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Synthesis, Characterization, and Anion Binding of Redox-Active Triarylborane Polymers

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ABSTRACT: Two new ferrocene-containing triarylborane polymers have been prepared from trimethylsilyl-substituted polystyrene via selective polymer modification reactions with organometallic reagents. The photophysical and electrochemical properties of the polymers have been investigated and compared with the respective molecular model compounds. Cyclic voltammetry studies reveal reversible ferrocene-centered oxidation and boron-centered reduction processes at similar potentials as for the molecular species. In contrast, binding studies indicate a distinct polymer effect in that the molecular species show a much larger affinity for fluoride.

Introduction

Transition metal containing polymers are an interesting class of materials in which the presence of the metal can lead to unusual electronic, magnetic, and optical properties.[1] Broad attention has been given especially to ferrocene polymers, in part due to the opportunity to reversibly switch between the oxidation states of Fe(II) and Fe(III), combined with the exceptionally high stability of ferrocene under ambient conditions.[2] The redox behavior of ferrocene-containing polymers has been widely studied, and a recent example that nicely illustrates this concept is that of block copolymers of polystyrene and poly(ferrocenylsilane) that reversibly form micellar structures upon oxidation of the iron centers.[3]

To combine organometallic moieties with electron-deficient (tricoordinate) organoboranes in one polymeric material is an attractive goal since overlap of the empty p orbital on boron with an organic or organometallic π-system is known to lead to extended π-conjugation and hence to dramatically alter the electronic and photophysical properties.[4,5] The resulting materials are therefore expected to exhibit unique electronic characteristics. For instance, polymers in which ferrocene moieties alternate with Lewis acidic boron sites have been reported by Wagner et al. to display an exceptionally high degree of electronic communication between the ferrocene moieties as indicated by large redox couplings measured by cyclic voltammetry.[6] Organometallic ruthenium complexes have been embedded into conjugated organoboron polymers by Chujo et al.[7] These hybrid organometallic polymers show interesting photophysical properties as a result of the push−pull effect between the electron-rich ruthenium and electron-poor boron centers and the occurrence of both $d_\pi-p_\pi^*$ and $\pi-\pi^*$ electronic transitions. In addition, the observation of a higher redox potential for the polymer in comparison to the Ru building block suggests that the organoborane moieties withdraw electron density from the transition metal complex.

Examples of polymers that contain organoborane moieties attached as pendant groups are comparatively rare. Lequan et al. described the attachment of triarylborane moieties to a polyurethane backbone through a diazo linker for applications as nonlinear optical (NLO) materials.[8] Moreover, Shirota et al. reported that polymerization of an organoborane-modified vinyltriphenylamine gives a polymeric material that acts as an efficient green emitter in a light-emitting device (LED).[9]

We have pioneered the attachment of electron-deficient boron centers to the side chain of polystyrene using a polymer modification strategy that involves the efficient replacement of trimethylsilyl groups with BBr_3.[10,11] This process provides an exceptionally high level of control over molecular weight, polymer architecture, and degree of functionalization. We have also demonstrated that subsequent attachment of bithiophene moieties to the borylated polystyrene PS-BBr_2 leads to strongly luminescent materials that can be used as chemosensors for the selective and highly efficient recognition of fluoride and cyanide.[12] In here we discuss the preparation of polystyrenes containing pendant electroactive ferrocenylborane moieties and compare their properties with those of the respective molecular model systems.

Experimental Section

Materials and General Methods. 2-Bromomesitylene, 1,3,5-triisopropylbenzene, and *n*-BuLi (1.6 M in hexanes) were purchased from Acros Organics and BBr_3 (99 + %) from Aldrich. BBr_3 was further purified by vacuum distillation. *Caution*! BBr_3 is toxic and highly corrosive and should be handled appropriately with great care. Fluorinated grease was used for ground glass joints in all reactions involving boron tribromide. The compounds trimethylstannylferrocene,[13] (4-*tert*-butylphenyl)dibromoborane,[14] and 2,4,6-triisopropylphenylmagnesium bromide[15] were synthesized according to literature procedures. Poly(4-trimethylsilylstyrene) of $M_n = 21\,100$, $M_w = 23\,800$, and PDI = 1.13 (GPC-RI) was prepared as previously reported.[11] All reactions were carried out under an inert atmosphere using Schlenk techniques or a glovebox (Innovative Technologies). Ether solvents were distilled from Na/benzophenone prior to use. Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies; alumina/copper columns for hydrocarbon solvents), and the chlorinated solvents were subsequently distilled from CaH_2 and degassed via several freeze−pump−thaw cycles.

Instrumentation. All 499.893 MHz ^1H, 125.7 MHz ^{13}C, and 160.4 MHz ^{11}B NMR spectra were recorded on a Varian

