Angewandte Chemie International Edition

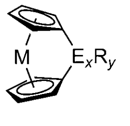
DOI: 10.1002/anie.201008184

Main-Chain Heterobimetallic Block Copolymers: Synthesis and Self-Assembly of Polyferrocenylsilane-*b*-Poly(cobaltoceniumethylene)**

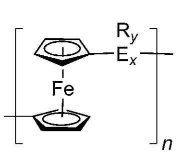
Joe B. Gilroy, Sanjib K. Patra, John M. Mitchels, Mitchell A. Winnik, and Ian Manners**

Metal-containing polymers are attracting growing attention as functional materials as a result of the useful physical and catalytic properties that arise from the presence of metal centers.[1] For example, metallopolymers with reversible redox properties are of interest for applications in electrocatalysis[2] and sensing,[3] as responsive surfaces[4] and capsules,[5] and as the active components of photonic crystal displays.[6] Block copolymers containing metal centers present additional features of considerable interest as a result of their ability to undergo self-assembly in the solid state or solution. Studies of such materials have led to applications as nanotemplates in lithography[7] and as precursors to patterned magnetic nanostructures[8] and nanocatalysts for carbon nanotube growth.[9] However, the synthesis of materials containing metalloblocks by living polymerization protocols presents substantial challenges as a result of undesirable side reactions of many metal centers with ionic and radical propagating sites. Herein, we describe our initial results on the synthesis and properties of unusual main-chain heterobimetallic diblock copolymers with different redox-active centers in each metalloblock.

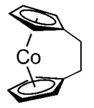
The ring-opening polymerization (ROP) of strained metallocenophanes **1** provides a well-studied route to functional metallopolymers **2**.[10–12] In particular, the ROP of 18-electron sila[1]ferrocenophanes (**1**, M = Fe, $E_xR_y = SiR_2$) represents a useful route to polyferrocenylsilanes (PFSs, **2**, M = Fe, $E_xR_y = SiR_2$) which exhibit many interesting characteristics.[13] Living anionic polymerization of sila[1]ferrocenophanes (**1**, M = Fe, $E_xR_y = SiR_2$) using organolithium initiators such as *n*BuLi proceeds by cleavage of the Si–Cp bond (Cp = cyclopentadienyl), and has been developed as a route to a variety of PFS block copolymers.[14] An alternative procedure, living photocontrolled ROP in the presence of cyclopentadienide anion initiators,[15] involves photoactivation and subsequent cleavage of the Fe–Cp bond. These living ROP routes have been extended to prepare block copolymers from several [1]- and [2]ferrocenophanes containing various bridges (**1**, M = Fe, $E_xR_y = GeR_2$,[16] PR,[17] or C_2R_4[18]); however, their use for analogous materials containing metals other than iron is unexplored. Here, we demonstrate the synthesis of PFS diblock copolymers with a poly(cobaltoceniumethylene) ($[PCE]^+$) coblock derived from the dicarba[2]cobaltococenophane **3**. Living photocontrolled ROP of **3**, which has not been previously reported, was explored because the previously demonstrated thermal ROP to afford $[PCE]^+$ homopolymer and also ring-opening oligomerizations of **3** appeared to proceed through Co–Cp bond cleavage.[19]



1



2



3

The successful synthesis of PFS-*b*-$[PCE]^+$ block copolymers was accomplished by sequential photocontrolled ROP of **1** (M = Fe, $E_xR_y = SiMe_2$) and **3** followed by oxidation of the 19-electron cobaltocene centers (Scheme 1).[19–22] The living PFS blocks were synthesized by addition of sodium cyclopentadienide (NaCp) as initiator to a solution of **1** (M = Fe, $E_xR_y = SiMe_2$) in tetrahydrofuran (THF) under anhydrous conditions, followed by prolonged irradiation (5–24 h) of the solutions at 5 °C. The living PFS chains were then combined with 19-electron cobaltocenophane **3**, and the solutions irradiated at 20 °C (to increase solubility) until the block copolymers precipitated from solution (15–24 h). The living polymer chains were quenched by, and the resulting product washed with degassed methanol, oxidized by air in the presence of ammonium triflate ([NH$_4$][OTf]), and dialyzed against water for 72 h. The yellow block copolymers were then filtered and dried in vacuo. The molecular weight (M_n) of the diblock copolymers was determined from the M_n of the PFS block (which was determined by gel permeation chromatography (GPC) analysis of an aliquot of the reaction solution before the addition of **3**) through comparison of the relative integrations of the -CH_2CH_2- signal from the $[PCE]^+$ block and the -$SiMe_2$- signal from the PFS block in the ^1H NMR spectra. In this study two materials were prepared:

