Synthesis, Characterization, and AFM Studies of Dendronized Polyferrocenylsilanes

Kyoung Taek Kim,[†] Junwon Han,[§] Chang Y. Ryu,[§] Frank C. Sun,[⊥] Sergei S. Sheiko,[⊥] Mitchell A. Winnik,*,[†] and Ian Manners*,[†,‡]

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada; The School of Chemistry, University of Bristol, Bristol BS8 1TS, England; Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, Troy, New York 12180; and Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

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ABSTRACT: Dendronized polyferrocenylsilanes were synthesized by a substitution reaction of reactive poly(ferrocenylchloromethylsilane) with monodendrons with a focal hydroxy group. The resulting dendronized polymers were studied by ^{1}H NMR, differential scanning calorimetry (DSC), and polarized optical microscopy (POM). To facilitate the direct visualization of single polymer chains by atomic force microscopy (AFM), an interaction chromatography technique (IC) was used to fractionate the polydisperse polymers to separate the high molecular weight dendronized PFSs. AFM studies of the fractionated high molecular weight PFSs revealed a spherical cocoon for the single chains of the dendronized polymer as well as elongated single-chain structures. The cocoon of the dendronized PFS could be interesting as a unimolecular micelle with the transition-metal-rich core which is isolated by the dense outer layer of the dendrons.

Introduction

Dendronized polymers are linear polymers that have dendritic side groups in every repeat unit.[1] As the size of the dendron (the generation of the dendron) increases, the steric repulsion between neighboring dendrons increases. Above the critical size of the dendron, the polymer backbone would be stiffened and turned into a cylindrical shape. This molecular cylinder could be a useful nanosized entity for building novel functional materials.[2] Also, because of the high density of the functional groups at the periphery of the dendron side chains, the dendronized polymers could be useful scaffolds for drug delivery.[3] Percec and co-workers demonstrated that the dendronized polymers possess either a spherical or a cylindrical conformation depending on the size and the generation number of the dendron side chain.[4] Because of the large size of the individual chains, the dendronized polymer chains could be directly visualized by techniques such as atomic force microscopy. The layer of the congested dendron side chains can effectively isolate the polymer main chain.[1] For example, Aida and co-workers reported this effect for dendronized luminescent poly(phenylene ethynylene)s (PPEs) with benzyl ether dendron side chains.[5] The luminescence intensity of the PPE backbone in the solution was preserved upon increasing the concentration of the polymer. The dense layer of the dendron side chains provided effective isolation for the PPE backbone by preventing collisonal quenching between the PPE chains.

Metal-containing polymers are a topic of interest due to their unique properties arising from the presence of transition metal atoms in the macromolecular structures.[6] Polyferrocenylsilanes (PFSs) are a class of metallopolymers containing iron atoms in the main chain.[7] Interesting properties of PFSs such as redox activity, semiconductivity, and the ability to function as precursors to catalysts for the growth of carbon nanotubes have been studied.[7,8] Since the discovery of thermal ring-opening polymerization of [1]-silaferrocenophanes,[9] various other polymerization techniques such as transition-metal-catalyzed, living anionic, and photolytic ring-opening polymerization have been developed.[7,10] The transition-metal-catalyzed polymerization of silaferrocenophanes is of particular interest because this technique allows the polymerization of the ferrocenophane monomer containing a reactive group such as Si−Cl group.[11] The resulting polymer, poly(ferrocenylchloromethylsilane), can be readily functionalized by the substitution reaction of the Si−Cl group with alkyllithiums and species with hydroxy groups.[12]

Dendronized polymers containing polyferrocenylsilane backbone could be an interesting class of materials due to the characteristics of the metallopolymer backbone.[13] Furthermore, the redox and catalytic activity of the PFS would be localized within spherical or columnar nanostructure isolated from the surroundings due to the dense outer layer consisting of bulky dendritic side chains. This could provide a unique environment for the PFS core with respect to the development of functional materials based on the templated growth of metal nanoparticles within localized environments via a redox process involving the Fe(II)/Fe(III) couple.[14]

In this paper we report the synthesis of dendronized PFSs by introducing the dendron side groups to the PFS backbone containing reactive Si−Cl groups. The resulting dendronized PFS were expected to possess a conformation dictated by the size and the generation number of the dendron side groups. We also attempted to directly visualize single dendronized PFS chains by using atomic force microscopy.

Experimental Section

General Methods. Chemicals were purchased from Aldrich and used as received. NMR spectra were recorded on a Varian Gemini 300 or Gemini 400 spectrometer with benzene-d_6 or chloroform-d as a solvent and internal standard. Mass spectra were obtained on

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* To whom correspondence should be addressed. E-mail: mwinnik@chem.utoronto.ca; ian.manners@bristol.ac.uk.

[†] University of Toronto.

[‡] University of Bristol.

[§] Rensselaer Polytechnic Institute.

[⊥] University of North Carolina at Chapel Hill.

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a Perseptive Biosystems Voyage MALDI-TOF mass spectrometer using a 337 nm nitrogen laser for desorption and dithranol as the matrix. FT-IR measurements were performed on a Perkin-Elmer Spectrum One spectrometer. Thermal characterization was performed on a TA Instruments DSC 2920 modulated DSC equipped with a refrigeration cooling unit. A Nikon Optiphoto2-Pol microscope equipped with a Mettler FP82HT hot stage and a Nikon digital camera were used for optical microscopy experiments. Molecular weights of polymers were measured on a Viscotek GPC max system (VE 2001 GPC solvent/sample module and TriSEC model 302 triple detector array) with THF as an eluent. AFM images were collected using a Nanoscope IIIa multimode atomic force microscope (Veeco Metrology Group) in tapping mode. The specimens were prepared by spin-casting of dilute polymer solutions on a mica substrate. For electrochemical measurements, cyclic voltammetry was performed using an Epsilon EC instrument equipped with an Au electrode and an Ag/AgCl reference electrode. All measurements were performed under a purified N_2 atmosphere. The working electrode, Au, was used in conjunction with a Pt wire as the counter electrode. The data were obtained with a scan rate of 100 mV/s at 22 °C. The solutions of polymer in CH_2Cl_2 (previously dried over CaH_2 and distilled under N_2) with a concentration of 5×10^{-3} M and 0.1 M in $[NBu_4][PF_6]$ (previously recrystallized from EtOH and vacuum-dried) were used for the experiments. Ferrocene was added as internal standard at the end of the each experiment, and potentials are reported vs the ferrocene/ferrocenium couple. Dynamic light scattering (DLS) measurements were performed using a wide-angle light scattering photometer from the ALV-5000 system. The light source was a JDS Uniphase He−Ne laser (632.8 nm, 35 mW). Data were collected at 25 °C and were analyzed using the CONTIN algorithm.

