

Supporting Information for:

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

Zhilian Zhou,¹ Zhibo Li,² Yu Ren,² Marc A. Hillmyer^{2*} and Timothy P. Lodge^{1,2*}

¹Department of Chemical Engineering and Materials Science, ²Department of Chemistry, University of Minnesota, Minneapolis, MN 55455

Received date; Email: hillmyer@chem.umn.edu, lodge@chem.umn.edu

Synthetic protocol for OSB and OSF

Materials: All materials were purchased from Aldrich and used without further purification unless noted. Styrene was stirred over CaH₂ at room temperature for 12 h and distilled into a flask containing dibutylmagnesium, and was then stirred over dibutylmagnesium for 5 h at room temperature. Butadiene was purified by stirring over dibutylmagnesium and *n*-butyllithium successively at 0 °C for 4 h. Ethylene oxide was stirred over dibutyl magnesium for 4 h in ice/water bath. Potassium naphthalenide solution was prepared according to the procedure described by Hillmyer and Bates.¹ Naphthalene was added to a stirring dispersion of freshly cut potassium in tetrahydrofuran (THF) under a purge of argon. The green color of the potassium naphthalenide appeared immediately, and the solution was stirred at room temperature for at least 12 h before use. The concentration of the potassium naphthalenide solution was determined by addition of a 10 mL aliquot of the dark green solution to water and titration with a standardized HCl solution using phenolphthalein as indicator. Cyclohexane and THF were purified by passing through an activated alumina column (Laroche) to remove protic impurities and through a supported copper catalyst (Engelhard) to remove trace oxygen, using a home-built solvent purification system.

Step 1: Synthesis of TBDMSO-PS-*b*-PB diblock precursor. A polystyrene-*b*-polybutadiene diblock precursor was first prepared by using 3-(*t*-butyldimethylsilyloxy)-1-proxy lithium (TBDMSOLi) as the initiator (TBDMSO-PS-*b*-PB). A 2 L round-bottom flask equipped with five internal ACETHREDS ports was heated to 250 °C at 5 mTorr overnight to remove any adsorbed water. After cooling, cyclohexane (ca. 1 L) and THF (ca. 20 mL, 30 fold excess relative to Li) was added to the flask. THF was used to avoid the slow initiation of styrene by the primary alkyl lithium initiator (TBDMSOLi) in pure cyclohexane and to control the microstructure of the resulting PB block. TBDMSOLi (19.5 mL, 0.0116 mol) and purified styrene (54.6g) were then added to the reactor and the rapid initiation was indicated by the quick appearance of the dark orange-red color. The reaction mixture was stirred at 45 °C for 4 h to achieve complete polymerization and was then cooled to 10 °C. Purified butadiene (15.1g) was slowly added. The reaction mixture was warmed to 18 °C and stirred for 3 h. The living chains were terminated by injection of excess degassed 2-propanol. The polymer was precipitated out in 1:1 mixture of 2-propanol and methanol and vacuum dried at room temperature.

Step 2: Deprotection of the TBDMSO end groups. To substitute the TBDMSO groups at the PS chain ends, the diblock precursor was mixed with 5 fold excess of tetrabutylammonium fluoride (TBAF) in THF and stirred at room temperature for 20 h. The reaction mixture was quenched with excess HCl solution in water.

*Step 3: Preparation of PEO-*b*-PS-*b*-1,2-PB triblock copolymer.* 9.0g diblock precursor was dissolved in anhydrous THF at room temperature. To transfer the hydroxy end groups to the corresponding potassium alkoxide, the polymer solution was slowly titrated with a THF/potassium naphthalenide mixture of known concentration. At the end point, a slight green color was observed and persisted for at least 30 min. After the titration, purified ethylene oxide monomer (18.6g) was added to the reaction flask slowly, and the reaction mixture was stirred at 45 °C for 20 h. Termination of the polymerization was accomplished by the addition of slightly acidic (HCl) methanol. The resulting hydroxy terminated block copolymers were isolated by filtration (KCl precipitated upon termination) and concentrated using a rotary evaporator. The block copolymers were purified by dissolving in chloroform and washing with distilled water.

*Step 4: Preparation of PEO-*b*-PS-*b*-1,2-PB:C₆F₁₃I triblock copolymer.* PEO-*b*-PS-*b*-1,2-PB:C₆F₁₃I (OSF) triblock copolymer was prepared by fluorinating the OSB triblock copolymer with *n*-perfluorohexyl iodine (C₆F₁₃I) following the procedure developed for PS-*b*-1,2-PB diblocks.² Before adding solvents and reactant, the 100 mL round bottom flask was purged with nitrogen for half an hour. The OSB triblock copolymer (2.9g, 0.0036mol of olefinic sites) was dissolved in 60 mL of 1:1 mixture of hexane and α,α,α -trifluorotoluene (BTF). 1 fold of *n*-perfluorohexyl iodine (C₆F₁₃I) and 0.5 fold triethylborane solution (1.0M in hexane) were injected into the reaction flask under nitrogen flow. The reaction mixture was stirred for 72 h under slow air flow (10cc/min) through a 3-way adapter connected to the reaction flask and a bubbler. The reaction mixture was concentrated using a rotary evaporator, precipitated in 0.6 L hexane, and dried under vacuum at room temperature for 48 h.

