

Redox-controlled micellization of organometallic block copolymers†

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

Received (in Berkeley, CA, USA) 19th March 2007, Accepted 16th July 2007

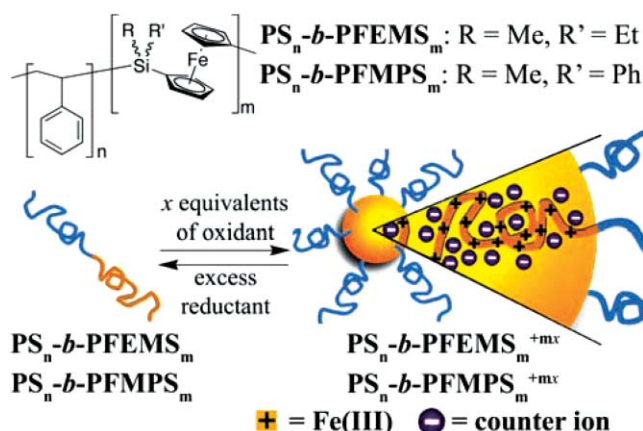
First published as an Advance Article on the web 3rd September 2007

DOI: 10.1039/b704200k

Polystyrene-*block*-polyferrocenylsilane (PS-*b*-PFS) diblock copolymers were stoichiometrically oxidized in solution using salts of the one-electron oxidant tris(4-bromophenyl)ammonium. Due to a redox-induced polarity change for the PFS block, self-assembly into well-defined spherical micelles occurs. The micelles are composed of a core of partially oxidized PFS segments and a corona of PS. When the micellar solutions were treated with the reducing agent decamethylcobaltocene, the spherical micelles disassemble and regenerate unassociated and pristine PS-*b*-PFS free chains.

The development of new methods to control the formation of self-assembled nanostructures is of considerable current interest.¹ Indeed, stimuli, such as pH, temperature, light, pressure, and concentration have already been investigated with respect to triggered self-assembly in various fields.² Diblock copolymers, comprised of two different polymer segments covalently linked at a common junction, are well-known to undergo solution state self-assembly to form spherical, cylindrical and plate-like micelles as well as many other morphologies. Typically, block selective solvents are used to induce insoluble polymer segments to form a core whilst creating a solvent-swollen corona from the solvent compatible block.³ In this communication we report a new conceptual approach to induce self-assembly of block copolymers which involves the reversible redox-triggered changes in polarity of a metal-containing block.⁴

Polyferrocenylsilane block copolymers contain iron centers in the main chain which can be reversibly interconverted between Fe(II) and Fe(III) states.^{5,6} This process is accompanied by a large change in polarity in which neutral hydrophobic organometallic chains become cationic polyelectrolytes and hydrophilic.⁷ Herein we studied the influence of the stoichiometric tuning of the degree of oxidation of the polyferrocenylsilane block on the solution state self-assembly of organic-organometallic polystyrene (PS) diblock copolymers with amorphous poly(ferrocenylmethylphenylsilane) (PFMPs) and poly(ferrocenylethylmethylsilane) (PFEMS) coblocks (see Scheme 1). The number average molecular weight (M_n) and polydispersity index (PDI) of PS₅₄₈-*b*-PFMPs₇₃ was 79,500 and 1.08, respectively. For PS₃₈₉-*b*-PFEMS₁₀₈, M_n = 67,900 and PDI = 1.04. The hexafluoroantimonate ([SbF₆][−]) salt



Scheme 1 Reversible redox controlled micelle formation in CH₂Cl₂ using PS-*b*-PFMPs and PS-*b*-PFEMS. The oxidants and reductant are [N(C₆H₄Br-4)₃][SbF₆] or [N(C₆H₄Br-4)₃][SbCl₆] and decamethylcobaltocene, respectively.

of the stoichiometric one-electron oxidant tris(4-bromophenyl)ammonium cation, [N(C₆H₄Br-4)₃]⁺, and decamethylcobaltocene, (Co(η-C₅Me₅)₂), were used as the oxidizing and reducing agents, respectively. Dichloromethane was the chosen solvent, given its high compatibility with all neutral polymeric segments and the redox agents.