Synthesis of Dendrons with Various Focal Groups. All reactions were performed under a nitrogen atmosphere. All dendrons with a focal carboxylic acid group (**D0-COOH**, **D1-COOH**, and **D2-COOH**) and a focal benzyl alcohol group (**D0** and **D1**) used in this paper were prepared following the methods reported by Percec et al.[15] but with slight modifications. The synthesis of D1-TEG has been reported by Percec et al.[16]

D0-Ph. D0-COOH (6.75 g, 10 mmol) and 1,1′-carbodiimidazole (CDI) (2.43 g, 11.5 mmol) were charged in a two-neck round-bottom flask equipped with a reflux condenser. 2-Butanone (60 mL) was added to the flask, and this solution was stirred for 4 h at room temperature. 4-Aminophenol (1.64 g, 15 mmol) was added to the reaction mixture, and the reaction was stirred for 6 h at 50 °C. Upon cooling the solution to room temperature, a white precipitate was formed. The precipitated powder was filtered, washed profusely with 2-butanone, and dissolved in chloroform (150 mL). The chloroform solution was extracted with dilute aqueous HCl twice. The organic layer was dried with anhydrous $MgSO_4$ and then concentrated. Upon recrystallization in $CHCl_3$/hexane (20/80 by volume), a white powder was obtained. Yield: 7.2 g (94%). ^{1}H NMR (δ = ppm, $CDCl_3$, 300 MHz): 0.94 (t, J = 6.9 Hz, CH_3CH_2−, 9H), 1.32 (s, CH_3CH_2−, 54H), 1.75−1.93 (m, −CH_2CH_2O−, 6H), 4.05−4.09 (m, −CH_2CH_2O−, 6H), 6.85 (d, J = 8.7 Hz, −CONH−*Ph*−OH, 2H), 7.09 (s, *Ph*−NHCO−PhOH, 2H), 7.44 (d, J = 8.7 Hz, Ph−CONH−*Ph*, 2H), 7.74 (br, NH, 1H). ^{13}C NMR (δ, $CDCl_3$, 100 MHz): 166.15, 153.37, 153.23, 141.43, 130.28, 129.69, 122.98, 115.93, 105.82, 73.61, 69.45, 31.96, 31.95, 30.34, 29.78, 29.75, 29.73, 29.69, 29.67, 29.61, 29.44, 29.42, 29.39, 26.11, 22.71, 14.13. Mass (MALDI-TOF) for $C_{49}H_{83}NO_5$: found 767.4 (M + H), 788.9 (M + Na).

D1-Ph. D1-COOH (4.96 g, 5 mmol), CDI (0.97 g, 6 mmol), and 4-aminophenol (0.65 g, 6 mmol) were reacted in the same manner for **D0-Ph**. After recrystallization in CH_2Cl_2/hexane (2:8 by volume), a white powder was obtained. Yield: 4.2 g (77%). ^{1}H NMR (δ = ppm, $CDCl_3$, 300 MHz): 0.91 (t, J = 7.2 Hz, CH_3-CH_2−, 9H), 1.28−1.55 (br, CH_3CH_2−, 54H), 1.75−1.87 (m, −CH_2-CH_2O−, 6H), 3.92−4.04 (m, −CH_2CH_2O−, 6H), 5.05 (s, Ph−CH_2O−Ph, 2H), 5.08 (s, Ph−CH_2O−Ph, 4H), 6.79 (d, J = 8.7 Hz, CONH−*Ph*−OH), 6.83 (d, J = 9 Hz, *Ph*−CH_2O−, 2H), 6.91 (d, J = 8.7 Hz, *Ph*−CH_2O−, 4H), 7.13 (s, *Ph*−COO−, 2H), 7.28 (d, J = 8.7 Hz, *Ph*−CH_2O−, 2H), 7.33 (d, J = 8.7 Hz, *Ph*−CH_2O−, 4H), 7.42 (d, J = 8.7 Hz, CONH−*Ph*−, 2H), 7.54 (s, NH, 1H). ^{13}C (δ, $CDCl_3$, 100 MHz): 171.96, 159.10, 159.05, 152.95, 152.71, 130.92, 130.33, 130.07, 129.39, 129.33, 128.54, 122.34, 115.77, 114.53, 114.17, 107.36, 74.79, 71.46, 68.11, 68.03, 31.94, 29.69, 29.64, 29.48, 29.45, 29.37, 29.34, 29.32, 26.09, 22.71, 14.14. Mass (MALDI-TOF) for $C_{70}H_{101}NO_8$: found 1086.9 (M + H).

D1-TEG. In a two-neck flask equipped with a reflux condenser, **D1-COOH** (4.96 g, 5 mmol) and CDI (0.97 g, 6 mmol) were reacted in THF (60 mL) at room temperature for 4 h. The solution was cooled to 0 °C, and then a solution of triethylene glycol (7.5 g, 50 mmol) in THF (50 mL) was added, while the temperature was kept at 0 °C. This solution was stirred for 1 h at 0 °C and then stirred at 50 °C for 8 h. The solvents were removed under reduced pressure. The crude mixture was dissolved in CH_2Cl_2 and extracted with water three times. The organic layer was dried with anhydrous $MgSO_4$. The concentrated solution was precipitated in acetone. A white glassy solid was obtained after filtering and drying under vacuum for 24 h. Yield: 5.1 g (91%). ^{1}H NMR (δ = ppm, $CDCl_3$, 300 MHz): 0.91−0.99 (m, CH_3CH_2−, 9H), 1.32 (s, CH_3CH_2−, 54H), 1.59−1.72 (m, −CH_2CH_2O−, 6H), 3.27−3.38 (m, −OCH_2CH_2O−, 6H), 3.42−3.45 (t, −OCH_2CH_2OH, 2H), 3.52−3.55 (t, −OCH_2CH_2OH, 2H), 3.61−3.72 (m, −OCH_2CH_2O−, 6H), 4.35−4.38 (t, −$COOCH_2CH_2O$−, 2H), 4.87 (s, Ph−CH_2O−Ph, 4H), 5.26 (s, Ph−CH_2O−Ph, 2H), 6.81 (d, J = 8.4 Hz, *Ph*CH_2O−, 2H), 6.88 (d, J = 8.4 Hz, *Ph*CH_2O−, 4H), 7.29 (d, J = 8.4 Hz, *Ph*CH_2O−, 4H), 7.44 (d, J = 8.4 Hz, *Ph*CH_2O−, 2H), 7.83 (s, *Ph*COO−, 2H). Mass (MALDI-TOF) for $C_{70}H_{108}O_{11}$: found 1126.1 (M + H).