---

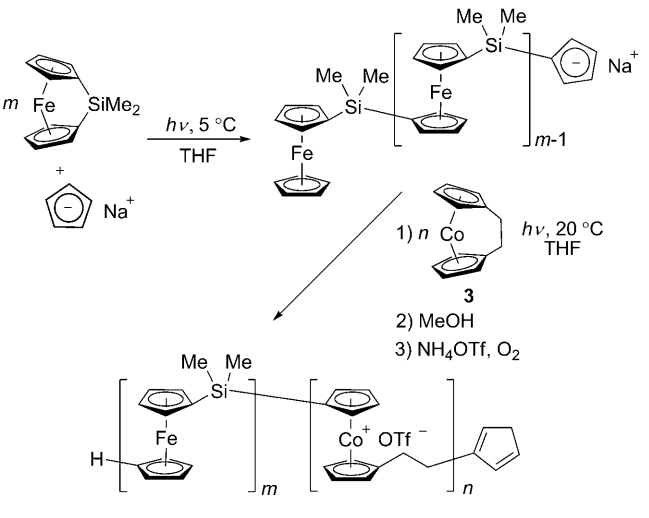
[*] Dr. J. B. Gilroy, Dr. S. K. Patra, Prof. I. Manners
School of Chemistry, University of Bristol
Cantock's Close, Bristol, BS8 1TS (UK)
E-mail: ian.manners@bristol.ac.uk

Dr. J. M. Mitchels
Microscopy and Analysis Suite, University of Bath
3 West 2.15, Bath, BA2 7AY (UK)

Prof. M. A. Winnik
Department of Chemistry, University of Toronto
80 St. George Street, Toronto, ON M5S 3H6 (Canada)
E-mail: mwinnik@chem.utoronto.ca

[**] J.B.G. and S.K.P. are grateful to the European Union (EU) for Marie Curie postdoctoral fellowships. J.B.G. also thanks the Natural Sciences and Engineering Research Council (NSERC) of Canada for a postdoctoral fellowship. We are grateful to Dr. Torben Gädt for the preparation of the block copolymer PFS$_{34}$-*b*-P2VP$_{272}$ and Dr. Paul A. Rupar for production of micelle graphics. I.M. thanks the EU for a Marie Curie Chair, a reintegration grant, and an advanced investigator grant and the Royal Society for a Wolfson research merit award. M.A.W thanks the NSERC for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201008184.



PFS$_m$-*b*-([PCE][OTf])$_n$

4a: $m = 50$, $n = 50$
4b: $m = 42$, $n = 75$

Scheme 1. Synthesis of heterobimetallic block copolymers through photocontrolled ROP (OTf^- = trifluoromethanesulfonate; triflate anion).

PFS$_{50}$-*b*-([PCE][OTf])$_{50}$ **4a** and PFS$_{42}$-*b*-([PCE][OTf])$_{75}$ **4b**, where the subscripts represent the number-average degree of polymerization.

The ^{1}H NMR spectrum of block copolymer **4a** in a 9:1 mixture of [D$_8$]THF and D_2O included well-resolved resonances corresponding to the two blocks (Figure 1 and Figure S1 in the Supporting Information).[23] The [PCE]$^+$ block contributed two resonances at $\delta = 5.73$ and 5.69 ppm because of the substituted Cp ligands, and a singlet at $\delta = 2.81$ corresponding to bridging methylene moieties. The remaining signals could be assigned to the PFS block, with peaks observed at $\delta = 4.22$ and 4.03 ppm for the substituted Cp ligands and a singlet at $\delta = 0.47$ ppm because of the methyl substituents of the SiMe$_2$ bridge. The ^{13}C NMR spectrum was consistent with the assigned structure, showing three unique signals for the Cp at $\delta = 107.0$, 85.4, 85.2 ppm and a signal at $\delta = 28.9$ ppm for the bridging methylene groups of the [PCE]$^+$ block. The Cp resonances at $\delta = 73.9$, 72.3, and 72.0 ppm and the signal for the -SiMe$_2$- bridge at $\delta = -0.5$ ppm were assigned to the PFS block. A single resonance at $\delta = -6.7$ ppm in the ^{29}Si NMR spectrum was observed for the −SiMe$_2$− bridge of the PFS block. A singlet in the ^{19}F NMR spectrum at $\delta = -79.0$ ppm and a strong IR band at 1257 cm^{-1} [$\nu_{as}(SO_3)$] confirmed the presence of the triflate anion [OTf]$^-$. The NMR spectra obtained for **4b** were consistent with the structure assigned for **4a** (Figure S2 in the Supporting Information).

