

Redox-Controlled Micellization of Organometallic Block Copolymers

David A. Rider,^a Mitchell A. Winnik^{a,*} and Ian Manners^{b,*}

Supplementary Information

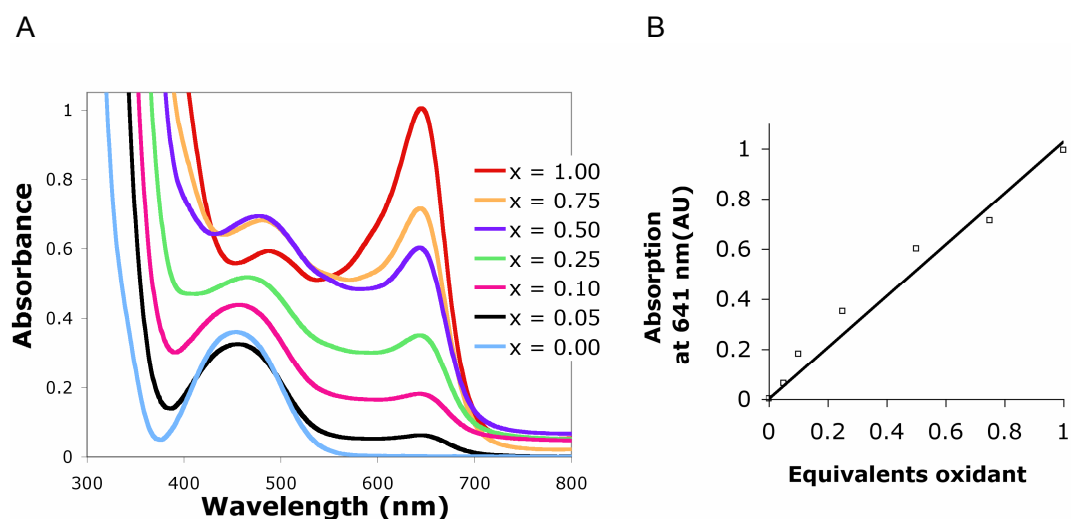


Figure S1. (A) UV-vis spectra of **PS₅₄₈-b-PFMPS₇₃** in CH₂Cl₂ for various molar ratios (x) of [N(C₆H₄Br-4)₃][SbF₆] as oxidant. (B) Dependence of absorbance of LMCT band on molar ratio of the oxidant.

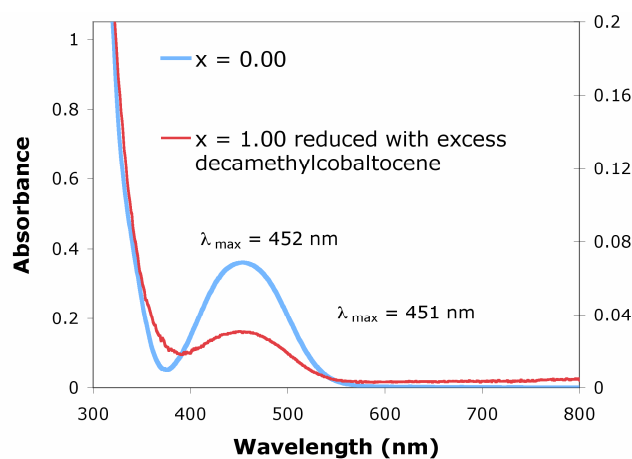


Figure S2. UV-vis spectra in CH₂Cl₂ of **PS₅₄₈-b-PFMPS₇₃** as synthesized ($x = 0.00$) and following oxidation ($x = 1.00$) with [N(C₆H₄Br-4)₃][SbF₆] and reduction with excess decamethylcobaltocene.