D2-Ph. D2-COOH (10.4 g, 5 mmol), CDI (0.97 g, 6 mmol), and 4-aminophenol (0.65 g, 6 mmol) were reacted in the same manner as for **D0-Ph**. After recrystallization in CH_2Cl_2/hexane (2:8 vol), a white powder was obtained. Yield: 6.7 g (61%). ^{1}H NMR (δ = ppm, $CDCl_3$, 400 MHz): 0.89−0.96 (m, CH_3CH_2−, 27H), 1.23−1.55 (m, CH_3CH_2−, 162H), 1.72−1.82 (m, −CH_2-CH_2O−, 18H), 3.79−3.82 (m, −CH_2CH_2O−, 4H), 3.89−4.01 (m, −CH_2CH_2O−, 14H), 5.06 (s, Ph−CH_2O−, 4H), 5.08 (s, Ph−CH_2O−, 2H), 6.65 (s, *Ph*−CH_2O−, 2H), 6.66 (s, *Ph*−CH_2O−, 4H), 6.76 (d, J = 8.8 Hz, CONH−*Ph*−OH, 2H), 7.20 (s, −*Ph*−CONH−, 2H), 7.35 (d, J = 8 Hz, CONH−*Ph*−OH, 2H), 7.70 (s, NH, 1H). ^{13}C (δ, $CDCl_3$, 100 MHz): 165.44, 153.46, 153.33, 153.04, 152.89, 141.52, 137.86, 137.77, 132.40, 131.74, 130.23, 122.61, 122.59, 115.86, 107.56, 106.36, 105.75, 75.22, 73.48, 73.42, 71.92, 69.15, 68.95, 31.98, 30.43, 29.83, 29.78, 29.73, 29.71, 29.62, 29.55, 29.53, 29.50, 29.45, 29.42, 26.27, 26.21, 22.73, 14.13. Mass (MALDI-TOF) for $C_{142}H_{245}NO_{14}$: found 2192.4 (M + H).

D2-TEG. D2-COOH (10.4 g, 5 mmol), CDI (0.97 g, 6 mmol), and triethylene glycol (7.5 g, 50 mmol) were reacted in the same manner as for **D1-TEG**. After precipitation in acetone, a white solid was obtained. The crude solid was separated by column chromatography (SiO_2, CH_2Cl_2/ethyl acetate (9:1 by vol)). A white glassy solid was obtained. Yield: 3.2 g (28%). ^{1}H NMR (δ = ppm, $CDCl_3$, 300 MHz): 0.88−0.095 (m, CH_3CH_2−, 27H), 1.25−1.56 (br, CH_3CH_2−, 162H), 1.70−1.83 (m, −CH_2CH_2O−, 18H), 3.62−3.65 (m, −CH_2CH_2−OH, 2H), 3.72−3.75 (m, −OCH_2CH_2O−, 6H), 3.76−3.80 (m, −$CH_2CH_2CH_2O$−, 4H), 3.84−3.87 (m, −OCH_2-CH_2OH, 2H), 3.90−4.02 (m, −$CH_2CH_2CH_2O$−, 14H), 4.49−4.52 (m, −Ph−COO−CH_2CH_2O−, 2H), 5.07 (s, Ph−CH_2O−, 6H), 6.36 (s, *Ph*−CH_2O−, 2H), 6.67 (s, *Ph*−CH_2O−, 4H), 7.46 (s, −*Ph*−COO−, 2H). ^{13}C (δ, $CDCl_3$, 100 MHz): 166.06, 153.28, 153.04, 152.06, 142.71, 137.87, 137.81, 132.41, 131.73, 125.17, 109.82, 106.21, 105.81, 105.74, 75.17, 73.41, 73.33, 72.51, 71.72, 70.71, 70.39, 69.31, 69.10, 68.91, 64.03, 61.78, 31.96, 30.46, 30.44, 31.96, 30.46, 30.44, 29.85, 29.82, 29.81, 29.80, 29.78, 29.72, 29.70, 29.62, 29.54, 29.49, 29.44, 29.43, 29.42, 26.25, 26.24, 26.20, 22.72, 14.13. Mass (MALDI-TOF) for $C_{142}H_{252}O_{17}$: found 2234.2 (M + H).

PFS-MeO. Poly(chloromethyl ferrocenylsilane) (**PFS-Cl**) was prepared and purified as reported previously.[11] For analytical purposes, the reactive chlorine group on the silicon atom was substituted with a methoxy group by a reaction with methanol: To a 25 mL of toluene solution of **PFS-Cl** (1 g) under a nitrogen atmosphere were added triethylamine (1 mL) and methanol (1 mL). The mixture was stirred for 24 h at room temperature and was then precipitated into methanol (200 mL). A yellow precipitant was collected, washed with methanol, and vacuum-dried for 24 h at room temperature. Yield: 0.82 g. ^{1}H NMR (δ = ppm, C_6D_6, 300 MHz): 0.66−0.73 (m, *CH*$_3$−Si, 3H), 3.50 (s, *CH*$_3$−O−Si, 3H), 4.21−4.43 (m, *Cp*, 8H). GPC (PS standard, THF): M_n = 24 550 g/mol, M_w/M_n = 2.13.

PFS-D0. The reaction was performed under a nitrogen atmosphere. Toluene (30 mL) and triethylamine (1 mL) were added in a Schlenk flask with **PFS-Cl** (0.52 g) and **D0** (1.58 g, 2.4 mmol). The reaction mixture was stirred for 24 h at room temperature. After 24 h, methanol (1 mL) was added in the flask, and the solution was further stirred for 4 h at room temperature. The resulting solution was precipitated into methanol (300 mL). An amber gummy solid was obtained, and the collected polymer was redissolved in THF (30 mL). THF solution was precipitated into methanol (250 mL). An amber polymer was collected and vacuum-dried for 24 h at room temperature. Yield: 1.18 g (66%). ^{1}H NMR (δ = ppm, C_6D_6, 300 MHz): 0.78−0.87 (br, *CH*$_3$−Si, 3H), 0.95−1.04 (m, *CH*$_3$−CH_2CH_2−, 9H), 1.39 (s, −CH_2*CH*$_2$$CH_2$, 54H), 1.57−2.02 (m, −*CH*$_2$$CH_2O$−, 6H), 3.99−4.03 (m, −$CH_2$*CH*$_2$O−, 6H), 4.24−4.57 (m, *Cp*, 8H), 4.94 (s, Ph−*CH*$_2$O−, 2H), 6.82 (s, *Ph*, 2H). GPC (PS standard, THF): M_n = 96 470 g/mol, M_w/M_n = 1.83.