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INOVA spectrometer equipped with a boron-free 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). Solution ^{1}H and ^{13}C NMR spectra were referenced internally to solvent signals. ^{11}B NMR spectra were referenced externally to $BF_3 \cdot Et_2O$ (δ = 0). ^{11}B NMR spectra were acquired with boron-free quartz NMR tubes. All NMR spectra were recorded at ambient temperature unless noted otherwise. The abbreviations Ph (phenyl), Fc (ferrocenyl), Mes (2,4,6-trimethylphenyl), and Tip (2,4,6-triisopropylphenyl) are used for the peak assignments. UV−vis measurements were performed in CH_2Cl_2 using a Varian Cary 500 scan UV−vis−NIR spectrophotometer with a 1 cm quartz cuvette. GC-MS spectra were acquired on a Hewlett-Packard HP 6890 Series GC system equipped with a series 5973 mass selective detector and a series 7683 injector. A temperature profile with a heating rate of 20 °C/min from 50 to 300 °C was used. GPC analyses were performed in THF (1 mL/min) using a Waters Empower system equipped with a 717plus autosampler, a 1525 binary HPLC pump, a 2998 photodiode array detector, and a 2414 refractive index detector. A series of styragel columns (Polymer Laboratories; two 5 μm Mix-C columns and a 5 μm Mix-D column in series; linear range 200−2 000 000), which were kept in a column heater at 35 °C, were used for separation. The columns were calibrated with PS standards (Polymer Laboratories). DSC measurements were performed on a Perkin-Elmer differential scanning calorimeter Pyris 1 system with ca. 10 mg of polymer using the specified scan rate. Thermogravimetric analyses were performed under a N_2 atmosphere using a Perkin-Elmer Pyris 1 system with ca. 5 mg of polymer at a heating rate of 20 °C/min from 50 to 800 °C. Elemental analyses were carried out by Quantitative Technologies (Whitehouse, NJ).

X-ray diffraction intensities were collected on a Bruker SMART APEX CCD diffractometer at T = 100(2) K using Cu Kα (1.541 78 Å) radiation. Numerical absorption correction was applied; the structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on $F2$. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. All software and source scattering factors are contained in the SHELXTL program package.[16]

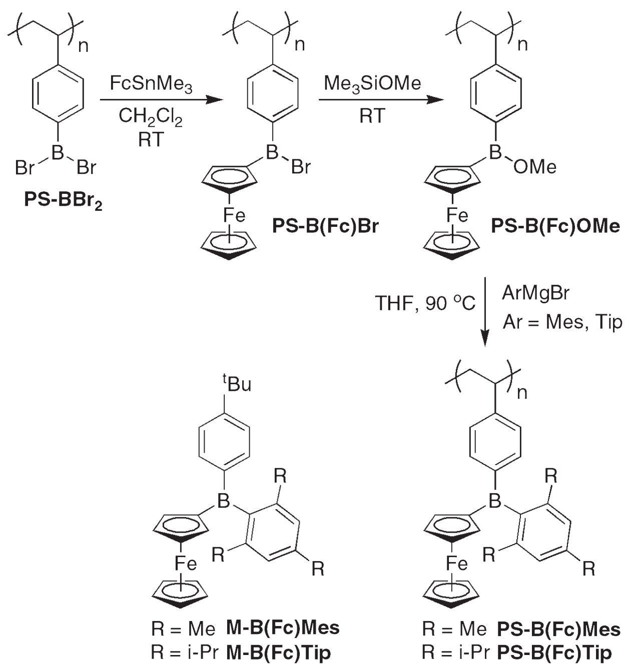
Cyclic voltammetry was carried out on a CV-50W analyzer from BAS. The three-electrode system consisted of an Au disk as working electrode, a Pt wire as secondary electrode, and an Ag wire as the reference electrode. The voltammograms were recorded with ca. $10^{-3}-10^{-4}$ M solutions in THF (reduction waves) or CH_2Cl_2 (oxidation waves) containing $[Bu_4N]PF_6$ (0.1 M) as the supporting electrolyte. The scans were referenced after the addition of a small amount of decamethylferrocene as internal standard. The potentials are reported relative to the ferrocene/ferrocenium couple (for decamethylferrocene vs ferrocene: −548 mV in CH_2Cl_2 and −452 mV in THF).

Synthesis of PS-B(Fc)Mes. A solution of BBr_3 (0.21 g, 0.84 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of PS-SiMe$_3$ (0.123 g, ca. 0.70 mmol of Me$_3$Si groups) in CH_2Cl_2 (10 mL) and stirred for 20 h. A solution of FcSnMe$_3$ (0.448 g, 1.28 mmol) in CH_2Cl_2 (10 mL) was added dropwise, and the reaction mixture turned dark red. The mixture was allowed to stir for 20 h at rt, Me$_3$SiOMe (0.25 mL, 1.81 mmol) was added neat, and the solution was stirred for another 24 h. All volatile components were removed under high vacuum. The orange-red solid residue was taken up in THF (10 mL), a solution of MesMgBr (0.5 M in THF, 2.8 mL, 1.4 mmol) was added, and the mixture was allowed to react for 1 h at rt and then kept at reflux for 5 days. The mixture was filtered, and the filtrate was concentrated to ca. 4 mL and precipitated into ether (350 mL). After filtration through a short alumina plug using dichloromethane as the solvent, the product was purified by repeated precipitation from THF into ether (350 mL). The precipitate was dried at 50 °C under high vacuum to obtain a fine orange-red powder (0.195 g, 67%). For *PS-B(Fc)Mes*: ^{11}B NMR (160.386 MHz, CDCl$_3$): δ = 57 ppm ($w_{1/2}$ = 1900 Hz). ^{1}H NMR (499.893 MHz, CDCl$_3$): δ = 7.6 (br, 2H, Ph$_o$), 6.9−6.4 (br, 4H, Ph$_m$ and Mes$_m$), 4.5, 4.3 (br, 2 × 2H, Fc-H3,4 and Fc-H2,5), 4.0 (br, 5H, C$_5$H$_5$), 2.3 (br, 3H, *p*-Me), 1.9 (br, 6H, *o*-Me), 2.0−1.4 (overlapping, polymer backbone protons). ^{13}C NMR (125.69 MHz, CDCl$_3$): δ = 149.0 (br), 143.7, 140.3 (br), 138.2, 136.5, 127.3 (aromatic C's), 75.0, 74.3 (Fc C's), 69.5 (C$_5$H$_5$), 42−40 (polymer backbone), 23.3 (*o*-Me), 21.5 (*p*-Me). GPC-RI (THF vs PS standards): M_n = 23 800, M_w = 27 400, PDI = 1.15; high-MW shoulder (17% area): M_n = 61 120, M_w = 65 210, PDI = 1.07. UV−vis (THF, mol^{-1} L^{-1} per repeat unit): λ_{max} = 295 nm (ε = 17 960), 368 nm (ε = 2540), 484 nm (ε = 1280). DSC (onset, 10 °C/min; second heating curve): T_g not observed. TGA (20 °C/min; N$_2$): 16% weight loss between 278 and 324 °C; 43% weight loss between 416 and 603 °C; 22% residual mass at 800 °C. Elemental analysis: calculated C 77.55, H 6.51; found C 77.04, H 6.71.