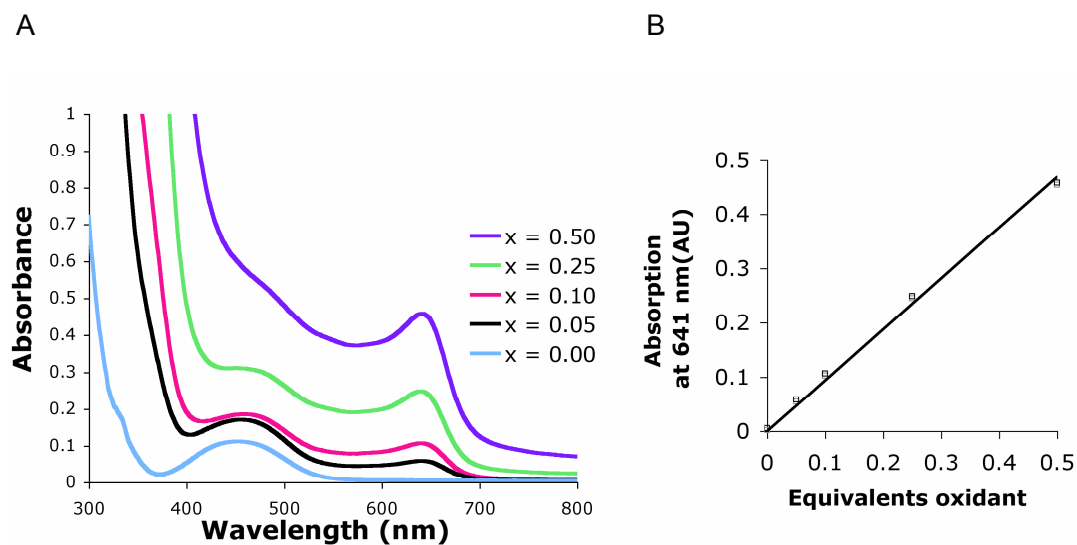


Figure S3. UV-vis spectra of $\text{PS}_{389}\text{-}b\text{-PFEMS}_{108}$ in CH_2Cl_2 for various molar ratios (x) of $[\text{N}(\text{C}_6\text{H}_4\text{Br}-4)_3][\text{SbCl}_6]$ as oxidant. (B) Dependence of absorbance of LMCT band on molar ratio of the oxidant.

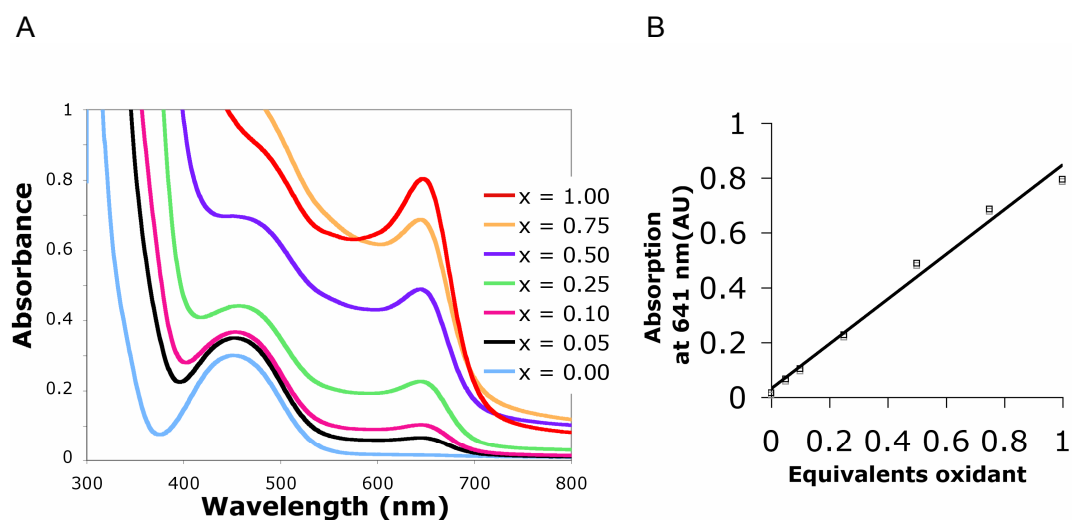


Figure S4. UV-vis spectra of $\text{PS}_{548}\text{-}b\text{-PFMPS}_{73}$ in CH_2Cl_2 for various molar ratios (x) of $[\text{N}(\text{C}_6\text{H}_4\text{Br}-4)_3][\text{SbCl}_6]$ as oxidant. (B) Dependence of absorbance of LMCT band on molar ratio of the oxidant.