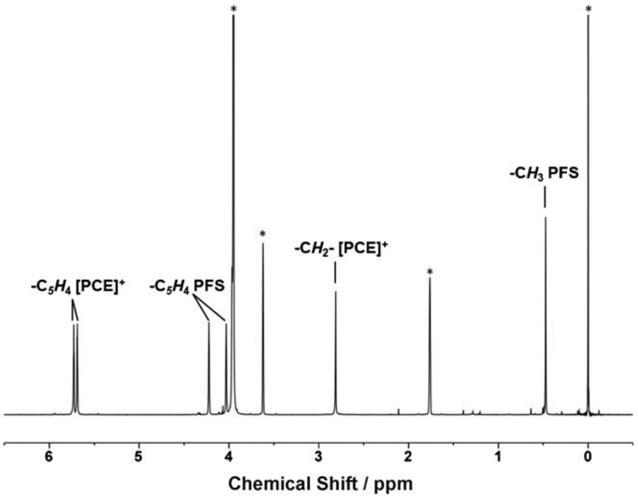


Figure 1. ^{1}H NMR spectrum of block copolymer **4a** in a 9:1 mixture of [D$_8$]THF and D_2O. The asterisks denote residual protonated NMR solvent signals and tetramethylsilane (TMS).

The electronic spectra of block copolymers **4a** and **4b** consist of broad absorptions between 375 and 600 nm ($\lambda_{max} = 407$ and 405 nm for **4a** and **4b**, respectively) attributed to d–d transitions in the 18-electron ferrocene (fc) and cobaltocenium repeat units (Figures S3 and S4 in the Supporting Information). To probe the redox properties of **4a** and **4b**, cyclic voltammetry experiments were conducted (Figure 2a and Figures S5 and S6 in the Supporting Information).

The cyclic voltammogram of **4a** in a 9:1 mixture of THF and water with supporting electrolyte [NBu$_4$][OTf] was characterized by three separate redox events. Two separate oxidation waves ($E_{1/2} = 0.17$ and 0.26 V vs. fc/fc$^+$) were assigned to the PFS block. The presence of two oxidation waves in the PFS polymers has previously been attributed to electronic communication between neighboring ferrocene units, resulting in sequential oxidation of alternating ferrocene moieties in the polymer backbone.[24] A third redox event corresponding to the reduction of the [PCE]$^+$ block was observed at a potential of −1.27 V vs. fc/fc$^+$, which was close to the edge of the electrochemical window of the solvent mixture employed. The reduction potential observed was consistent with that reported for ([PCE][NO$_3$])$_n$ (ca. −1.3 V vs. fc/fc$^+$) prepared by thermal ROP.[19] The electrochemical properties of **4b** were similar to those of **4a**, with a larger current response observed because of the relatively longer [PCE]$^+$ block. A significant feature of these materials is the ability to access three different polymeric species based on the redox events observed (PFS-*b*-PCE, PFS-*b*-[PCE]$^+$, and [PFS]$^+$-*b*-[PCE]$^+$; Figure 2b).