Synthesis of PS-B(Fc)Tip. The polymer was prepared in analogy to the procedure for *PS-B(Fc)Mes* from BBr$_3$ (0.82 g, 3.27 mmol), PS-SiMe$_3$ (0.50 g, ca. 2.84 mmol of Me$_3$Si groups), FcSnMe$_3$ (1.56 g, 4.47 mmol), Me$_3$SiOMe (1.4 mL, 10.2 mmol), and TipMgBr (0.5 M in THF, 20 mL, 10.0 mmol). Yield: 0.89 g, 62%. For *PS-B(Fc)Tip*: ^{11}B NMR (160.386 MHz, CDCl$_3$): δ = 56 ppm ($w_{1/2}$ = 2100 Hz). ^{1}H NMR (499.893 MHz, CDCl$_3$): δ = 7.6 (br, 2H, Ph$_o$), 6.9 (br, 2H, Tip$_m$), 6.4 (br, 2H, Ph$_m$), 4.4 (br, 4H, Fc-H2−5), 4.0 (br, 5H, C$_5$H$_5$), 2.9 (br, 1H, *p*-C*H*Me$_2$), 2.5 (br, 2H, *o*-C*H*Me$_2$), 1.45, 1.27, 0.93 (br, 21H, *p*-CH*Me*$_2$, *o*-CH*Me*$_2$, polymer backbone protons). ^{13}C NMR (125.69 MHz, CDCl$_3$): δ = 148.9, 147.9, 142.0 (br), 137.2, 126.8, 119.9 (aromatic C's), 76.0, 73.5 (Fc C's), 69.5 (C$_5$H$_5$), 42−40 (polymer backbone), 35.0 (*p*-*C*HMe$_2$), 34.3 (*o*-*C*HMe$_2$), 24.5 (*o*- and *p*-CH*Me*$_2$). GPC-RI (THF vs PS standards): M_n = 30 400, M_w = 33 700, PDI = 1.11; high-MW shoulder (9% area): M_n = 70 850, M_w = 73 710, PDI = 1.04. UV−vis (THF, mol^{-1} L^{-1} per repeat unit): λ_{max} = 295 nm (ε = 15 850), 366 nm (ε = 1990), 486 nm (ε = 1020). DSC (onset, 10 °C/min; second heating curve): T_g = 132 °C; TGA (20 °C/min; N$_2$): 19% weight loss between 294 and 360 °C; 4% weight loss between 431 and 459 °C; 15% residual mass at 800 °C. Elemental analysis: calculated C 78.90, H 7.83; found C 77.38, H 7.42.

Synthesis of M-B(Fc)Mes. A solution of FcSnMe$_3$ (0.290 g, 0.83 mmol) in CH$_2$Cl$_2$ (5 mL) was cooled to ca. −10 °C and added dropwise to a precooled solution (−10 °C) of 4-^{t}BuPhBBr$_2$ (0.253 g, 0.83 mmol) in CH$_2$Cl$_2$ (5 mL). The dark red reaction mixture was allowed to warm to rt and then stirred for 1 h. Me$_3$SiOMe (0.24 mL, 1.74 mmol) was added neat, and the resulting orange-red solution was stirred for another 1 h. All volatile components were removed under high vacuum. The residue was taken up in THF (10 mL), and a solution of MesMgBr (0.5 M in THF, 1.70 mL, 0.85 mmol) was added. The reaction mixture was stirred at rt for 30 min and then heated to 60 °C for 3 days. The solvent was removed under high vacuum to leave behind a red solid, which was extracted with hexanes. Purification by column chromatography using alumina as the stationary phase and hexanes as the eluent gave the pure product as a red crystalline material (0.260 g, 70%). For *M-B(Fc)Mes*: ^{11}B NMR (160.386 MHz, CDCl$_3$): δ = 70 ppm ($w_{1/2}$ = 1300 Hz). ^{1}H NMR (499.893 MHz, CDCl$_3$): δ = 7.89 (d, ^3J = 8.5 Hz, 2H, Ph$_o$), 7.44 (d, ^3J = 8.5 Hz, 2H, Ph$_m$), 6.86 (s, 2H, Mes$_m$), 4.69, 4.45 (2 × pst, $^{3/4}J$ = 1.5 Hz, 2 × 2H, Fc-H2,5 and Fc-H3,4), 4.26 (s, 5H, C$_5$H$_5$), 2.36 (s, 3H, *p*-Me), 2.12 (s, 6H, *o*-Me), 1.39 (s, 9H, CMe$_3$). ^{13}C NMR (125.69 MHz, CDCl$_3$): δ = 154.8 (Ph$_p$), 143.9, 139.6 (Ph$_i$ and Mes$_i$), 138.5 (Mes$_o$), 136.8 (Ph$_o$), 136.7 (Mes$_p$), 127.2 (Ph$_m$), 125.0 (Mes$_m$), 77.8, 74.3 (Fc C's), 69.5 (C$_5$H$_5$), 35.2 (*C*Me$_3$), 31.4 (C*Me*$_3$), 23.2 (*o*-Me), 21.4 (*p*-Me). UV−vis (THF, mol^{-1} L^{-1}): λ_{max} = 292 nm

Scheme 1. Synthesis of Ferrocenylborane-Modified Polystyrene and Model Systems



(ε = 23 250), 366 nm (ε = 3240), 485 nm (ε = 1630). GC-MS (*t* = 20.34 min): *m*/*z*: 448 [M^+] (100%). Elemental analysis: calculated C 77.71, H 7.42; found C 77.68, H 7.46.