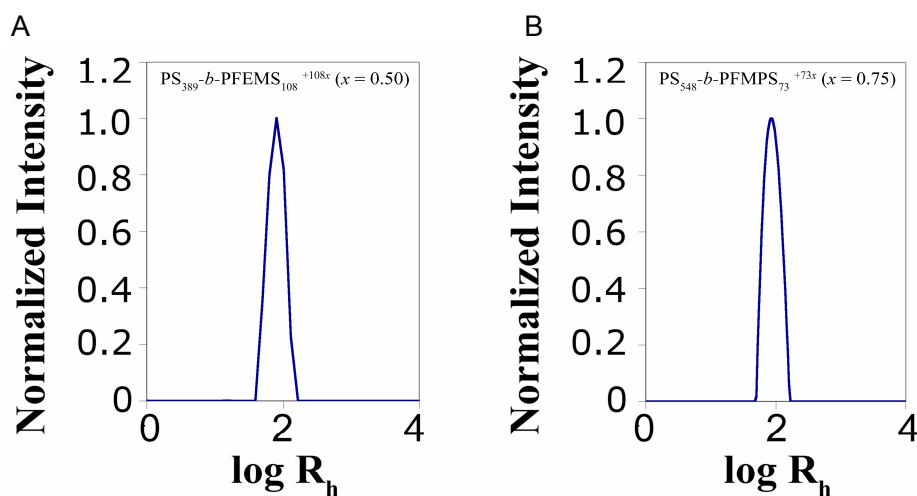


Figure S5. Dynamic light scattering CONTIN plots for (A) $\text{PS}_{389}\text{-}b\text{-PFEMS}_{108}$ following oxidation ($x = 0.50$) with $[\text{N}(\text{C}_6\text{H}_4\text{Br-4})_3][\text{SbCl}_6]$ in CH_2Cl_2 ($R_h = 79$ nm, % PD $\sim 3\%$) and (B) $\text{PS}_{548}\text{-}b\text{-PFMPS}_{73}$ following oxidation ($x = 0.75$) with $[\text{N}(\text{C}_6\text{H}_4\text{Br-4})_3][\text{SbCl}_6]$ in CH_2Cl_2 and ($R_h = 89$ nm, %PD $\sim 3\%$).

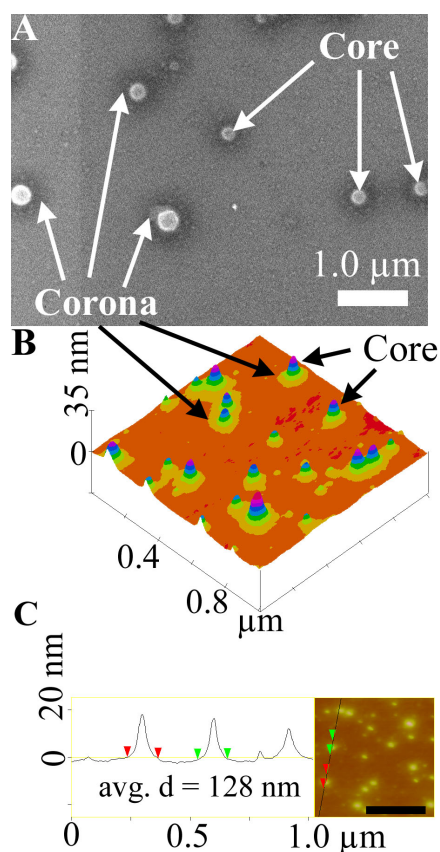


Figure S6. (A) SEM and (B) 3-D AFM height images of $\text{PS}_{548}\text{-}b\text{-PFMPS}_{73}^{+73x}$ ($x = 0.75$) micelles produced from oxidation with $[\text{N}(\text{C}_6\text{H}_4\text{Br-4})_3][\text{SbCl}_6]$ in CH_2Cl_2 . The polystyrene corona of the micelles is observed as a halo surrounding each PFMPS^+ core. (C) Width estimate of structures at zero height as defined by line trace in 2-D AFM image at right (inset scale bar = 500 nm).