Treatment of a series dichloromethane solutions of PS₅₄₈-*b*-PFMPs₇₃ (the concentration of ferrocenyl units was ~10^{−2} M in all cases) with increasing amounts of [N(C₆H₄Br-4)₃][SbF₆] (~10^{−3} M in CH₂Cl₂) afforded the corresponding solutions of PS₅₄₈-*b*-PFMPs₇₃^{+73x} (0.00 ≤ *x* ≤ 1.00; *x* = moles oxidant per mole ferrocenyl units). After ~6 h, UV-vis spectra were obtained for the series and confirmed the quantitative consumption of the oxidant (λ_{max} ≈ 700 nm) and an increasing concentration of polymer-based ferrocenium centers (λ_{max} ≈ 641 nm).⁸

Dark field transmission electron microscopy (DF-TEM) and dynamic light scattering (DLS) were used to confirm solution state self-assembly. The DF-TEM of PS₅₄₈-*b*-PFMPs₇₃^{+73x} (*x* = 0.75) shown in Fig. 1A reveals well-defined, electron-rich spherical PFMPs-based micellar cores presumably surrounded by “invisible” PS coronas in a close packed array. DLS of this sample also confirmed the presence of well-defined aggregates in solution (see Fig. 1B) with no evidence for unassociated diblock copolymer chains (hydrodynamic radius (*R*_h) ~ 6 nm). An apparent *R*_h of 33 nm and a percent polydispersity (% PD) of ~4%, were found by cumulant analysis.

In attempt to reverse the self-assembly of the spherical micelles and thus to regenerate the unassociated PS-*b*-PFMPs chains, chemical reduction was conducted. By treating the PS₅₄₈-*b*-PFMPs₇₃^{+73x} (0.00 ≤ *x* ≤ 1.00) solutions with an excess of

^aDepartment of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6.

E-mail: mwinnik@chem.utoronto.ca; Fax: +1 416 978 0541;

Tel: +1 416 978 6495

^bSchool of Chemistry, University of Bristol, Bristol, England BS8 1TS.

E-mail: ian.manners@bristol.ac.uk; Fax: +44(0) 117 929 0509;

Tel: +44(0) 117 928 7650

† Electronic supplementary information (ESI) available: detailed experimental procedures and characterization. See DOI: 10.1039/b704200k

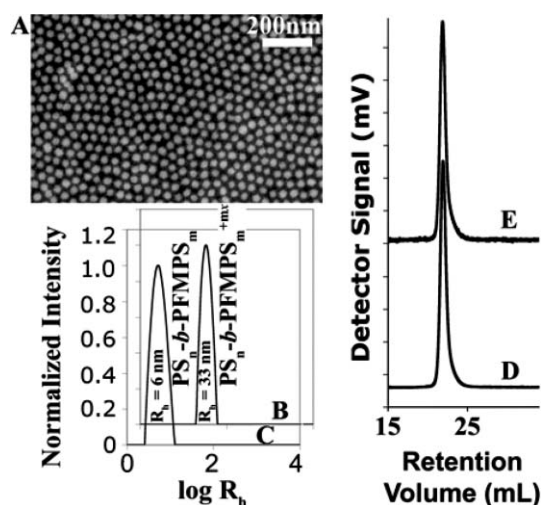


Fig. 1 DF-TEM image (A) and DLS CONTIN plot (B) of $\text{PS}_{548}\text{-}b\text{-PFMPS}_{73}^{+73x}$ ($x = 0.75$) produced using $[\text{N}(\text{C}_6\text{H}_4\text{Br-4})_3][\text{SbF}_6]$. (C) DLS CONTIN plot of product acquired by reduction of sample from (B) using excess decamethylcobaltocene. (D and E) GPC traces of $\text{PS}_{548}\text{-}b\text{-PFMPS}_{73}$ as synthesized and following oxidation/reduction using $[\text{N}(\text{C}_6\text{H}_4\text{Br-4})_3][\text{SbF}_6]$ ($x = 1.00$) and excess decamethylcobaltocene, respectively.