Synthesis of M-B(Fc)Tip. The compound was prepared in analogy to the procedure for *M-B(Fc)Mes* from $FcSnMe_3$ (0.499 g, 1.43 mmol), 4-^{t}BuPhBBr$_2$ (0.425 g, 1.40 mmol), Me_3SiOMe (0.50 mL, 3.63 mmol), and TipMgBr (0.5 M in THF, 4.2 mL, 2.1 mmol). Yield: 0.485 g, 65%. For *M-B(Fc)Tip*: ^{11}B NMR (160.386 MHz, $CDCl_3$): δ = 70 ppm ($w_{1/2}$ = 1750 Hz). ^{1}H NMR (499.893 MHz, $CDCl_3$): δ = 7.96 (d, ^3J = 8.5 Hz, 2H, Ph$_o$), 7.45 (d, ^3J = 8.5 Hz, 2H, Ph$_m$), 6.97 (s, 2H, Tip$_m$), 4.64, 4.47 (2 × pst, $^{3/4}J$ = 1.5 Hz, 2 × 2H, Fc-H2,5 and Fc-H3,4), 4.26 (s, 5H, C_5H_5), 2.93 (m, 1H, *p*-C*H*Me$_2$), 2.67 (m, 2H, *o*-C*H*Me$_2$), 1.38 (s, 9H, CMe$_3$), 1.33 (d, ^3J = 7.0 Hz, 6H, *o*-CH*Me*$_2$), 1.11 (d, ^3J = 7.0 Hz, 6H, *p*-CH*Me*$_2$), 0.98 (d, ^3J = 7.0 Hz, 6H, *p*-CH*Me*$_2$). ^{13}C NMR (125.69 MHz, $CDCl_3$): δ = 154.8 (Ph$_p$), 149.0 (Tip$_o$), 148.0 (Tip$_p$), 142.0, 140.3 (Ph$_i$ and Tip$_i$), 137.3 (Ph$_o$), 124.7 (Ph$_m$), 119.9 (Tip$_m$), 77.8, 73.4 (Fc C's), 75 (br, Fc-C1), 69.5 (C_5H_5), 35.2 (*C*Me$_3$), 34.4 (*o*-*C*H and C*Me*$_3$), 31.4 (*p*-*C*H), 24.7 (*o*-CH*Me*$_2$), 24.4 (*p*-CH*Me*$_2$). UV–vis (CH_2Cl_2, mol^{-1} L^{-1}): λ_{max} = 293 nm (ε = 15 880), 366 nm (ε = 2050), 486 nm (ε = 1100). GC-MS (*t* = 35.78 min): *m*/*z*: 532 [M^+] (100%). Elemental analysis: calculated C 78.96, H 8.52; found C 78.77, H 8.54.

Results and Discussion

The synthetic strategy is outlined in Scheme 1. Initial reaction of PS-BBr$_2$, which was prepared in situ by essentially quantitative replacement of the SiMe$_3$ groups in PS-SiMe$_3$ (M_w = 23 800, PDI = 1.13) with BBr_3,[10,11] with the mild organotin reagent $FcSnMe_3$ (Fc = ferrocenyl) in CH_2Cl_2 at rt gave the monosubstituted intermediate PS-B(Fc)Br. This reaction was accompanied by an immediate color change to red, which is indicative of successful installment of the ferrocene moiety at boron. High selectivity for the desired monofunctionalization was confirmed for the model reaction of (4-^{t}BuPh)BBr$_2$ with $FcSnMe_3$ by ^{1}H NMR spectroscopy, which showed only (4-^{t}BuPh)B(Fc)Br and no evidence of formation of the doubly substituted species (4-^{t}BuPh)B(Fc)$_2$ (see Supporting Information). The presence of a sterically demanding group like the 2,4,6-trimethylphenyl (mesityl, Mes) or 2,4,6-triisopropylphenyl (Tip) substituent is known to enhance the stability of the otherwise hydrolytically sensitive boron center.[4] Attachment of these bulky substituents was achieved by reaction with the respective Grignard reagents. The bromine substituents were first replaced with methoxy groups by treatment with a slight excess of methoxytrimethylsilane in CH_2Cl_2. Then the solvent was replaced with THF, the chosen Grignard reagent ArMgBr (Ar = Mes, Tip) was added, and the mixture was kept at reflux for ca. 5 days. The products were purified by column chromatography on alumina and then repeatedly precipitated from THF into ether. The ferrocenylborane polymers PS-B(Fc)Ar (Ar = Mes, Tip) were isolated as red powdery solids in ca. 60–70% yield. The polymers showed excellent solubility in common organic solvents like CH_2Cl_2, THF, and toluene. A series of molecular model compounds (M-B(Fc)Ar; Ar = Mes, Tip) that mimic one repeating unit of the polymer chain were prepared for comparison through similar procedures. They were readily purified by column chromatography and isolated by recrystallization.