The thermal properties of block copolymers **4a** and **4b** were studied by thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC) to assess their thermal stability and to probe for thermal transitions common to polymeric materials. TGA studies revealed two distinct decomposition steps for each block copolymer (Figures S7 and S8 in the Supporting Information) before each sample reached a steady state at temperatures above 600 °C. The char yields of the resulting magnetically responsive black powders were 33 % for **4a** and 44 % for **4b**. DSC studies over a temperature range of −40 to 250 °C revealed glass-transition temperatures (T_g) of around 32 and 34 °C because of the PFS block in **4a** and **4b** and broad features, which may be associated with glass transitions of the [PCE]$^+$ blocks, between 35 and 150 °C (Figures S9 and S10 in the Supporting Information). No melting endotherm was

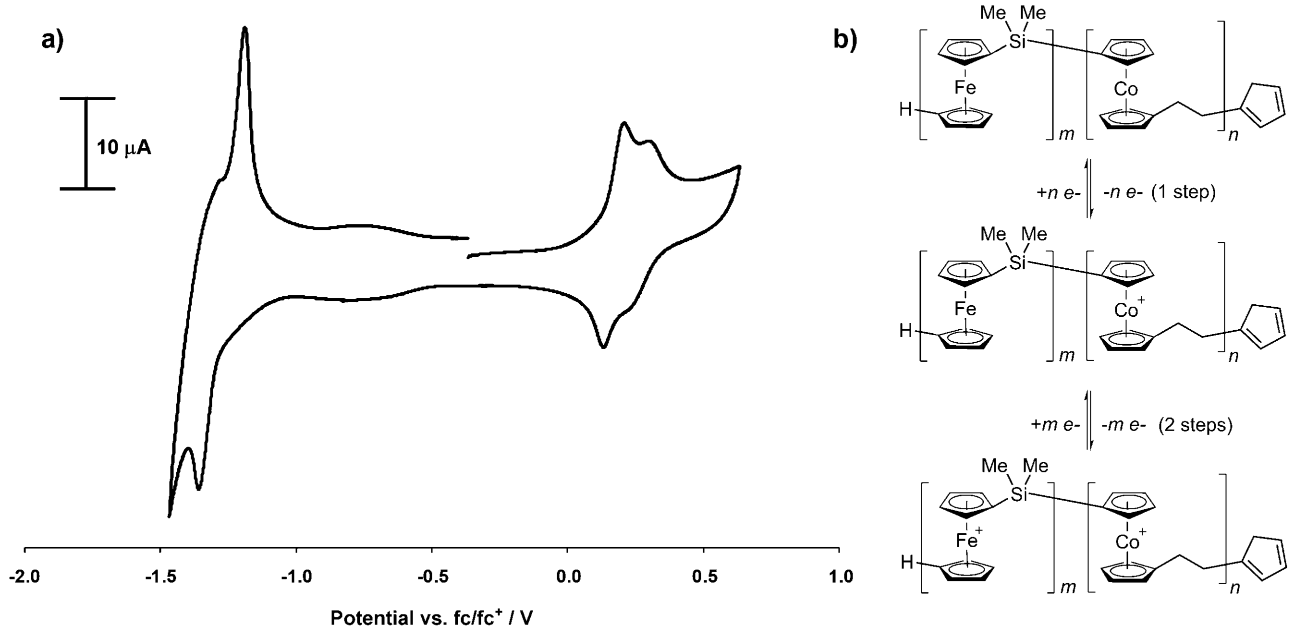


Figure 2. a) Cyclic voltammogram of a 1 mM (with respect to repeat units) solution of **4a** in a 9:1 mixture of THF and H_2O at a scan rate of 100 mV s^{-1} with 0.1 M $[Bu_4N][OTf]$ as the supporting electrolyte (the working electrode was a 3 mm Pt disk, the reference electrode was Ag/AgCl, and the auxiliary electrode was a Pt wire). b) Relevant species in the redox switching of PFS_m-*b*-([PCE][OTf]$)_n$ block copolymers.

observed for PFS, even upon prolonged isothermal annealing (70 °C, 24 h). Wide-angle X-ray scattering (WAXS) studies of **4a** and **4b** (Figures S11 and S12 in the Supporting Information) were consistent with the absence of crystalline domains of PFS, and contained only very weak signals ($d = 4.78$ Å) associated with the $[PCE]^+$ block (Figure S13 in the Supporting Information). The absence of crystalline domains of PFS in block copolymers **4a** and **4b** contrasts with the crystallinity detected by DSC and WAXS studies of a sample of the PFS homopolymer corresponding to the first block of **4a** (Figures S14 and S15 in the Supporting Information). This may be associated with inhibition of the crystallization because of the incompatibility of the PFS and $[PCE]^+$ blocks and the lack of chain mobility in the latter.