Dynamic Light Scattering (DLS)

DLS measurements were conducted on a home-built instrument equipped with a Lexel 95-2 Ar laser operating at 488 nm, a Brookhaven BI-DS photomultiplier, and a Brookhaven BI-9000 correlator.

Small Angle Neutron Scattering (SANS)

SANS experiments were carried out on the NG-7 30 m instrument of the Cold Neutron Research Facility at the National Institute of Standards and Technology (NIST). A sample to detector distance of 15 m was used to cover the scattering vector (*q*) range of $0.004 \text{ \AA}^{-1} < q < 0.03 \text{ \AA}^{-1}$. Here the scattering vector magnitude *q* is defined as $q = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle. The monochromated neutron wavelength (λ) was 6 Å and the wavelength spread ($\Delta\lambda/\lambda$) was 0.11. The resulting data were corrected for background electronic noise, nonuniform detector efficiency, solvent plus empty cell scattering, and sample transmission. For the mixed solvent of H₂O and D₂O, the scattering length density of the solvent is

$$\rho_0 = \phi(\text{D}_2\text{O}) \rho(\text{D}_2\text{O}) + (1 - \phi(\text{D}_2\text{O})) \rho(\text{H}_2\text{O})$$

where $\phi(\text{D}_2\text{O})$ is the volume fraction of D_2O .

Small Angle X-ray Scattering (SAXS)

SAXS measurements were performed using beam line 5ID-D, in the Dupont-Northwestern-Dow (DND-CAT) synchrotron research facility at the Advanced Photon Source, Argonne National Laboratory. A sample to detector distance of 6.8 m was used to access the necessary q range, and the exact q values were calibrated by a standard diblock copolymer. Two-dimensional SAXS images were collected by a charge-coupled device detector (Roper), and the scattering data were corrected for solvent plus cell scattering.

Transmission Electron Microscopy (TEM)

TEM samples were prepared in the following way: a droplet of polymer solution was placed on a microperforated TEM grid and was then soaked by filter paper. This resulted in the formation of thin liquid film of 10-300 nm thickness freely spanning across the micropores in a carbon-coated lacelike polymer layer supported by a meshy metal grid. The liquid film was left in air at room temperature to evaporate solvent. Since the glass transition of the PS block is far above room temperature, the micelle structure is retained as the solvent evaporates. TEM images were taken with a JEOL 1210 operating at 120 kV. Adequate phase contrast was obtained at a nominal underfocus of 3-26 μm . Images were recorded on a Gatan 724 multiscan digital camera and processed with Digital Micrographs version 3.1. Examination of many more micelles by TEM indicates an apparent polydispersity that is similar for both OSB and OSF micelles, but moderately greater (due to some even larger objects) than indicated by any of the scattering results. The scattering results are deemed to be more reliable, both because they were made on quiescent solutions rather than after a deposition/evaporation process, and because of the known sensitivity of scattering to any population of larger aggregates.

Reference:

- (1) Hillmyer, M. A.; Bates, F. S. *Macromolecules* **1996**, 29, 6994-7002.
- (2) Ren, Y.; Lodge, T. P.; Hillmyer, M. A. *Macromolecules* **2001**, 34, 4780-4787.