Table 1. ^{11}B NMR Shifts (ppm) of Organoboron Polymers and Molecular Model Compounds[a]

polymer	$\delta(^{11}B)/w_{1/2}$ (Hz)	molecular model	$\delta(^{11}B)/w_{1/2}$ (Hz)
PS-B(Fc)Mes	57/1900	M-B(Fc)Mes	70/1300
PS-B(Fc)Tip	56/2100	M-B(Fc)Tip	70/1750

[a] Data were obtained at rt in $CDCl_3$ (ca. 8 × 10^{-3} M).

The polymers were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy (Table 1). The assignments of the proposed polymeric structures were confirmed by comparison with the respective model compounds. The presence of a broad ^{11}B NMR signal at ca. 56–57 ppm is typical of triarylborane polymers.[12,17] However, for both polymers we observe an upfield shift of almost 15 ppm relative to the molecular species. This may be the result of shielding effects due to neighboring aryl groups in the case of the polymers and is consistent with prior observations for polymers that feature bithiophene borane pendant groups.[12] For both polymers, integration of the ferrocenyl region in the ^{1}H NMR spectra relative to the aromatic and aliphatic regions was in agreement with close to quantitative attachment of the –B(Fc)Ar pendant groups to the polystyrene (see Supporting Information). This is consistent with the model reactions described above where we found highly selective attachment of only one ferrocenyl group in the reaction of (4-^{t}BuPh)BBr$_2$ with an excess of $FcSnMe_3$.

The polymers were further analyzed by gel permeation chromatography (GPC) in THF against PS standards. For both polymers a narrow band was found in the expected molecular weight range (PS-B(Fc)Mes, M_w = 27 400, PDI = 1.15; PS-B(Fc)Tip, M_w = 33 700, PDI = 1.11). A small high molecular weight shoulder was apparent in both cases, and a Gaussian fit suggested that the MW of this fraction is about double that of the main peak. This slight bimodality with still very narrow dispersities indicates that homocoupling at the Br end groups may have occurred to a small extent (radical coupling). Such a process has, for example, been reported by Matyjaszewski to take place in the presence of Cu(I) species and has explicitly been exploited for the generation of telechelic polymers.[18] The high temperature employed during the installment of the bulky aryl groups likely favors this small extent of coupling (< 15%) detected for the products.[19]

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed to examine the thermal characteristics and stability. While for PS-B(Fc)Mes no clear glass transition (T_g) could be detected up to 250 °C, PS-B(Fc)Tip shows a T_g of 132 °C, which is at slightly higher temperature compared to polystyrene (T_g = 110 °C);[20] this may indicate that

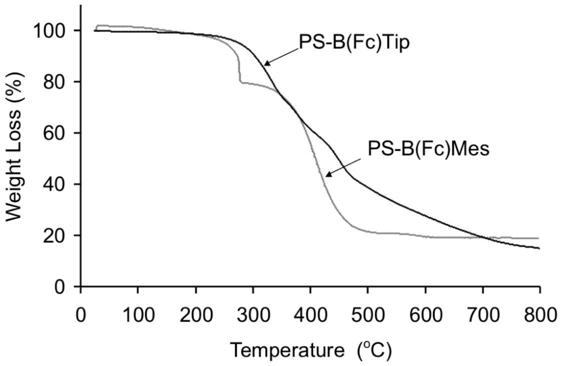


Figure 1. Thermogravimetric analysis (TGA) plots of PS-B(Fc)Mes and PS-B(Fc)Tip (20 °C/min).

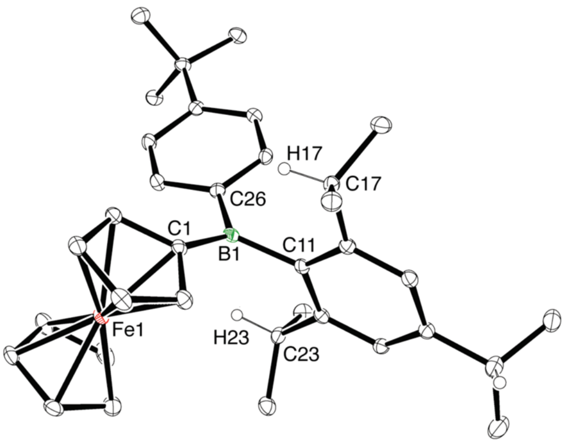


Figure 2. Molecular structure of M-B(Fc)Tip (ORTEP, 50% probability). All hydrogens except for those on the $CHMe_2$ groups are omitted for clarity. Selected bond lengths (Å): B1−C1 = 1.542(3), B1−C11 = 1.587(3), B1−C26 = 1.562(3).

the polymer structure is more rigid due to the presence of bulky triisopropylphenyl groups. The TGA data demonstrate high thermal stability of the polymers with no apparent decomposition up to ca. 275 °C (Figure 1). Above this temperature multistep decomposition processes were observed. The residual weights of polymers PS-B(Fc)Mes and PS-B(Fc)Tip at 800 °C were 22% and 15%, respectively.

To investigate their oxidative stability, the polymers were exposed to air and moisture in wet $CDCl_3$ and C_6D_6. They were also kept under air as solids for a period of 1 month, and the degradation was monitored by ^1H NMR spectroscopy. In $CDCl_3$ as the solvent the polymer PS-B(Fc)Mes was perfectly stable for ca. 9 days and PS-B(Fc)Tip for over 3 weeks. In contrast, no substantial degradation was observed in the solid state for over 3 weeks for PS-B(Fc)Mes, and the polymer PS-B(Fc)Tip remained stable for more than 1 month. A similar trend was observed for the model compounds M-B(Fc)Mes and M-B(Fc) Tip. This indicates that the stability of the boron center is primarily determined by the steric effect of the substituent.