The solution self-assembly of block copolymers comprising a crystalline poly(ferrocenyldimethylsilane) core-forming block and a solubilizing organic block (e.g., polyisoprene, poly(2-vinylpyridine) (P2VP), or polydimethylsiloxane) have recently received significant attention because of the ability of micelles based on these materials to grow through a crystallization-driven living self-assembly mechanism. The growth mechanism, which arises because of the crystallinity of the PFS block, has been exploited in the realization of block co-micelles,[25] scarflike micelles, micelle brushes,[26] and monodisperse cylindrical micelles.[27] Access to the PFS_m-*b*-([PCE][OTf]$)_n$ block copolymers **4a** and **4b** prompted us to study the solution self-assembly behavior of these materials as a possible route to new heterobimetallic micelle architectures.

Dissolution of **4a** in solvent mixtures chosen to be selective for the $[PCE]^+$ block such as MeOH or H_2O failed to give aggregates of consistent size and shape when samples were drop-cast onto carbon-coated copper grids and screened by TEM. However, spherical micelles (radius ca. 8 nm) were observed in a 0.5 mg mL^{-1} solution of **4a** in a 9:1 MeOH/water mixture (Figure S16 in the Supporting Information). The formation of spherical micelles in hydrophilic nonsolvents is typical for block copolymers with poly(ferrocenyldimethylsilane) core-forming blocks which, because of their hydrophobicity, are unable to crystallize under the self-assembly conditions.[28]

We have previously shown that crystalline poly(ferrocenyldimethylsilane) cores of cylinders formed by the self-assembly of block copolymers such as PFS-*b*-P2VP can be used to template crystalline PFS from PFS block copolymers that normally form spherical micelles with amorphous cores.[29] We therefore explored an alternative self-assembly strategy whereby block copolymer **4a** was added to a solution of short cylindrical micelle seeds (ca. 100–200 nm) to seed the self-assembly of **4a**. The seed micelles were obtained by sonicating a 0.5 mg mL^{-1} solution of long (> 5 μm) PFS_{34}-*b*-$P2VP_{272}$ cylindrical micelles for 1 h at −78 °C with a titanium sonotrode (Figures S17 and S18 in the Supporting Information). The seeded self-assembly of **4a** was studied by addition of 2.5 mg of **4a** (added as a 10 mg mL^{-1} solution in THF) to 12.5 μg of PFS_{34}-*b*-$P2VP_{272}$ seed micelles in 2.5 mL of methanol, a good solvent for P2VP and [PCE][OTf]. After aging for 48 h, the resulting aggregates were studied by TEM and AFM (Figure 3 and Figure S19 in the Supporting Information). Addition of **4a** to the cylindrical seed micelles (the height at the middle of the seed micelle is ca. 8 nm (AFM) and the height at the ends of the seed micelle is ca. 10 nm (AFM); Figure S18 in the Supporting Information) resulted in elongation of the cylindrical seed micelles, presumably through epitaxial growth of the PFS block in **4a** from the PFS core of the seed micelle. However, based on AFM height studies, the growth upon addition of **4a** was not