PFS-D0-Ph. The polymer was synthesized in the same manner as for **PFS-D0**. A reaction mixture comprising **PFS-Cl** (0.52 g) and **D0-Ph** (1.83 g, 2.4 mmol) in toluene was precipitated into methanol. A yellow powder was collected and redissolved in THF (30 mL). The THF solution was precipitated into acetone (250 mL). A yellow powder was collected, washed with acetone, and vacuum-dried for 24 h at room temperature. Yield: 1.7 g (85%). ^{1}H NMR (δ = ppm, C_6D_6, 300 MHz): 0.70−0.90 (br, *CH*$_3$Si, 3H), 0.90−1.09 (m, *CH*$_3$$CH_2$−, 9H), 1.30−2.05 (br, CH_3*CH*$_2$−, −*CH*$_2$$CH_2O$−, 60H), 3.75−4.05 (br, −CH_2*CH*$_2$O−, 6H), 4.05−4.70 (br, *Cp*, 8H), 7.05−7.12 (br, −CONH−*Ph*−OSi, 2H), 7.50−7.73 (br, −*Ph*−OSi, 2H), 7.80−8.05 (br, *Ph*, 2H). FT-IR (cyclohexane, cm^{-1}): 1640 (amide I), 1581 (amide II), 3300 (NH stretching). GPC (PS standard, THF) M_n = 91 540 g/mol, M_w/M_n = 1.77.

PFS-D1. PFS-Cl (0.52 g) and **D1** (2.25 g, 2.3 mmol) were reacted for 48 h as described above. During the reaction, the flask was cooled to 0 °C and warmed to room temperature several times to force the reaction to completion by the precipitation of resulting ammonium chloride salt. The polymer solution was precipitated into methanol and acetone. Yield: 0.98 g (40%). ^{1}H NMR (δ = ppm, C_6D_6, 300 MHz): 0.81−0.86 (br, *CH*$_3$Si, 3H), 0.95−0.99 (m, *CH*$_3$$CH_2$−, 9H), 1.35 (s, CH_3*CH*$_2$−, 54H), 1.66−1.70 (m, −*CH*$_2$-CH_2O−, 6H), 3.62−3.78 (m, −CH_2*CH*$_2$O−, 6H), 4.28−4.62 (m, *Cp*, 8H), 4.91 (s, Ph−*CH*$_2$O−Si, 2H), 5.02 (s, Ph−*CH*$_2$O−Ph, 4H), 5.22 (s, Ph−*CH*$_2$O−Ph, 2H), 6.83 (d, J = 8.4 Hz, −O−*Ph*-CH_2−, 2H), 6.86 (s, −*Ph*−O−Si, 2H), 6.92 (d, J = 8.4 Hz, O−*Ph*-CH_2−, 4H), 7.39 (d, J = 8.1 Hz, O−*Ph*−CH_2, 4H), 7.49 (d, J = 8.4 Hz, O−*Ph*−CH_2, 2H). GPC (PS standard, THF): M_n = 138 400 g/mol, M_w/M_n = 1.77.

PFS-D1-Ph. PFS-Cl (0.26 g) and **D1-Ph** (1.24 g, 1.15 mmol) were reacted for 48 h in toluene with occasional cooling to 0 °C. The solution was precipitated into methanol, and the collected polymer was dissolved in THF. The THF solution was precipitated into acetone. The collected polymer was washed with acetone. Vacuum drying yielded a yellow solid. Yield: 0.54 g (41%). ^{1}H NMR (δ = ppm, C_6D_6, 300 MHz): 0.70−0.80 (br, *CH*$_3$Si, 3H), 0.90 (CH_3, 9H), 1.25−1.53 (br, CH_3*CH*$_2$−, 54H), 1.62−1.80 (br, −*CH*$_2$$CH_2O$−, 6H), 3.63−0.3.80 (br, −CH_2*CH*$_2$O−, 6H), 4.2−4.6 (br, *Cp*, 8H), 4.83 (s, Ph−*CH*$_2$O−Ph, 4H), 5.28 (s, Ph−*CH*$_2$O−Ph, 2H), 6.55−6.95 (br, *Ph*), 7.26−7.55 (br, *Ph*). FT-IR (cyclohexane, cm^{-1}): 1640 (amide I), 1585 (amide II), 3287 (NH stretching). GPC (PS standard, THF): M_n = 110 500 g/mol, M_w/M_n = 1.90.

PFS-D1-TEG. PFS-Cl (0.26 g) and **D1-TEG** (1.29 g, 1.15 mmol) were reacted for 48 h with occasional cooling to 0 °C. The polymer was purified in the same manner as for **PFS-D1-Ph**. Yield: 0.53 g (39%). ^{1}H NMR (δ = ppm, C_6D_6, 300 MHz): 0.74−0.83 (br, *CH*$_3$Si, 3H), 0.93−1.02 (m, *CH*$_3$$CH_2$−, 9H), 1.35 (s, CH_3*CH*$_2$−, 54H), 1.83−1.77 (m, −CH_2*CH*$_2$$CH_2O$−, 6H), 3.59 (br s, −O*CH*$_2$*CH*$_2$O−, 6H), 3.60−3.80 (m, −*CH*$_2$O−(alkyl), 6H, −O*CH*$_2$*CH*$_2$OSi, 4H), 3.93 (br, −CH_2*CH*$_2$OSi, 2H), 4.23−4.58 (m, *Cp*, 8H), 4.87 (s, Ph−*CH*$_2$O−Ph, 4H), 5.23 (s, Ph−*CH*$_2$O−Ph, 2H), 6.82 (d, J = 8.4 Hz, −O−*Ph*−CH_2O−, 2H), 6.91 (d, J = 8.4 Hz, −O−*Ph*−CH_2O−, 4H), 7.33 (d, J = 8.4 Hz, −O−*Ph*−CH_2O−, 4H), 7.44 (d, J = 8.4 Hz, −O−*Ph*−CH_2O−, 2H), 7.77 (s, *Ph*−COO−CH_2−, 2H). GPC (PS standard, THF): M_n = 145 000 g/mol, M_w/M_n = 2.00.