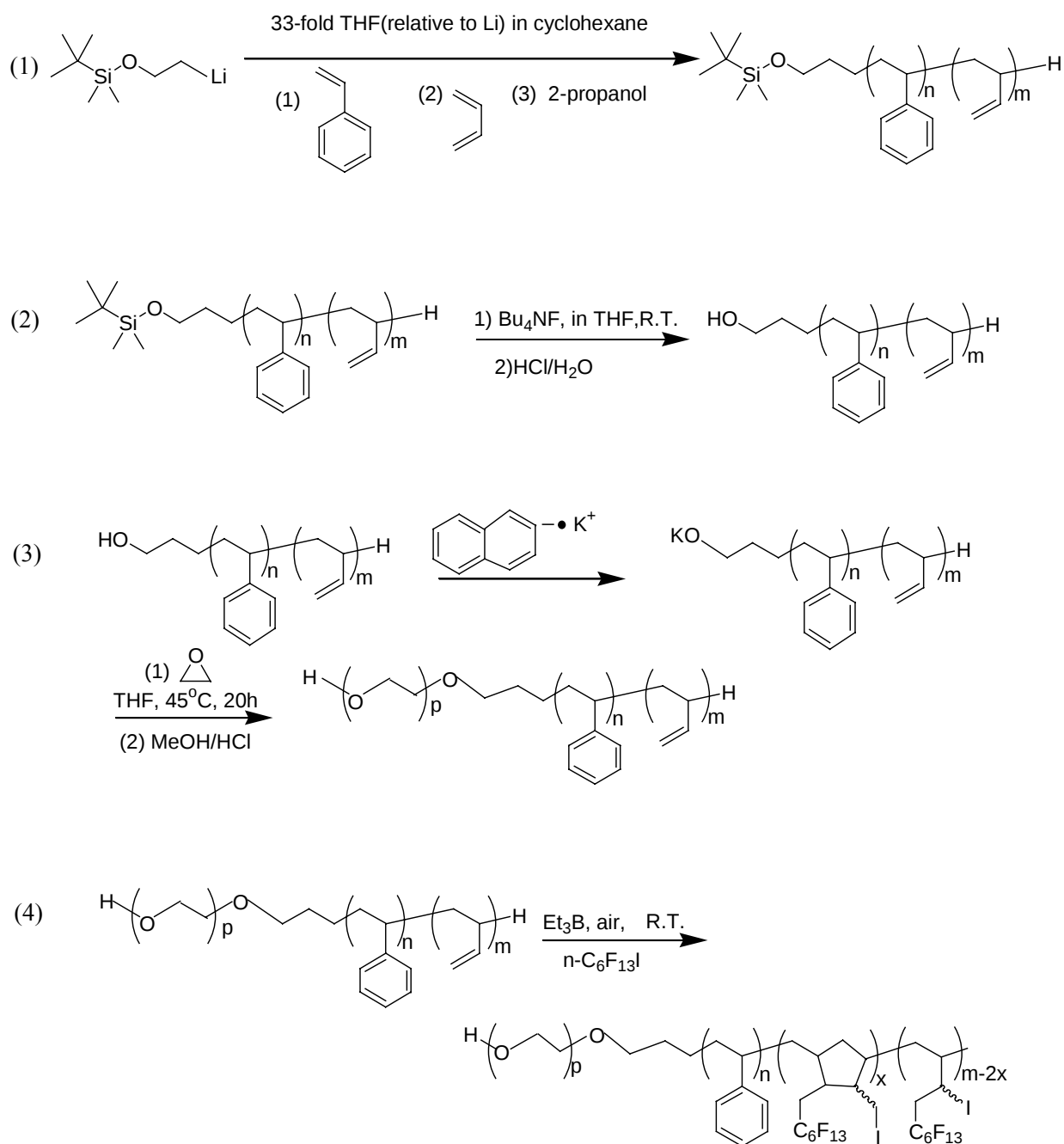


Figure S1. Synthesis route for the preparation of OSB and OSF triblock copolymers. (1) Preparation of TBDMSO-PS-*b*-1,2-PB diblock precursor. (2) Deprotection of the TBDMSO end groups. (3) Preparation of PEO-*b*-PS-*b*-1,2-PB triblock copolymer. (4) Preparation of PEO-*b*-PS-*b*-1,2-PB:C₆F₁₃I triblock copolymer.

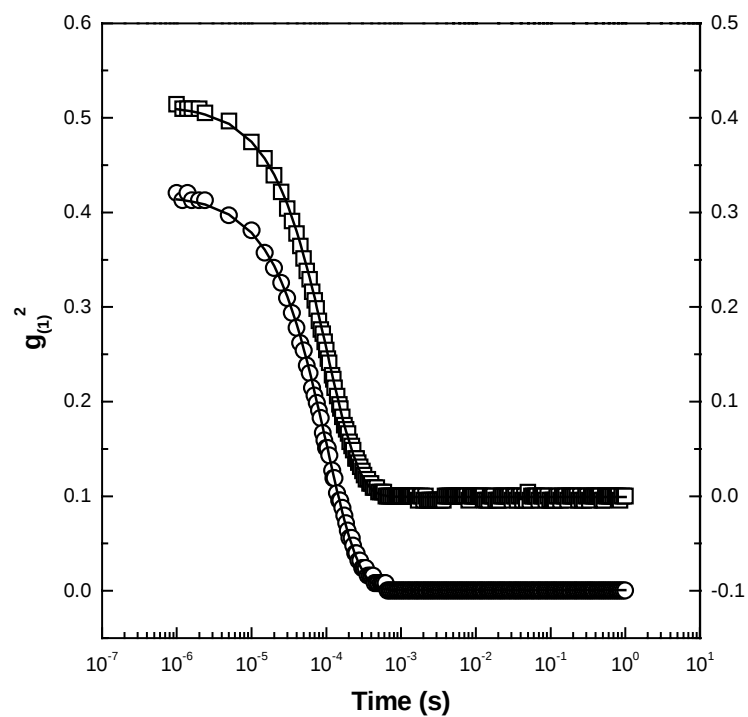


Figure S2. Intensity auto correlation functions ($\theta=110^\circ$) of OSB ($\square$) and OSF ($\circ$) aqueous solutions and corresponding single exponential fits.