The steric protection of the boron center by the isopropyl groups in the *ortho*-positions of the Tip substituent is also evident from an X-ray structure determination that was performed on dark red single crystals of M-B(Fc)Tip obtained from hexanes at −20 °C. Two independent molecules are found in the unit cell, the geometric parameters of which are similar to one another; hence, only one of them is displayed in Figure 2. The molecular structure of M-B(Fc)Tip shows clearly that the isopropyl groups are positioned in close proximity to the empty p orbital on boron, thereby hindering attack of nucleophiles at the boron center. The boron atom is only slightly bent out of the Cp plane with Cp (centroid)−C1−B1 = 177.6° and 176.7° for the two independent molecules. This is in contrast to the strong tilting of the electron-deficient organoborane moiety toward the electron-rich Fe center typically observed for ferrocenylboranes[21] and thus indicates that steric strain prevents more pronounced interaction with the Fe d orbitals. Steric effects are also reflected in the B−C bond lengths; the B−C bonds to the bulky Tip group of 1.587(3) and 1.583(3) Å are significantly longer that those to the *tert*-butylphenyl group (1.562(3) and 1.566(3) Å). The B−C(Cp) bond lengths of 1.542(3) Å are comparatively even shorter, but in a similar range as for other ferrocenylborane species (e.g., $FcB(C_6F_5)_2$,[22] 1.501(4) Å; $FcB(Mes)_2$,[23] 1.546(7) Å).

The electronic structure of the polymers was examined by UV−vis spectroscopy and cyclic voltammetry (Table 2). They exhibit a band at ca. 485 nm in THF, which is characteristic of a d−d transition of the ferrocene moiety with charge transfer character and is also observed for the model systems. Cyclic voltammetry studies were carried out in THF (cathodic scans) and CH_2Cl_2 (anodic scans) using $[Bu_4N]PF_6$ as the electrolyte (Figure 3). The polymers PS-B(Fc)Mes and PS-B(Fc)Tip exhibit a redox process at 131 and 129 mV, respectively, which originates from the ferrocene oxidation. The redox potentials are similar to those determined for the respective molecular species M-B(Fc) Mes ($E_{1/2}$ = 133 mV) and M-B(Fc)Tip ($E_{1/2}$ = 118 mV). However, the shape of the redox waves for the polymers show signs of deposition of the oxidized polymeric material on the electrode. An additional redox process is observed in THF at $E_{1/2} = -2.83$ V for PS-B(Fc)Mes and at $E_{1/2} = -2.81$ V for PS-B (Fc)Tip, respectively; this process is attributed to the reduction of the organoborane moieties. Again, similar redox potentials were recorded for the molecular model systems (M-B(Fc)Mes, $E_{1/2} = -2.76$ V; M-B(Fc)Tip, $E_{1/2} = -2.73$ V).

Tricoordinate organoboranes are well-known to form complexes with Lewis basic substrates, a property that has been widely exploited for chemosensor applications.[24] Notable in the case of ferrocenylboranes is the work by Aldridge and others on their use for the colorimetric and electrochemical detection of fluoride.[23,25] Binding studies performed on PS-B(Fc)Mes and the respective model compound indicate that the boron centers do not significantly bind to pyridine as evident from a lack of a significant change in the ^{11}B NMR shift upon addition of a large excess of pyridine (> 10 equiv). In contrast, Bu_4NF binds to the boron centers easily as indicated by a significant upfield shift in the ^{11}B NMR to ca. 4 ppm (see Supporting Information). The selectivity for fluoride over pyridine is attributed to the steric bulk provided by the mesityl group. A similar result is obtained for PS-B(Fc)Tip and the model M-B(Fc)Tip. UV−vis titrations were performed to determine the fluoride binding constants for the polymers (Figure 4). Noteworthy is that the binding constants determined for polymers PS-B(Fc)Mes (2.9×10^4 M^{-1}) and PS-B(Fc)Tip (2.7×10^4 M^{-1}) are similar,[26] but both are considerably smaller than the ones for the model compounds, indicating a distinct polymer effect on the binding strength. This is attributed to the fact that fluoride binding leads to a change from a trigonal to a tetrahedral geometry at boron, which should strongly enhance steric interactions with neighboring arylborane moieties.[27] From the binding constants determined for the model compounds, it can be inferred that binding of the fluoride to the model compound M-B(Fc)Mes (4.7×10^6 M^{-1}) is only slightly stronger than to M-B(Fc)Tip (3.4×10^6 M^{-1}).

In summary, we have prepared two electroactive borylated polystyrene derivatives that bear an electron-rich ferrocene moiety on boron along with a mesityl or a triisopropylphenyl group for steric protection. The polymer with the bulkier triisopropylphenyl group is relatively more stable than that with a mesityl group attached to boron. According to cyclic voltammetry studies both polymers undergo oxidation at a potential close

Table 2. Comparison of UV−vis and Cyclic Voltammetry Data

	absorption[a]		boron redox[b]		ferrocene redox[c]	
	λ_{max}	log ε	$E_{1/2}$ (V)	ΔE_p (mV)	$E_{1/2}$ (V)	ΔE_p (mV)
PS-B(Fc)Mes	295/368/484	4.3/3.4/3.1	−2.83	217	0.131	65
PS-B(Fc)Tip	295/366/486	4.2/3.3/3.0	−2.81	51	0.129	76
M-B(Fc)Mes	292/366/485	4.4/3.5/3.2	−2.76	257	0.133	117
M-B(Fc)Tip	293/366/486	4.2/3.3/3.0	−2.73	150	0.118	133

[a] Data were acquired in THF at rt. [b] In THF/0.1 M Bu_4NPF_6. [c] In CH_2Cl_2/0.1 M $[Bu_4N]PF_6$.