Results and Discussion

Synthesis of the Dendrons and Dendronized PFSs. The parent polymer, poly(chloromethylferrocenylsilane) (**PFS-Cl**), was prepared by a transition-metal-catalyzed polymerization of chloromethyl-[1]-silaferrocenylsilane in toluene in the presence of Karstedt's catalyst and triethylsilane as a capping agent.[11] For the molecular weight analysis, **PFS-Cl** was further reacted with the excess of methanol to yield air- and moisture-stable polymer, **PFS-MeO**. The complete substition of Si−Cl groups on the polymer backbone was confirmed by comparison of the ^{1}H NMR integration of the methoxy peak (3.5 ppm) and the methyl peak (0.7 ppm) of the polymer backbone. The molecular weight (M_n) obtained by GPC in a triple detection mode was 24 450 g/mol, and the polydispersity index (PDI) was 2.13. We calculated the number-average degree of polymerization of 95 based on the molecular weight of **PFS-MeO**.

The alkoxy benzyl ether dendrons were synthesized by the literature method reported by Percec and co-workers.[14] We prepared the dendrons up to the second generation. For the macromolecular reaction between **PFS-Cl** and the dendrons, the carboxylic acid group at the focal point of the dendron was changed to a hydroxy group. The dendrons with a focal carboxylic acid group were reacted with 1,1′-carbonyldiimidazole (CDI) and then an excess amount of 4-aminophenol or triethylene glycol. After purification, the dendrons with a focal hydroxy group were obtained in good to moderate yields. Figure 1 shows the structures of the dendrons used in this study.

The synthesized dendrons with a focal hydroxy group were reacted with the parent polymer, **PFS-Cl**, in toluene. The series of the dendrons based on the second-generation dendron with 3,4,5-tris(alkoxybenzyl) groups at the periphery (**D2**) did not give a high degree of substitution under any reaction conditions. Compared to the dendrons with 4-alkoxybenzyl peripheral groups (**D1**), the dendrons based on **D2** would be bulkier than **D1** due to the presence of the long alkoxy chains at the 3- and 5-positions of the peripheral phenyl groups.[17] The severe steric hindrance and repulsion between the dendrons based on **D2** might be the reason for the low substitution yield.

The reaction between the dendrons based on **D0** and **D1** and the **PFS-Cl** gave the dendronized polymers with high degrees of substitution. The substitution reaction was performed by stirring **PFS-Cl** and the corresponding dendrons in toluene in the presence of triethylamine for 24−48 h. After the reaction, the remaining Si−Cl groups of **PFS-Cl** were quenched by adding excess of methanol to the reaction mixture. ^{1}H NMR spectra of the synthesized dendronized polymers showed no trace of the signal from the unreacted Si−Cl groups (Figure 2). Molecular weights of dendronized polymers showed reasonable agreements with the calculated molecular weights obtained from the degree of polymerization of the parent **PFS-MeO**. The GPC traces also showed no significant change in the polydispersity indices, suggesting that the substitution was complete (Table 1).

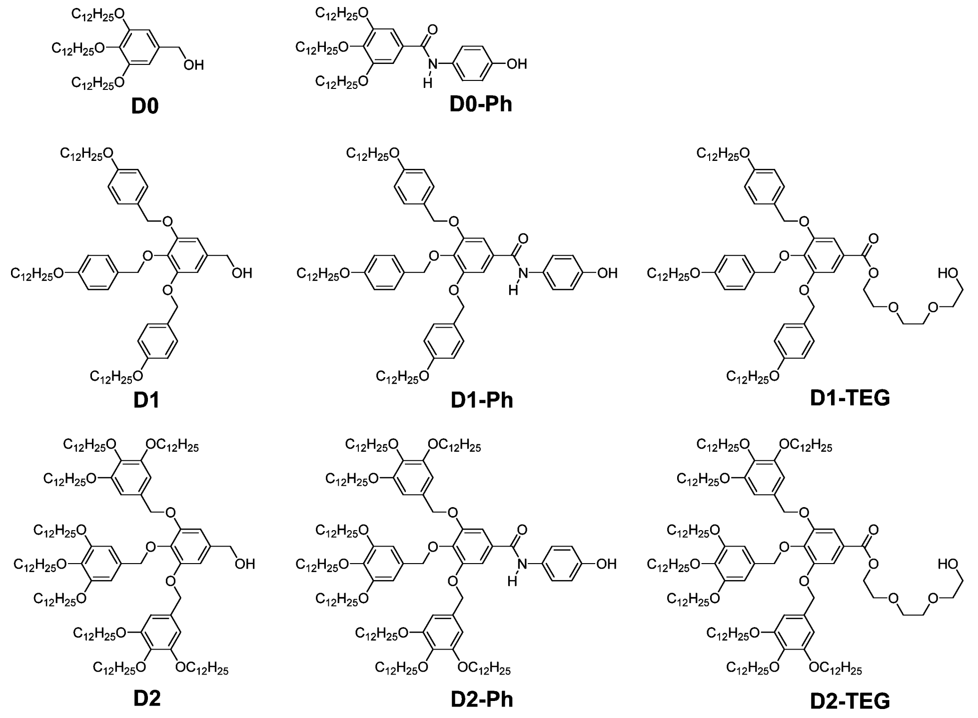
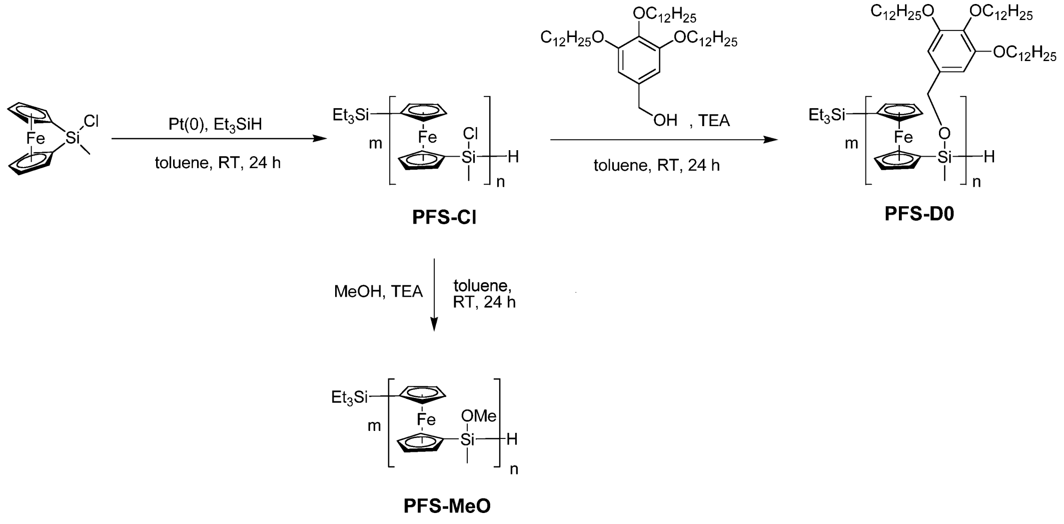


Figure 1. Alkoxy benzyl ether dendrons with various focal hydroxy groups.