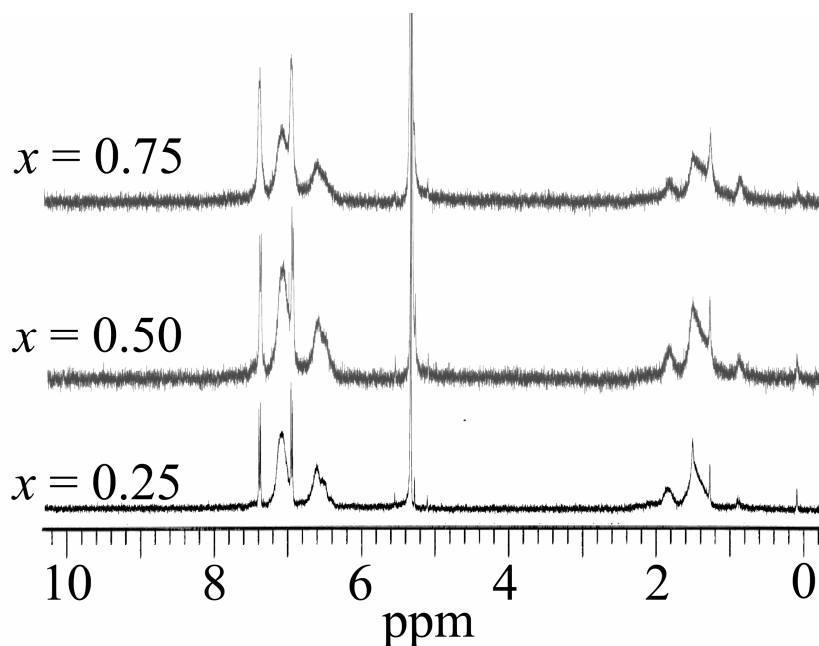


Figure S7. $^1\text{H-NMR}$ of $\text{PS}_{548}\text{-b-PFMPS}_{73}^{+73x}$ ($x = 0.25, 0.50, 0.75$) micellar solutions produced from oxidation with $[\text{N}(\text{C}_6\text{H}_4\text{Br-4})_3][\text{SbCl}_6]$ in CD_2Cl_2 . $^1\text{H-NMR}$ (d, CD_2Cl_2): 1.49 (br, $\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)$), 1.82 (br, $\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)$), 6.60, 7.07 (br, $\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)$), 6.96, 7.40 (s, $\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3$). The polystyrene $^1\text{H-NMR}$ signals persist with increasing degrees of oxidation suggesting a well solvated polystyrene corona is present for the $\text{PS}_{548}\text{-b-PFMPS}_{73}^{+73x}$ ($x = 0.25, 0.50, 0.75$) micellar solutions.