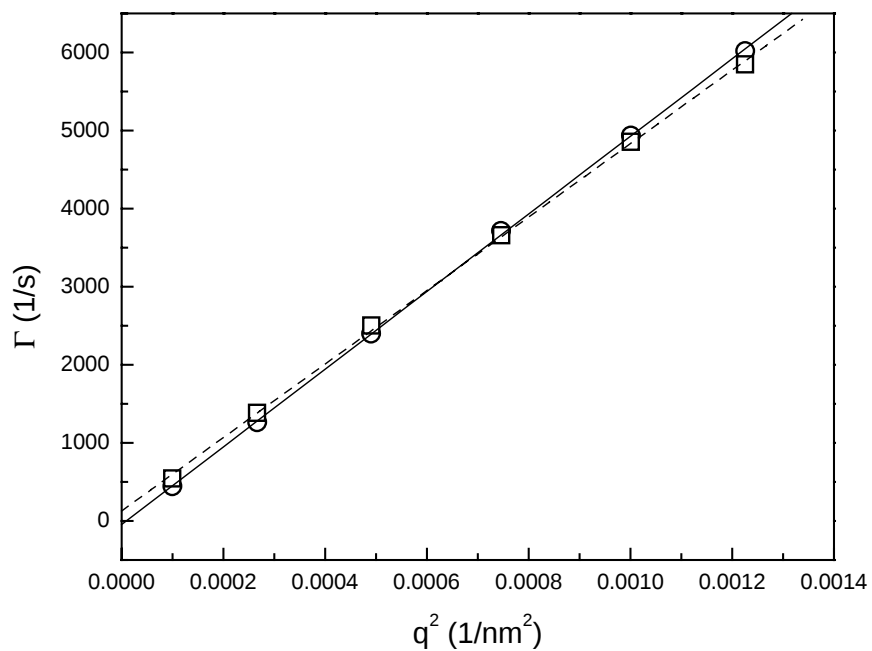


Figure S3. Angle dependence of decay rates (Γ) of OSB ($\square$) and OSF ($\circ$) aqueous solutions and corresponding linear fits.

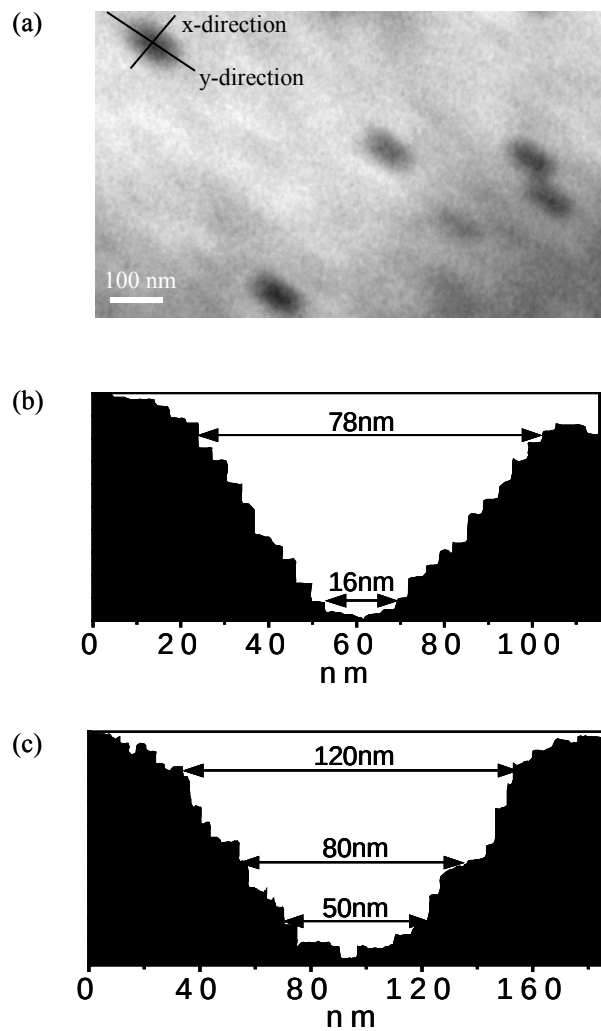


Figure S4. TEM image of OSF micelles and optical density profiles of a typical micelle along two orthogonal directions: (b) x-direction; (c) y-direction. The plateaus in (c) hint at the three-layer structure of OSF micelles.