Scheme 1. Synthesis of the Parent Polymers, PFS-Cl and PFS-MeO, and the Dendronized Polymer, PFS-D0, by the Substitution Reaction with PFS-Cl and the Dendron with a Focal Hydroxy Group



Solubility of Synthesized Dendronized Polymers in Organic Solvents. All dendronized polymers were easily soluble in organic solvents such as CH_2Cl_2, $CHCl_3$, THF, and cyclohexane. Since the parent polymers, **PFS-Cl** and **PFS-MeO**, are insoluble in cyclohexane, the good solubility of dendronized polymers in cyclohexane could be an indication of the high degree of substitution of the cyclohexane-soluble dendrons with flexible alkoxy chains on the PFS backbone. The apparent hydrodynamic radii of **PFS-D1** and **PFS-D1-TEG** in cyclohexane were determined by dynamic light scattering. **PFS-D1** showed a hydrodynamic radius of 6.6 nm (polydispersity: 0.14), and **PFS-D1-TEG** showed an apparent hydrodynamic radius of 6.8 nm (polydispersity: 0.18). The results suggest that both **PFS-D1** and **PFS-D1-TEG** are soluble in cyclohexane without significant aggregation.

$CDCl_3$ solutions of dendronized polymers **PFS-D0-Ph** and **PFS-D1-Ph** showed significant peak broadness in the ^{1}H NMR. We therefore suspected that the amide group of the **D0-Ph** and **D1-Ph** might hydrogen bond with the amide groups of neighboring dendrons. The presence of the hydrogen bonding was confirmed by the FT-IR result of cyclohexane solutions of **PFS-D0-Ph** and **PFS-D1-Ph**. Both solutions showed amide bands at 1644−1645 and 1540−1545 cm^{-1}, which are characteristic for the hydrogen-bonded amide group. The apparent hydrodynamic radii of **PFS-D0-Ph** and **PFS-D1-Ph** in cyclohexane were measured by dynamic light scattering. Compared to the hydrodynamic radius of **PFS-D1-TEG** in cyclohexane (6.8 nm), larger hydrodynamic radii were observed (12 nm for **PFS-D0-Ph** and 37 nm for **PFS-D1-Ph**).

Considering the chemical structure of the dendronized PFS, especially **PFS-D1-Ph**, which has amide groups near the junction between PFS backbone and the focal point of the dendrons, the interaction between the amide groups of the dendrons would favor intramolecular hydrogen bonding over intermolecular

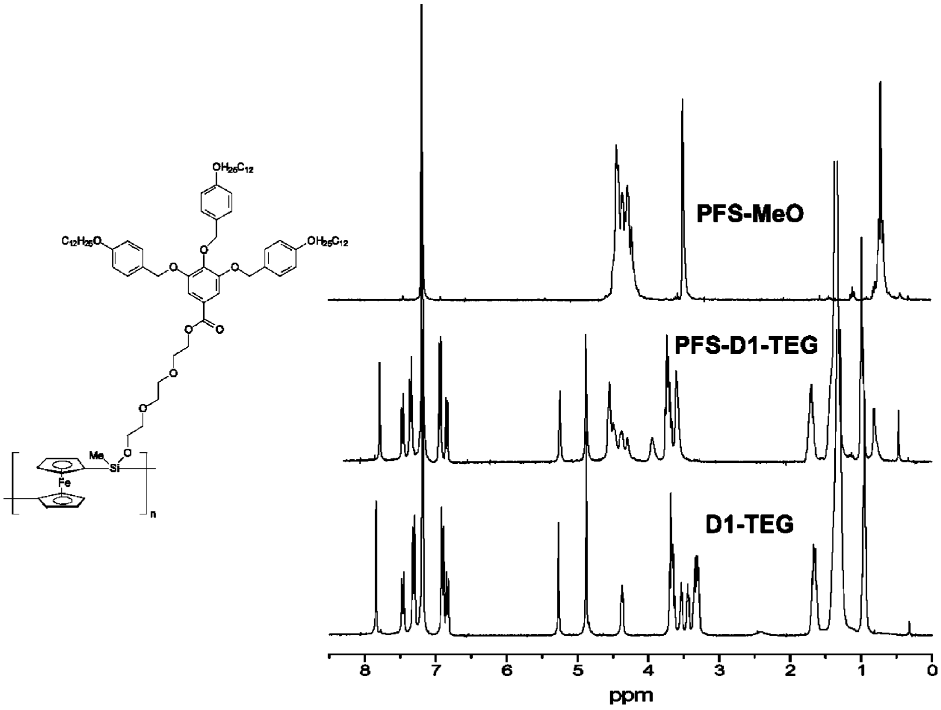


Figure 2. Comparison of ^{1}H NMR spectra (in C_6D_6) of the parent PFS (**PFS-MeO**), the dendron (**D1-TEG**), and the dendronized PFS (**PFS-D1-TEG**). The dendronized PFS shows no trace of MeO−Si protons at 3.5 ppm, indicating the complete reaction between Si−Cl and hydroxyl group of the dendron.

Table 1. Molecular Weight Characterization of a Parent and Dendronized Polymers

polymer	M_n (g/mol)[a]	PDI[a]	DP_n[b]	theor MW[c]
PFS-MeO	24 500	2.13	95	na
PFS-D0	96 400	1.83	95	85 000
PFS-D0-Ph	91 500	1.77	95	94 500
PFS-D1	138 400	1.77	95	114 500
PFS-D1-Ph	110 500	1.90	95	124 000
PFS-D1-TEG	145 000	2.00	95	128 200

[a] Molecular weights and polydispersity indices were obtained from the GPC in a triple detection mode. [b] The number-average degree of polymerization was calculated based on the number-average molecular weight of parent polymer PFS-MeO. [c] Theoretical molecular weights were calculated based on the degree of polymerization of PFS-MeO.