decamethylcobaltocene, reversion to the unassociated $\text{PS}_{548}\text{-}b\text{-PFMPS}_{73}$ chains occurred. The DLS in Fig. 1C confirmed the disappearance of the spherical micelles and the reappearance of the unimers with $R_h = 6$ nm. To ensure that the complete oxidation and reduction cycle was non-destructive to the diblock copolymer, the gel permeation chromatograms (GPC, right angle light scattering detection) of the as-synthesized $\text{PS}_{548}\text{-}b\text{-PFMPS}_{73}$ material and the polymer isolated from the reduction of the fully oxidized $\text{PS}_{548}\text{-}b\text{-PFMPS}_{73}^{+73x}$ ($x = 1.00$) micellar solution were compared (Fig. 1D and 1E). The molecular weight and PDI of the two samples were within experimental error of one another thus confirming the reversibility of the redox-controlled self-assembly process.⁸

We expanded our studies of redox-controlled self-assembly to other block copolymers. In addition, the oxidant counteranion was changed to $[\text{SbCl}_6]^-$ to permit energy dispersive X-ray (EDX) analysis. Oxidation of a series of $\text{PS}_{389}\text{-}b\text{-PFEMS}_{108}$ and $\text{PS}_{548}\text{-}b\text{-PFMPS}_{73}$ solutions with increasing amounts (x) of $[\text{N}(\text{C}_6\text{H}_4\text{Br-4})_3][\text{SbCl}_6]$ was performed. Precipitation of a blue oxidized material was observed for $\text{PS}_{389}\text{-}b\text{-PFEMS}_{108}^{+108x}$ ($x > 0.50$) thus preventing solution characterization. For the remaining samples, UV-vis and DLS confirmed the stoichiometric oxidation and micellization. Shown in Fig. 2A and 2B are the DF-TEM images of illustrative well-defined electron-rich micellar cores for the $\text{PS}_{389}\text{-}b\text{-PFEMS}_{108}^{+108x}$ and $\text{PS}_{548}\text{-}b\text{-PFMPS}_{73}^{+73x}$ solutions ($x = 0.50, 0.75$ respectively). By DLS, the micellar R_h values were 79 nm (% PD $\sim 3\%$) and 89 nm (% PD $\sim 3\%$), respectively.⁸ For chemical analysis of the micellar core, elemental spectra from an EDX line trace intersecting 6 individually isolated $\text{PS}_{548}\text{-}b\text{-PFMPS}_{73}^{+73x}$ ($x = 0.75$) micelles was obtained (Fig. 2C, aqua line is C-trace). Shown in Fig. 2D–G are the EDX plots for Fe, Si, Sb and Cl signals, respectively. The well-defined traces for 6 differently sectioned micelles verify the chemical uniformity of the micellar core. Given the coinciding signals for these elements, a