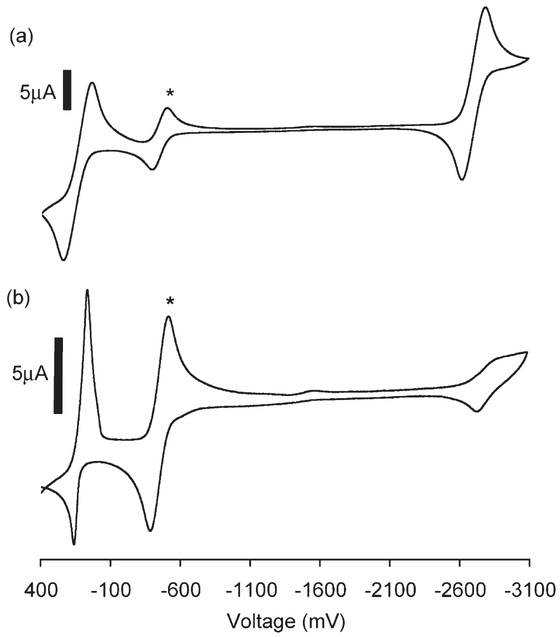


Figure 3. Cyclic voltammograms of (a) M-B(Fc)Mes and (b) PS-B(Fc)Mes (1.2×10^{-3} M) with 0.1 M $[Bu_4N]PF_6$ in THF as the supporting electrolyte (scan rate 100 mV/s). Asterisk (∗) denotes decamethylferrocene used as a reference.

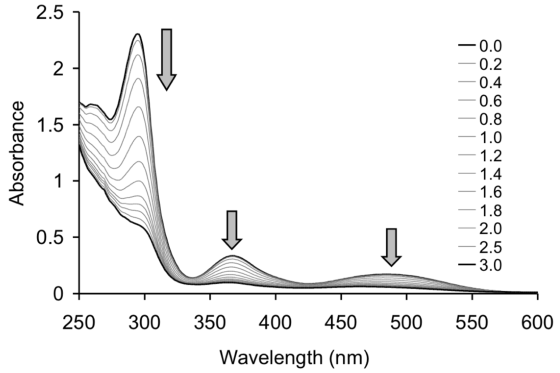


Figure 4. Spectral titration of PS-B(Fc)Mes (1.20×10^{-4} M for boron sites) with aliquots of a 3.62×10^{-3} M solution of $[Bu_4N]F$ in THF; added equiv are given relative to borane units.

to, but slightly higher than, that of ferrocene itself, while reduction of the boron centers occurs at highly negative potentials of ca. −2.8 V relative to the ferrocene/ferrocenium couple. Anion complexation studies suggest that the polymers bind fluoride less effectively than the molecular model systems, an aspect that is attributed to pronounced neighboring group effects. An enhancement of the anion binding ability is expected upon oxidation of the ferrocene sites[28] in the polymer and studies in this regard are currently under way.

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Supporting Information Available: ^{1}H NMR data for polymers PS-B(Fc)Mes and PS-B(Fc)Tip; ^{1}H NMR data for the model reaction of (4-*tert*-butylphenyl)dibromoborane with $FcSnMe_3$; comparison of ^{11}B NMR spectra of PS-B(Fc)Mes after fluoride and pyridine addition; spectral titration plots for the fluoride binding to M-B(Fc)Tip and PS-B(Fc)Tip. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Archer, R. D. *Inorganic and Organometallic Polymers*; Wiley-VCH: New York, 2001. (b) Abd-El-Aziz, A. S.; Carraher Jr., C. E.; Pittman Jr., C. U.; Sheats, J. E.; Zeldin, M. *Macromolecules Containing Metal and Metal-Like Elements*; John Wiley & Sons: Hoboken, NJ, 2003; Vol. *1*. (c) Manners, I. *Synthetic Metal-Containing Polymers*; Wiley-VCH: New York, 2004. (d) Abd-El-Aziz, A. S., Manners, I., Eds.; *Frontiers in Transition Metal-Containing Polymers*; Wiley-Interscience: Hoboken, NJ, 2007.

(2) (a) Manners, I. *Chem. Commun.* **1999**, 857–865. (b) Hudson, R. D. A. *J. Organomet. Chem.* **2001**, *637*–*639*, 47–69. (c) Stepnicka, P., Ed. *Ferrocenes: Ligands, Materials and Biomolecules*; Wiley-VCH: Weinheim, 2008.

(3) Rider, D. A.; Winnik, M. A.; Manners, I. *Chem. Commun.* **2007**, 4483–4485.

(4) (a) Entwistle, C. D.; Marder, T. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2927–2931. (b) Entwistle, C. D.; Marder, T. B. *Chem. Mater.* **2004**, *16*, 4574–4585.

(5) (a) Jäkle, F. Boron: Organoboranes. In *Encyclopedia of Inorganic Chemistry*, 2nd ed.; King, R. B., Ed.; Wiley: Chichester, 2005; pp 560−598. (b) Jäkle, F. *Coord. Chem. Rev.* **2006**, *250*, 1107–1121. (c) Matsumi, N.; Chujo, Y. *Polym. J.* **2008**, *40*, 77–89. (d) Elbing, M.; Bazan, G. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 834–838.

(6) (a) Heilmann, J. B.; Scheibitz, M.; Qin, Y.; Sundararaman, A.; Jäkle, F.; Kretz, T.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 920–925. (b) Heilmann, J. B.; Qin, Y.; Jäkle, F.; Lerner, H. W.; Wagner, M. *Inorg. Chim. Acta* **2006**, *359*, 4802–4806.