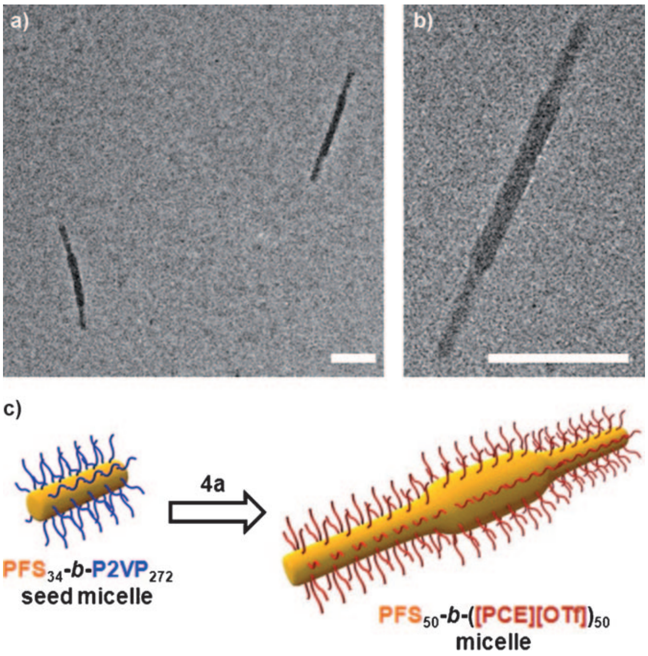


Figure 3. a,b) Bright-field TEM images of cylindrical micelles resulting from the addition of **4a** to PFS$_{34}$-*b*-P2VP$_{272}$ seed micelles. c) Idealized graphical representation of the micelle structures shown in (a) and (b). PFS$_{50}$-*b*-([PCE][OTf])$_{50}$ **4a** grew in three dimensions around the PFS$_{34}$-*b*-P2VP$_{272}$ seed micelle (middle), burying it within the hierarchical micelle structures. The PFS core is represented in orange, the [PCE][OTf] corona is represented in red, and the P2VP corona is represented in blue. For AFM height images of the PFS$_{50}$-*b*-([PCE]-[OTf])$_{50}$ micelles and the PFS$_{34}$-*b*-P2VP$_{272}$ seed micelles, see the Supporting Information (Figures S18 and S19). Scale bars correspond to 200 nm.

restricted to the ends of the seed micelles, but rather occurred in three dimensions (3D) around the seed micelle (the height at the middle of the seed micelle is ca. 12 nm (AFM), the height at the ends of the seed micelle is ca. 14 nm (AFM), and the height at the cylinder ends is ca. 11 nm; Figure S19 in the Supporting Information). A similar 3D growth mechanism was recently observed when PFS-*b*-polyphosphazene block copolymers were grown from PFS-*b*-P2VP seed micelles.[29] The "dumbbell-shaped" central portion of the micelle observed after addition of **4a** appears to have originated from the seed micelle (Figure S18 in the Supporting Information), and may be due to structural changes in the seed micelle core during the sonication process.

In summary, we have successfully synthesized novel heterobimetallic block copolymers based on ferrocene and cobaltocenium repeat units by living photocontrolled ROP, a process that has not previously been demonstrated for **3**. The block copolymers have interesting redox properties because of the electroactive ferrocene and cobaltocenium centers, which yield oxidation and reduction waves separated by around 1.5 V. As a result, the block copolymers described in this study may have utility as three-stage switches in polymer-based functional materials. The self-assembly behavior was also studied and allows access to new heterobimetallic block co-micelle architectures through living self-assembly. Future work in this area will focus on detailed studies of a range of PFS-*b*-[PCE]$^+$ block copolymers and exploration of their properties, self-assembly, and functional polymer-based applications.

Received: December 25, 2010
Revised: March 30, 2011

Keywords: block copolymers · living polymerization · metallopolymers · micelles · self-assembly

---

[1] a) K. A. Williams, A. J. Boydston, C. W. Bielawski, *Chem. Soc. Rev.* **2007**, *36*, 729–744; b) G. R. Whittell, I. Manners, *Adv. Mater.* **2007**, *19*, 3439–3468; c) V. Marin, E. Holder, R. Hoogenboom, U. S. Schubert, *Chem. Soc. Rev.* **2007**, *36*, 618–635; d) W.-Y. Wong, P. D. Harvey, *Macromol. Rapid Commun.* **2010**, *31*, 671–713; e) G. R. Whittell, M. D. Hager, U. S. Schubert, I. Manners, *Nat. Mater.* **2011**, *10*, 176–188.

[2] a) D. J. Caruana, A. Heller, *J. Am. Chem. Soc.* **1999**, *121*, 769–774; b) N. Gajovic, G. Binyamin, A. Warsinke, F. W. Scheller, A. Heller, *Anal. Chem.* **2000**, *72*, 2963–2968.

[3] a) C. Valério, J.-L. Fillaut, J. Ruiz, J. Guittard, J.-C. Blais, D. Astruc, *J. Am. Chem. Soc.* **1997**, *119*, 2588–2589; b) M.-C. Daniel, J. Ruiz, D. Astruc, *J. Am. Chem. Soc.* **2003**, *125*, 1150–1151; c) R. Djeda, A. Rapakousiou, L. Liang, N. Guidolin, J. Ruiz, D. Astruc, *Angew. Chem.* **2010**, *122*, 8328–8332; *Angew. Chem. Int. Ed.* **2010**, *49*, 8152–8156.

[4] M. Péter, R. G. H. Lammertink, M. A. Hempenius, G. J. Vancso, *Langmuir* **2005**, *21*, 5115–5123.