Experimental

Equipment and materials. Dichloromethane was dried by refluxing over calcium hydride followed by distillation under reduced pressure. Tris(4-bromophenyl)-ammoniumyl hexachloroantimonate ($[\text{N}(\text{C}_6\text{H}_4\text{Br-4})_3][\text{SbCl}_6]$) was used as received from Aldrich. The $^1\text{H-NMR}$ spectra were obtained from a Varian Gemini 300 spectrometer. Molecular weights were determined by gel permeation chromatography (GPC) using a Viscotek GPC MAX liquid chromatograph equipped with a Viscotek Triple Detector Array. The triple detector array consists of a refractometer, a four-capillary differential viscometer, a 90° angle laser and a low-angle laser (7°) light scattering detector ($\lambda_0 = 670$ nm). The triple-detector system has been shown to provide absolute M_w values for PFS homopolymers,¹ and we assume that it provides accurate values of M_w/M_n . A molecular weight versus elution time calibration curve was generated from 12-15 narrow molecular weight polystyrene standards ($2\text{k} < M_n < 220\text{k}$, $\text{PDI} < 1.10$, Aldrich). A flow rate of 1.0 mL/min was used with THF as the eluent. Transmission electron microscopy (TEM) images were obtained using a Hitachi HD2000 electron microscope with an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4500 Field-Emission scanning electron microscope operating at 1.0 kV. Samples were not coated with any conductive coating prior to imaging. Dynamic light scattering (DLS) measurements were performed using a wide-angle light scattering photometer from ALV. The light source was a JDS Uniphase He-Ne laser ($\lambda_0 = 632.8$ nm, 35 mW) emitting vertically polarized light. The cells were placed into the ALV/DLS/SLS-5000 Compact Goniometer System and sat in a vat of thermostated *cis*-decahydronaphthalene, which matched the index of refraction of the glass cells. The angular range of the goniometer is $12\text{-}155^\circ$. The scattered light was detected by a Dual ALV-High Q.E. APD avalanche photodiode module. This detector was interfaced to the ALV-5000/EPP multiple tau digital correlator with 288 exponentially spaced channels that measured the correlation function in real time. Upon a cumulant analysis, we obtained a first order cumulant from which apparent hydrodynamic radii of the micelles were obtained and a second order cumulant, indicating width of the size distribution that can be used as an polydispersity index of the micelles. All measurements were carried out at room

Supplementary Material (ESI) for Chemical Communications

This journal is (c) The Royal Society of Chemistry 2007

temperature (r.t.). DLS experiments were performed at an angle of 90°. Atomic force microscopy (AFM) operated in tapping mode was performed on a Multimedia Nanoscope IIIa AFM (Digital instrument/Veeco-Metrology Group). The AFM tips had resonant frequencies close to 170 kHz.

Synthesis of tris(4-bromophenyl)-ammoniumyl hexafluoroantimonate. The complete synthetic details concerning the synthesis of tris(4-bromophenyl)-ammoniumyl hexafluoroantimonate ($[\text{N}(\text{C}_6\text{H}_4\text{Br}-4)_3][\text{SbF}_6]$) used in this study have been published elsewhere.²

Synthesis of polystyrene-*block*-polyferrocenylsilane diblock copolymers. The complete synthetic details concerning the synthesis of the **PS-*b*-PFMPS** materials used in this study have been published elsewhere.³ The complete synthetic details concerning the synthesis of **PS-*b*-PFEMS** materials used in this study have been published elsewhere.⁴ By size exclusion chromatography (based on absolute molecular weight analysis using the combination of ¹H-NMR and GPC, error approx. = 10%), Mn (PDI) of **PS-*b*-PFMPS** as synthesized = 79.5K (1.08) and Mn (PDI) of **PS-*b*-PFEMS** as synthesized = 68.2k (1.04).

Sample Preparation for Transmission and Scanning Electron Microscopy and Atomic Force Microscopy. TEM samples were prepared at room temperature (23 °C) by placing a drop of the micelle sample solution onto a precoated copper grid which was placed on filter paper. Excess fluid was then removed with a clean piece of filter paper. Before every TEM session, the electron beam was aligned to minimize optical artifacts. For SEM and AFM characterization of isolated micelles, a 10 fold dilution of the above solution was done followed by the immersion of a precleaned silicon wafer.

Sample preparation for dynamic light scattering measurements. Disposable 10 mm × 75 mm glass cells for light scattering were purchased from Fisher Scientific Chemicals. These were cleaned in an acetone still for 15 min. The cells were then removed from the still, and the open end was immediately tightly wrapped with Al foil. Sealed cells were placed in an oven at 120 °C for 1 h to evaporate any residual acetone trapped in the cell. Micelle solutions of oxidized **PS-*b*-PFMPS** in CH₂Cl₂ for light scattering studies were prepared by transferring the filtered solutions (0.45 μm pore size) to the cleaned glass cells. The cells were capped with a rubber septa to avoid any solvent evaporation or infiltration of dust.