Table 2. Thermal Properties of Dendrons and Dendronized PFSs[a]

dendron/ polymer	phase transition	note
D0-Ph	k: 101.6 °C: Hex: 113.9 °C: I	
	I: 104.8 °C: Hex: 73.6 °C: k	5 °C ramp rates
D1-Ph	k: 52.4 °C: k: 89.2 °C: Hex: 104.9 °C: I	5 °C ramp rates
D2-Ph	k: 88.9 °C: M: 125.3 °C: I	
	I: 119.0 °C: M: 89.2 °C: k	5 °C ramp rates
D1-TEG	k: 50.4 °C: Hex: 59.3 °C: I	
	I: 57.7 °C: Hex: 38.4 °C: k	5 °C ramp rates
PFS-D0	T_g: −6.2 °C	10 °C ramp rates
PFS-D0-Ph	T_g: 78.0 °C	10 °C ramp rates
PFS-D1	T_g: 31.9 °C	10 °C ramp rates
PFS-D1-Ph	T_g: 55.3 °C	10 °C ramp rates
PFS-D1-TEG	T_g: 14.3 °C	10 °C ramp rates

[a] k = crystalline, Hex = hexagonal phase identified by polarized optical microscopy, M = unidentified mesophase, and I = isotropic melt.

hydrogen bonding. We assumed that the intramolecular hydrogen bonding of **PFS-D1-Ph** could stiffen the overall chain conformation of the dendronized PFS so that the shape of the **PFS-D1-Ph** would be cylindrical. Therefore, the large apparent hydrodynamic radius of the dendronized PFS in cyclohexane probably reflects the rotational motion of the cylindrical chain of the dendronized PFS, even though we could not completely rule out the possibility of the aggregation of the chains via intermolecular hydrogen bonding between the dendronized PFS chains.

Characterization of Liquid Crystalline Properties of Dendronized PFS. The alkoxy benzyl ether dendrons used in this study are thermotropic mesogens.[17] For examples, the dendrons **D0-Ph**, **D1-Ph**, and **D1-TEG** showed a focal conic birefringent texture under the polarized optical microscopy, suggesting that the dendrons form a hexagonal-packed liquid crystalline structure (Table 2).

We anticipated that the dendronized PFS with the liquid crystalline dendron side groups could also form thermotropic liquid crystalline phases. However, the DSC traces of the dendronized polymers did not show any first-order transition but only showed a glass transition of the polymer. Frechét and co-workers reported that some liquid crystalline polymers form a liquid crystalline phase without showing the phase transition signal in DSC.[18] Therefore, we looked for the thermal transition of the dendronized PFSs with a polarized optical microscope. Only weak birefringence of the polymer **PFS-D1-Ph** was observed by polarized optical microscopy after cooling the polymer from 120 to 100 °C and annealing at 100 °C for 2 h (Figure 3). Longer annealing times did not increase the birefringence of **PFS-D1-Ph**. For a hexagonal packed liquid crystalline phase, the alkoxy benzyl ether dendrons should be stacked at less than a 4 Å distance.[17] The large distance (ca. 6.4 Å) between the neighboring silicon atoms in the PFS backbone[19] might prevent the dendrons from stacking into a dense liquid crystalline phase.

AFM Studies of the Dendronized PFSs. Because of the presence of bulky dendron side groups on the backbone, dendronized polymers could offer the possibility of direct visualization by scanning force microscopy (SFM) and atomic force microscopy (AFM). We chose dendronized PFSs with bulkier dendrons based on **D1** for the AFM observation. The polydisperse nature of the dendronized PFSs ($M_w/M_n \sim 2$) was expected

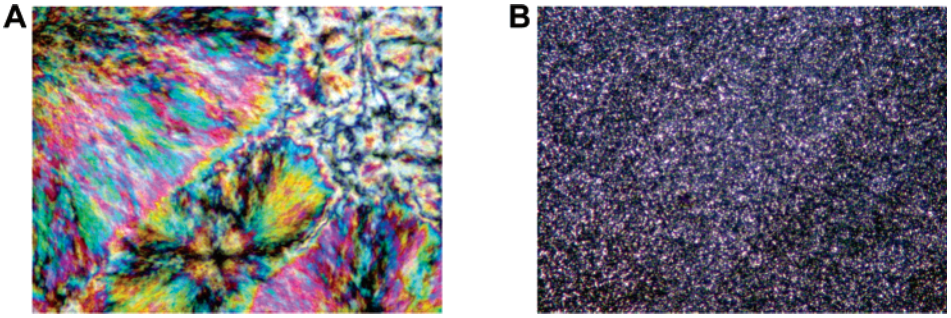
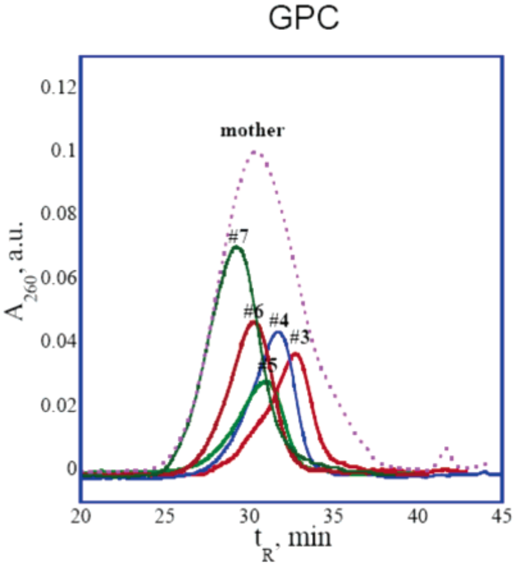


Figure 3. Optical birefringence texture of dendron **D1-Ph** (A) and the dendronized polymer **PFS-D1-Ph** (B). **PFS-D1-Ph** was annealed at 100 °C for 2 h.



PFS-D1-TEG

fraction	M_w (kg/mol)	PDI
mother	126.2	1.90
#3	71	1.71
#4	94	1.24
#5	118	1.22
#6	140	1.25
#7	190	1.32

Figure 4. GPC traces of fractionated dendronized polymer **PFS-D1-TEG** by IC-HPLC.

to hamper the observation of the conformation of the single chain of the dendronized PFS because the conformation of the dendronized polymer could also be affected by the degree of the polymerization of the backbone.[4] Therefore, we fractionated the polydisperse dendronized PFSs by an interaction-controlled HPLC (IC) technique with CH_2Cl_2/CH_3CN as an eluent and C_{18}-bonded silica HPLC columns (Figure 4). IC is a unique technique to separate polydisperse polymers by using the specific interaction between the analyte and the column, which is sensitive to the chemical structures of the polymer.[20] High molecular weight fractions of the dendronized PFSs were used for the AFM experiments.