[5] Y. Ma, W.-F. Dong, M. A. Hempenius, H. Möhwald, G. J. Vancso, *Nat. Mater.* **2006**, *5*, 724–729.

[6] D. P. Puzzo, A. C. Arsenault, I. Manners, G. A. Ozin, *Angew. Chem.* **2009**, *121*, 961–965; *Angew. Chem. Int. Ed.* **2009**, *48*, 943–947.

[7] a) J. Y. Cheng, C. A. Ross, V. Z.-H. Chan, E. L. Thomas, R. G. H. Lammertink, G. J. Vancso, *Adv. Mater.* **2001**, *13*, 1174–1178; b) J. Y. Cheng, A. M. Mayes, C. A. Ross, *Nat. Mater.* **2004**, *3*, 823–828; c) C.-A. Fustin, B. G. G. Lohmeijer, A.-S. Duwez, A. M. Jonas, U. S. Schubert, J.-F. Gohy, *Adv. Mater.* **2005**, *17*, 1162–1165; d) I. Korczagin, R. G. H. Lammertink, M. A. Hempenius, S. Golze, G. J. Vancso, *Adv. Polym. Sci.* **2006**, *200*, 91–117; e) J. Lu, D. Chamberlin, D. A. Rider, M. Liu, I. Manners, T. P. Russell, *Nanotechnology* **2006**, *17*, 5792–5797.

[8] D. A. Rider, K. Liu, J.-C. Eloi, L. Vanderark, L. Yang, J.-Y. Wang, D. Grozea, Z.-H. Lu, T. P. Russell, I. Manners, *ACS Nano* **2008**, *2*, 263–270.

[9] a) C. Hinderling, Y. Keles, T. Stöckli, H. F. Knapp, T. de Los Arcos, P. Oelhafen, I. Korczagin, M. A. Hempenius, G. J. Vancso, R. Pugin, H. Heinzelmann, *Adv. Mater.* **2004**, *16*, 876–879; b) S. Lastella, Y. J. Jung, H. Yang, R. Vajtai, P. M. Ajayan, C. Y. Ryu, D. A. Rider, I. Manners, *J. Mater. Chem.* **2004**, *14*, 1791–1794; c) J. Q. Lu, T. E. Kopley, N. Moll, D. Roitman, D. Chamberlin, Q. Fu, J. Liu, T. P. Russell, D. A. Rider, I. Manners, M. A. Winnik, *Chem. Mater.* **2005**, *17*, 2227–2231.

[10] D. E. Herbert, U. F. J. Mayer, I. Manners, *Angew. Chem.* **2007**, *119*, 5152–5173; *Angew. Chem. Int. Ed.* **2007**, *46*, 5060–5081.

[11] For recent work in the area of strained sandwich and related complexes, see: a) T. Mizuta, Y. Imamura, K. Miyoshi, *J. Am. Chem. Soc.* **2003**, *125*, 2068–2069; b) H. K. Sharma, F. Cervantes-Lee, K. H. Pannell, *J. Am. Chem. Soc.* **2004**, *126*, 1326–1327; c) P. Chadha, J. L. Dutton, M. J. Sgro, P. J. Ragogna, *Organometallics* **2007**, *26*, 6063–6065; d) H. Braunschweig, M. Gross, K. Radacki, C. Rothgaengel, *Angew. Chem.* **2008**, *120*, 10127–10129; *Angew. Chem. Int. Ed.* **2008**, *47*, 9979–9981;

e) M. Tamm, *Chem. Commun.* **2008**, 3089–3100; f) D. M. Khramov, E. L. Rosen, V. M. Lynch, C. W. Bielawski, *Angew. Chem.* **2008**, *120*, 2299–2302; *Angew. Chem. Int. Ed.* **2008**, *47*, 2267–2270; g) B. Bagh, J. B. Gilroy, A. Staubitz, J. Müller, *J. Am. Chem. Soc.* **2010**, *132*, 1794–1795; h) H. Braunschweig, T. Kupfer, *Acc. Chem. Res.* **2010**, *43*, 455–465.

