morphology, consistent with an equilibrium, closed-association self-assembly process. The resulting decay rates varied linearly with squared scattering vector (Figure S3), yielding hydrodynamic radii of 55 and 52 nm for OSB and OSF, respectively. These dimensions are quite large, especially given the relatively low molar masses, but are not unexpected given the strong hydrophobicity of S, B, and F. DLS measurements made at 70 °C on the OSB micelles, above the estimated  $T_g$  of the mixed S/B core, gave equivalent results.

Figure 1 shows small-angle X-ray and neutron scattering (SAXS, SANS) data for 1% OSB and OSF aqueous solutions, along with fits to various micelle form factor expressions. An H<sub>2</sub>O/D<sub>2</sub>O mixture was used to contrast-match the scattering length density of the O block, and therefore the SANS curves reflect solely the structural features of the S/B and S/F cores (see Supporting Information). The SANS data for OSB are well fit by a monodisperse uniform sphere model,<sup>22</sup> with a core radius  $R_c$  of 21 nm. This suggests that the micelle core formed by S and B is homogeneous and spherical in shape. In SAXS (see Supporting Information), all three components of OSB contribute, necessitating a more elaborate approach. Pederson and Gerstenberg<sup>23</sup> modeled the micelle corona by non-interacting Gaussian chains, associated with a hard sphere core. This model fits the OSB SAXS data very well, giving a core radius of 13.5 nm, an interfacial thickness between core and shell of 13 nm, and an end-to-end length of the O blocks of 20 nm. Attributing one-half of the interfacial thickness to the micelle core, the overall core is 20 nm, in excellent agreement with the SANS result of 21

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**Figure 2.** TEM images of (a) OSB and (b) OSF micelles, and schematic illustration of (c) a core–corona spherical micelle formed by OSF and (d) a core–shell–corona oblate elliptical micelle formed by OSF.

nm. Summing the fitting parameters of the Pederson model gives an overall micelle radius of about 47 nm, slightly smaller than, but not inconsistent with, the hydrodynamic radius of 55 nm.

The results for OSF were quantitatively and qualitatively different. Because the SANS contrast of the F block with the solvent is more than 4 times that of S, the SANS data are fit first by a simple ellipsoid model,<sup>24</sup> containing only the F component. This model describes the data and assigns the elliptical F core principal radii of 6, 25, and 25 nm. If the model is enhanced to include a distinct S shell,<sup>25</sup> the fit results in radii of 5, 25, and 25 nm for the elliptical F core, surrounded by a 5 nm thick S shell. Within an estimated uncertainty of  $\pm 0.5$  nm in each linear dimension, these core and shell volumes match the relative volume fractions of the two blocks precisely. The SAXS scattering contrast of the F block is approximately 50 times greater than that of either S or O, and so here the simple ellipsoid core model is employed. The resulting radii of 5, 25, and 25 nm are equivalent to the SANS results.<sup>26</sup>

The structures and dimensions of the OSB and OSF micelles deduced from scattering measurements were further confirmed by direct observation with transmission electron microscopy (TEM). The 1% solutions were deposited on Formvar grids, the solvent was evaporated in air, and the resulting films were imaged at 120 kV (see Supporting Information). As shown in Figure 2a, core–corona spherical micelles are observed for OSB triblock copolymers, and both the core and the overall micelle sizes are consistent with the scattering analysis. The elliptical shape of the OSF micelles is clearly evident in the TEM image in Figure 2b. The asymmetry of the OSF micelles is illustrated by the optical density profiles of a typical micelle along two orthogonal directions (Figure S4). TEM gives approximate overall micelle principal radii of 39, 60, and 60 nm, which imply a hydrodynamic radius of 53 nm for an oblate ellipsoid, in excellent agreement with the measured value of 52 nm.

The DLS, SAXS, SANS, and TEM analyses all point to spherical core/corona micelles for OSB and oblate elliptical core/shell/corona micelles for OSF. The former requires intimate mixing of S and B segments in the core, which is consistent with the known degree of segregation of these two blocks.<sup>27</sup> The product of degree of polymerization  $N$  and interaction parameter  $\chi$  is about 5 for the SB pair,<sup>27</sup> well below the mean-field theory value required for microphase separation of 12.<sup>28</sup> The dramatic shape change induced by chemical modification of the B block is also in harmony with this picture. The degree of segregation between S and F is at least 50, based on previous analysis for SF diblocks.<sup>27</sup> Thus, F and S should be very well segregated. Furthermore, for this composition, an S–F diblock would be expected to adopt a lamellar phase, with

a flat interface. The ellipticity can therefore be understood as a compromise between the desired interfacial curvatures of S/F in the core, and S/water+O in the corona. The core dimensions of both micelles imply very large aggregation numbers, ca. 3000, and significant stretching of the individual blocks (typically by a factor of 2–3); both observations also support a very strongly segregated micellar system.

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**Supporting Information Available:** Experimental details and Figures S1–S4 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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