Oxidation of PS-*b*-PFMPS and PS-*b*-PFEMS block copolymers with tris(4-bromophenyl)ammoniumyl hexafluoroantimonate and tris(4-bromophenyl)ammoniumyl hexachloroantimonate and subsequent treatment with decamethylcobaltocene. The following standard procedure for oxidation of 5 mol % of the ferrocene units in the **PS-*b*-PFMPS** block copolymer using a corresponding amount of $[\text{N}(\text{C}_6\text{H}_4\text{Br}-4)_3][\text{SbF}_6]$ as a one electron oxidant is typical. Similarly, a series of experiments involving 0.10, 0.25, 0.50, 0.75, and 1.00 mol equivalents of $[\text{N}(\text{C}_6\text{H}_4\text{Br}-4)_3][\text{SbF}_6]$ were carried out so that the reaction mixture had the same final concentration of monomer units. An analogous procedure was used for experiments using $[\text{N}(\text{C}_6\text{H}_4\text{Br}-4)_3][\text{SbCl}_6]$ or the **PS-*b*-PFEMS** block copolymer. 0.5 mL of a 1×10^{-3} M CH₂Cl₂ solution of $[\text{N}(\text{C}_6\text{H}_4\text{Br}-4)_3][\text{SbF}_6]$ was added to a 10.5 mL stirred CH₂Cl₂ solution of the **PFMPS** block copolymer (0.01 mmol of **PFMPS** monomer units). The yellow/amber color of polymer solutions changed within the first hour to light green or dark green depending on the molar ratio of the added oxidizing agent. After 6 h no precipitate formation was observed in all cases except for oxidations of **PS-*b*-PFEMS** block copolymer with 0.75, and 1.00 mol equiv of $[\text{N}(\text{C}_6\text{H}_4\text{Br}-4)_3][\text{SbCl}_6]$. At this point the UV-vis spectra of the polymeric salt solutions were acquired. UV-vis (25 °C, CH₂Cl₂): λ_{max} = 440–450 nm, 641 nm (for x mol equivalents higher than 0.25). For reduction, an excess of decamethylcobaltocene (> 10 fold excess to moles of oxidant) was added directly to CH₂Cl₂ solutions of the semi-oxidized **PS-*b*-PFMPS** block copolymers and stirred for 24–48 hrs in an inert atmosphere glove box. After precipitation and washing using pentane and methanol, an orange powder was isolated (25–50% yield). By size exclusion chromatography (based on PS standards, error approx. = 10%), Mn (PDI) of **PS-*b*-PFMPS** as synthesized = 49.6K (1.15); Mn (PDI) of **PS-*b*-PFMPS** oxidized to $x = 1.00$ mol equivalents with $[\text{N}(\text{C}_6\text{H}_4\text{Br}-4)_3][\text{SbF}_6]$ then reduced with excess decamethylcobaltocene = 45.7K (1.19).

Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2007

References:

- (1) Massey, J. A.; Kulbaba, K.; Winnik, M. A.; Manners, I. *J. Polym. Sci., Polym. Phys.* **2000**, *38*, 3032.
- (2) Engel, P. S.; Robertson, D. M.; Scholz, J. N.; Shine, H. J. *J. Org. Chem.* **1992**, *57*, 6178-6187.
- (3) Temple, K.; Massey, J. A.; Chen, Z.; Vaidya, N.; Berenbaum, A.; Foster, M. D.; Manners, I. *J. Inorg. Organomet. Polym.* **1999**, *9*, 189.
- (4) Rider, D. A.; Cavicchi, K. A.; Power-Billard, K. N.; Russell, T. P.; Manners, I. *Macromolecules* **2005**, *38*, 6931.