(7) Matsumi, N.; Chujo, Y.; Lavastre, O.; Dixneuf, P. H. *Organometallics* **2001**, *20*, 2425–2427.

(8) (a) Branger, C.; Lequan, M.; Lequan, R. M.; Large, M.; Kajzar, F. *Chem. Phys. Lett.* **1997**, *272*, 265–270. (b) Branger, C.; Lequan, M.; Lequan, R. M.; Large, M.; Kajzar, F.; Barzoukas, M.; Fort, A. *MCLC S&T, Sect. B: Nonlinear Opt.* **1997**, *17*, 281–303.

(9) Mutaguchi, D.; Okumoto, K.; Ohsedo, Y.; Moriwaki, K.; Shirota, Y. *Org. Electron.* **2003**, *4*, 49–59.

(10) (a) Qin, Y.; Cheng, G.; Sundararaman, A.; Jäkle, F. *J. Am. Chem. Soc.* **2002**, *124*, 12672–12673. (b) Qin, Y.; Sukul, V.; Pagakos, D.; Cui, C.; Jäkle, F. *Macromolecules* **2005**, *38*, 8987–8990.

(11) Qin, Y.; Cheng, G.; Parab, K.; Achara, O.; Jäkle, F. *Macromolecules* **2004**, *37*, 7123–7131.

(12) Parab, K.; Venkatasubbaiah, K.; Jäkle, F. *J. Am. Chem. Soc.* **2006**, *128*, 12879–12885.

(13) (a) Lenze, N.; Neumann, B.; Salmon, A.; Stammler, A.; Stammler, H.-G.; Jutzi, P. *J. Organomet. Chem.* **2001**, *619*, 74–87. (b) Rebiere, F.; Samuel, O.; Kagan, H. B. *Tetrahedron Lett.* **1990**, *31*, 3121–3124.

(14) Qin, Y.; Kiburu, I.; Shah, S.; Jäkle, F. *Org. Lett.* **2006**, *8*, 5227–5230.

(15) (a) Scott, Natalie M.; Schareina, T.; Tok, O.; Kempe, R. *Eur. J. Inorg. Chem.* **2004**, *2004*, 3297–3304. (b) Miller, A. R.; Curtin, D. Y. *J. Am. Chem. Soc.* **1976**, *98*, 1860–1865.

(16) Sheldrick, G. SHELXTL (5.10); Bruker XRD, Madison, WI.

(17) Li, H.; Sundararaman, A.; Venkatasubbaiah, K.; Jäkle, F. *J. Am. Chem. Soc.* **2007**, *129*, 5792–5793.

(18) Sarbu, T.; Lin, K.-Y.; Spanswick, J.; Gil, R. R.; Siegwart, D. J.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 9694–9700.

(19) Other possibilities, which are less likely although we can not fully rule them out, are (i) the presence of a trace amount of 1,1′-bis(trimethylstannyl)ferrocene in the tin reagent that may act as a cross-linker and (ii) incomplete substitution of the PS-B(Fc)Br intermediate with the aryl Grignard reagent and subsequent hydrolysis with formation of B−O−B cross-links. However, the ^{11}B and ^{1}H NMR data provide no evidence of the latter.

(20) Rieger, J. *J. Therm. Anal.* **1996**, *46*, 965–972.

(21) Scheibitz, M.; Bolte, M.; Bats, J. W.; Lerner, H.-W.; Nowik, I.; Herber, R. H.; Krapp, A.; Lein, M.; Holthausen, M.; Wagner, M. *Chem.—Eur. J.* **2005**, *11*, 584–603.

(22) Carpenter, B. E.; Piers, W. E.; Parvez, M.; Yap, G. P. A.; Rettig, S. J. *Can. J. Chem.* **2001**, *79*, 857–867.

(23) Broomsgrove, A. E. J.; Addy, D. A.; Bresner, C.; Fallis, I. A.; Thompson, A. L.; Aldridge, S. *Chem.—Eur. J.* **2008**, *14*, 7525–7529.

(24) (a) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2000**, *122*, 6335–6336. Miyata, M.; Chujo, Y. *Polym. J.* **2002**, *34*, 967–969. (b) Solé, S.; Gabbaï, F. P. *Chem. Commun.* **2004**, 1284–1285. (c) Sun, Y.; Ross, N.; Zhao, S. B.; Huszarik, K.; Jia, W. L.; Wang, R. Y.; Macartney, D.; Wang, S. *J. Am. Chem. Soc.* **2007**, *129*, 7510–7511.

(25) (a) Yamamoto, H.; Ori, A.; Ueda, K.; Dusemund, C.; Shinkai, S. *Chem. Commun.* **1996**, 407–408. (b) Bresner, C.; Aldridge, S.; Fallis, I. A.; Jones, C.; Ooi, L.-L. *Angew. Chem., Int. Ed.* **2005**, *44*, 3606–3609.

(26) The polymer analysis assumes close to quantitative attachment of −B(Fc)Ar pendant groups, which is supported by ^{1}H NMR data and elemental analysis results.

(27) As pointed out by a reviewer, another possibility for the differences in the binding constants of the polymers and molecular systems is that the fluoride anions bridge different boryl pendant groups in the polymers. However, on the basis of our prior studies on related bithiopheneborane polymers, this is unlikely; see ref 12.

(28) (a) Venkatasubbaiah, K.; Nowik, I.; Herber, R. H.; Jäkle, F. *Chem. Commun.* **2007**, 2154–2156. (b) Kaufmann, L.; Vitze, H.; Bolte, M.; Lerner, H. W.; Wagner, M. *Organometallics* **2008**, *27*, 6215–6221.