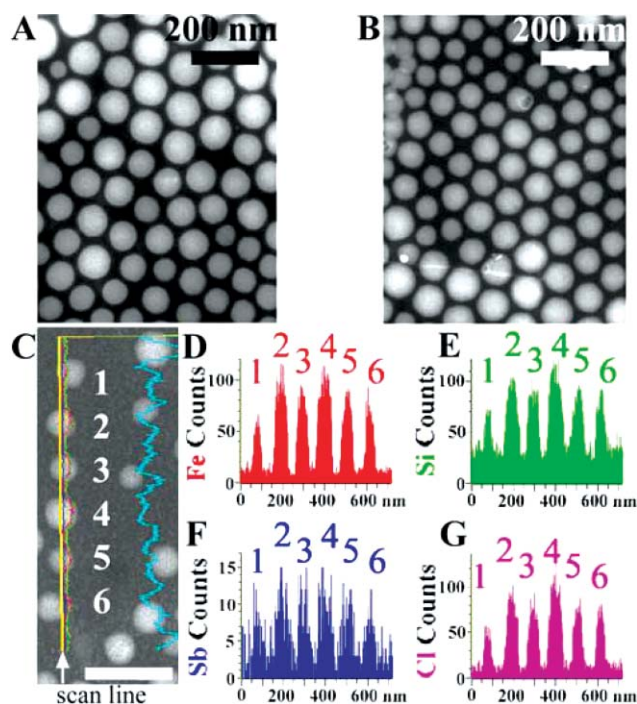


Fig. 2 DF-TEM images of (A) $\text{PS}_{389}\text{-}b\text{-PFEMS}_{108}^{+108x}$ ($x = 0.50$) and (B) $\text{PS}_{548}\text{-}b\text{-PFMPS}_{73}^{+73x}$ ($x = 0.75$) produced using $[\text{N}(\text{C}_6\text{H}_4\text{Br-4})_3][\text{SbCl}_6]$. EDX traces for Fe, Si, Sb, and Cl (D–G respectively) defined by scan line in DF-TEM image (C) for $\text{PS}_{548}\text{-}b\text{-PFMPS}_{73}^{+73x}$ ($x = 0.75$) (scale bar = 200 nm).

core rich in partially oxidized polymeric PFMPS_m^{+mx} with $[\text{SbCl}_6]^-$ counterions is proposed. Structural investigations using $^1\text{H-NMR}$, scanning electron microscopy (SEM), atomic force microscopy (AFM) verified that the anticipated corona of PS is also present in these micelles.⁸

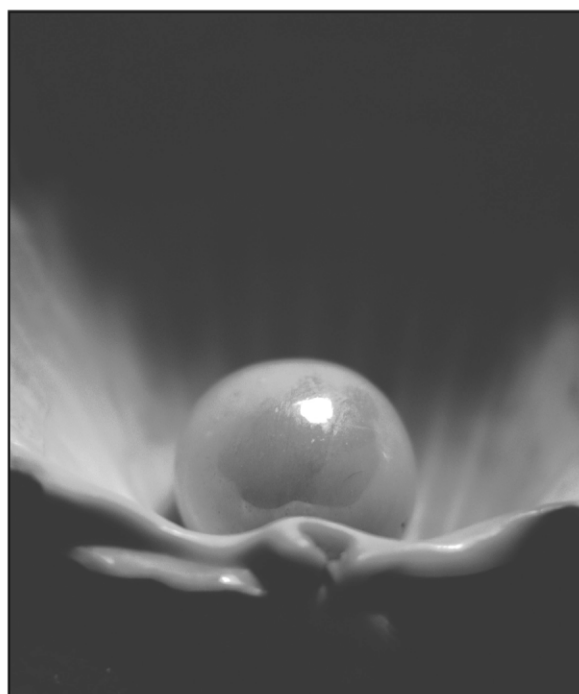
In summary, the chemical oxidation of $\text{PS-}b\text{-PFS}$ diblock copolymers successfully induces a spontaneous self-assembly into well-defined spherical micelles. The micelles were fully characterized by UV-vis, DLS, TEM, $^1\text{H-NMR}$, SEM and EDX, and comprise a PFS^+ core with $[\text{SbX}_6]^-$ ($X = \text{F}$ or Cl) counterions and a corona of PS. When reduced with decamethylcobaltocene, disassembly of the micelles occurs accompanied by release of free chains of the neutral diblock copolymer. A reversible redox-controlled micellization has been confirmed. Our future work will include a detailed investigation of the redox-driven self-assembly mechanism and an exploration of potential applications. This will include the development of catalysts which can be controllably tuned between homogeneous and heterogeneous states, and the potential for the redox-controlled release of encapsulants.

We thank Hai Wang for DLS measurements and the Ontario Government for fellowships to D.A.R. I.M. also acknowledges the support of a Marie Curie Chair from the European Union and a Royal Society Wolfson Research Merit Award at Bristol.