[12] a) L. Kaufmann, J.-M. Breunig, H. Vitze, F. Schödel, I. Nowik, M. Pichlmaier, M. Bolte, H.-W. Lerner, R. F. Winter, R. H. Herber, M. Wagner, *Dalton Trans.* **2009**, 2940–2950; b) M. Scheibitz, H. Li, J. Schnorr, A. S. Perucha, M. Bolte, H.-W. Lerner, F. Jäkle, M. Wagner, *J. Am. Chem. Soc.* **2009**, *131*, 16319–16329.

[13] a) I. Manners, *Chem. Commun.* **1999**, 857–865; b) V. Bellas, M. Rehahn, *Angew. Chem.* **2007**, *119*, 5174–5197; *Angew. Chem. Int. Ed.* **2007**, *46*, 5082–5104.

[14] Y. Ni, R. Rulkens, I. Manners, *J. Am. Chem. Soc.* **1996**, *118*, 4102–4114.

[15] M. Tanabe, G. W. M. Vandermeulen, W. Y. Chan, P. W. Cyr, L. Vanderark, D. A. Rider, I. Manners, *Nat. Mater.* **2006**, *5*, 467–470.

[16] N. S. Ieong, I. Manners, *Macromol. Chem. Phys.* **2009**, *210*, 1080–1086.

[17] a) T. J. Peckham, J. A. Massey, C. H. Honeyman, I. Manners, *Macromolecules* **1999**, *32*, 2830–2837; b) S. K. Patra, G. R. Whittell, S. Nagiah, C.-L. Ho, W.-Y. Wong, I. Manners, *Chem. Eur. J.* **2010**, *16*, 3240–3250.

[18] D. E. Herbert, U. F. J. Mayer, J. B. Gilroy, M. J. López-Gómez, A. J. Lough, J. P. H. Charmant, I. Manners, *Chem. Eur. J.* **2009**, *15*, 12234–12246.

[19] U. F. J. Mayer, J. B. Gilroy, D. O'Hare, I. Manners, *J. Am. Chem. Soc.* **2009**, *131*, 10382–10383.

[20] U. F. J. Mayer, J. P. H. Charmant, J. Rae, I. Manners, *Organometallics* **2008**, *27*, 1524–1533.

[21] For recent work on high molecular weight side chain cobaltocenium polymers prepared via ATRP, see: a) L. Ren, C. G. Hardy, C. Tang, *J. Am. Chem. Soc.* **2010**, *132*, 8874–8875; b) L. Ren, C. G. Hardy, S. Tang, D. B. Doxie, N. Hamidi, C. Tang, *Macromolecules* **2010**, *43*, 9304–9310.

[22] For dendrimers containing cobaltocenium centers, see: a) B. González, C. M. Casado, B. Alonso, I. Cuadrado, M. Morán, Y. Wang, A. E. Kaifer, *Chem. Commun.* **1998**, 2569–2570; b) C. Ornelas, J. Ruiz, D. Astruc, *Organometallics* **2009**, *28*, 2716–2723; c) for layer-by-layer assembly of Fe- and Co-containing polyelectrolyte bilayers see: W. Liu, W. Huang, M. Pink, D. Lee, *J. Am. Chem. Soc.* **2010**, *132*, 11844–11846.

[23] When **4a** and **4b** were suspended in THF, the solutions remained colorless, confirming the absence of the PFS hompolymer in the samples.

[24] R. Rulkens, A. J. Lough, I. Manners, S. R. Lovelace, C. Grant, W. E. Geiger, *J. Am. Chem. Soc.* **1996**, *118*, 12683–12695.

[25] X. Wang, G. Guerin, H. Wang, Y. Wang, I. Manners, M. A. Winnik, *Science* **2007**, *317*, 644–647.

[26] T. Gädt, N. S. Ieong, G. Cambridge, M. A. Winnik, I. Manners, *Nat. Mater.* **2009**, *8*, 144–150.

[27] J. B. Gilroy, T. Gädt, G. R. Whittell, L. Chabanne, J. M. Mitchels, R. M. Richardson, M. A. Winnik, I. Manners, *Nat. Chem.* **2010**, *2*, 566–570.

[28] H. Wang, M. A. Winnik, I. Manners, *Macromolecules* **2007**, *40*, 3784–3789.

[29] A. Presa Soto, J. B. Gilroy, M. A. Winnik, I. Manners, *Angew. Chem.* **2010**, *122*, 8396–8399; *Angew. Chem. Int. Ed.* **2010**, *49*, 8220–8223.