Notes and references

- I. W. Hamley, *Angew. Chem., Int. Ed.*, 2003, **42**, 1692.
- For example: (a) pH response: S. Liu and S. P. Armes, *Angew. Chem., Int. Ed.*, 2002, **41**, 1413; (b) temperature response: M. Arotçaràna, B. Heise, S. Ishaya and A. Laschewsky, *J. Am. Chem. Soc.*, 2002, **124**, 3787; (c) response to light: J. Jiang, X. Tong and Y. Zhao, *J. Am. Chem.*

- Soc.*, 2005, **127**, 8290; (d) pressure response: A. Raudino, F. Lo Celso, A. Triolo and R. Triolo, *J. Chem. Phys.*, 2004, **120**, 3489; (e) salt concentration response: J.-F. Gohy, S. K. Varshney, S. Antoun and R. Jérôme, *Macromolecules*, 2000, **33**, 9298.
- 3 (a) Z. Tuzar and P. Kratochvil, *Adv. Colloid Interface Sci.*, 1976, **6**, 201; (b) A. Halperin, M. Tirrell and T. P. Lodge, *Adv. Polym. Sci.*, 1992, **100**, 31; (c) S. Förster and T. Plantenberg, *Angew. Chem., Int. Ed.*, 2002, **41**, 688.
- 4 For prior work on small molecule surfactant based approaches for (a) redox-controlled viscoelasticity see: K. Tsuchiya, Y. Orihara, Y. Kondo, N. Yoshino, T. Ohkubo, H. Sakai and M. Abe, *J. Am. Chem. Soc.*, 2004, **126**, 12282; (b) redox-controlled motions and positions of aqueous and organic liquids see: B. S. Gallardo, V. K. Gupta, F. D. Eagerton, L. I. Jong, V. S. Craig, R. R. Shah and N. L. Abbott, *Science*, 1999, **283**, 57; (c) redox-controlled assembly see: N. Aydogan and N. L. Abbott, *Langmuir*, 2001, **17**, 5703; (d) For an example of the irreversible redox-triggered disassembly of polymerosomes see: A. Napoli, M. J. Boerakker, N. Tirelli, R. J. M. Nolte, N. A. J. M. Sommerdijk and J. A. Hubbell, *Langmuir*, 2004, **20**, 3487.
- 5 I. Manners, *Chem. Commun.*, 1999, 857.
- 6 For examples of redox-tunable properties of PFS materials see: (a) phase separation in block copolymers in bulk: H. B. Eitouni and N. P. Balsara, *J. Am. Chem. Soc.*, 2004, **126**, 7446; (b) gel swellability: A. C. Arsenault, H. Miguez, V. Kitaev, G. A. Ozin and I. Manners, *Adv. Mater.*, 2003, **15**, 503; (c) capsule permeability: Y. Ma, W.-F. Dong, M. A. Hempenius, H. Möhwald and G. J. Vancso, *Nature Mater.*, 2006, **5**, 724; (d) microspheres: K. Kulbaba, A. Cheng, A. Bartole, S. Greenberg, R. Resendes, N. Coombs, A. Safa-Sefat, J. E. Greedan, H. D. H. Stover, G. A. Ozin and I. Manners, *J. Am. Chem. Soc.*, 2002, **124**, 12522; (e) nanoparticle synthesis: X.-S. Wang, H. Wang, N. Coombs, M. A. Winnik and I. Manners, *J. Am. Chem. Soc.*, 2005, **127**, 8924.
- 7 (a) R. Rulkens, A. J. Lough, I. Manners, S. R. Lovelace, C. Grant and W. E. Geiger, *J. Am. Chem. Soc.*, 1996, **118**, 12683; (b) G. Masson, P. Beyer, P. W. Cyr, A. J. Lough and I. Manners, *Macromolecules*, 2006, **39**, 3720; (c) M. Péter, R. G. H. Lammertink, M. A. Hempenius and G. J. Vancso, *Langmuir*, 2005, **21**, 5115.
- 8 See Supplementary Information.†



Looking for that **special** chemical science research paper?

TRY this free news service:

Chemical Science

- highlights of newsworthy and significant advances in chemical science from across RSC journals
- free online access
- updated daily
- free access to the original research paper from every online article
- also available as a free print supplement in selected RSC journals.*

*A separately issued print subscription is also available.

Registered Charity Number: 207890

RSCPublishing

www.rsc.org/chemicalscience