Our dynamic light scattering results for the solutions of the dendronized PFS suggest that the polymer **PFS-D1-TEG** could exist as a single chain with a spherical shape in cyclohexane by showing a hydrodynamic radius of 7 nm with a narrow polydispersity. For AFM experiments, dilute cyclohexane solutions of high molecular weight fractions of **PFS-D1-TEG** (fraction 6 in Figure 4) were spin-cast on a fresh-cleaved mica substrate. We observed slightly elongated particles with a lateral size of ca. 16 nm and the height of ca. 2.4 nm (Figure 5B). It should be noted that the observed dimensions could be affected by tip-induced and surface-induced deformation. We inferred that the actual shape of **PFS-D1-TEG** would be a small cocoon-shaped ellipsoid with a longer diameter of ca. 8 nm and a shorter diameter of ca. 6 nm. In cyclohexane, **PFS-D1-TEG** (fraction 6) showed an apparent hydrodynamic radius of 7 nm by DLS measurements.

Considering the incompatibility of the PFS backbone with cyclohexane and the good solubility of the dendron in this solvent, the cocoon of the single chains of **PFS-D1-TEG** may consist of the outer layer of densely packed dendron side chains and an inner domain of the compressed PFS backbone.[21] This structure could be regarded as a single chain micelle which has the dendron corona and the PFS chain core. Unimolecular micelles of dendrimers have been reported by Newkome et al. and Fréchet et al.[22] The observed cocoon of the single dendronized PFS chain could be interesting to study as a functional material due to the isolated core containing redox-active ferrocene units (Figure 6).

We also investigated the conformation of the chains of **PFS-D1** and **PFS-D1-Ph**. DLS measurements for **PFS-D1-Ph** in cyclohexane showed a hydrodynamic radius of 37 nm. The cyclohexane solution of **PFS-D1-Ph** was spin-cast on a fresh-cleaved mica substrate and then studied by AFM. We observed dendronized polymer chains as an elongated bar shape. The lengths of the observed chains were 38−76 nm. The height of the observed polymer chain was ca. 1.5 nm (Figure 5C). The elongated conformation of **PFS-D1-Ph** could be a result of dominant intramolecular hydrogen bonding between the amide groups of the dendrons. However, the large distance between two neighboring dendrons (ca. 6.4 Å) on the PFS backbone may prevent a **PFS-D1-Ph** chain from being folded into a dense stiff structure assisted by the close packing of the liquid crystalline dendrons. **PFS-D1** did not reveal any defined conformations by AFM experiments. Figure 5A shows the AFM images observed from the dendronized PFSs on a mica substrate. We observed spherical objects from **PFS-D1** dispersed on a mica substrate but only in a low population. We did not observe any ordered state of dendronized PFS on a mica substrate by AFM

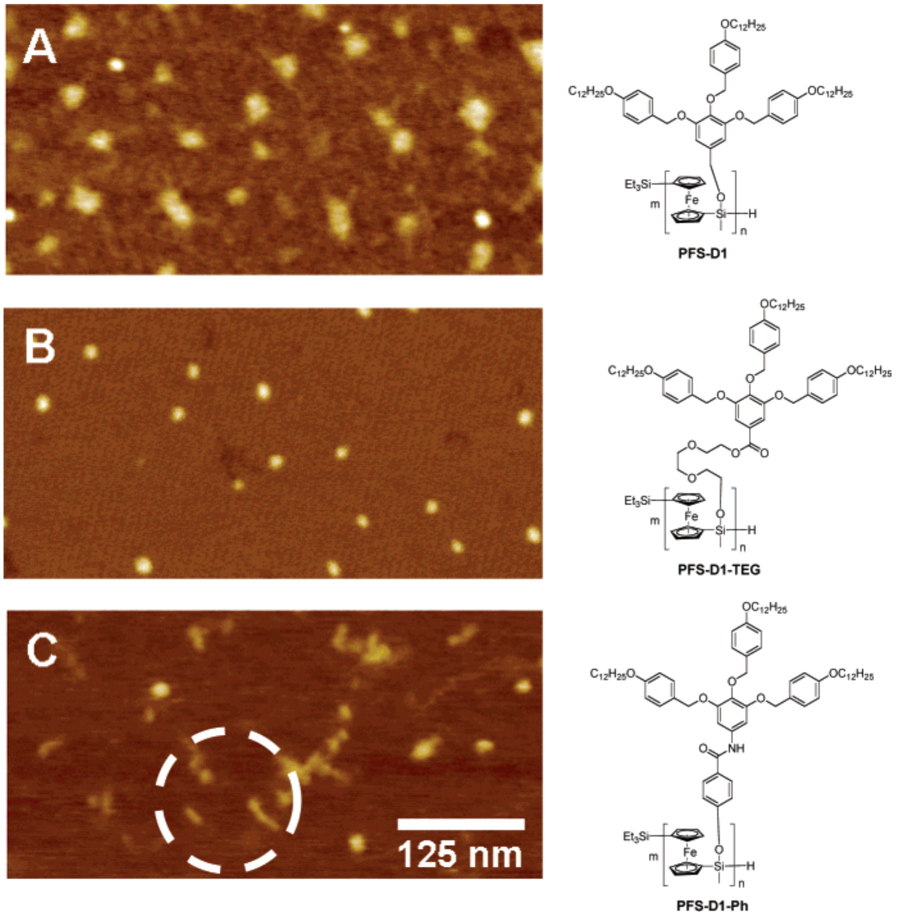


Figure 5. AFM images of fractionated and unfractionated dendronized polymers. The sample specimens were prepared by spin-casting the solutions of polymers on a freshly cleaved mica substrate. (A) **PFS-D1** (fractionated, M_w = 121 000 g/mol, $CHCl_3$ solution). (B) **PFS-D1-TEG** (fractionated, M_w = 140 000 g/mol, cyclohexane solution). (C) **PFS-D1-Ph** (unfractionated, M_w = 110 000 g/mol, cyclohexane solution). The elongated objects in the circles in (C) indicate the polymer chains of 38 nm long (left) and 75 nm long (right).

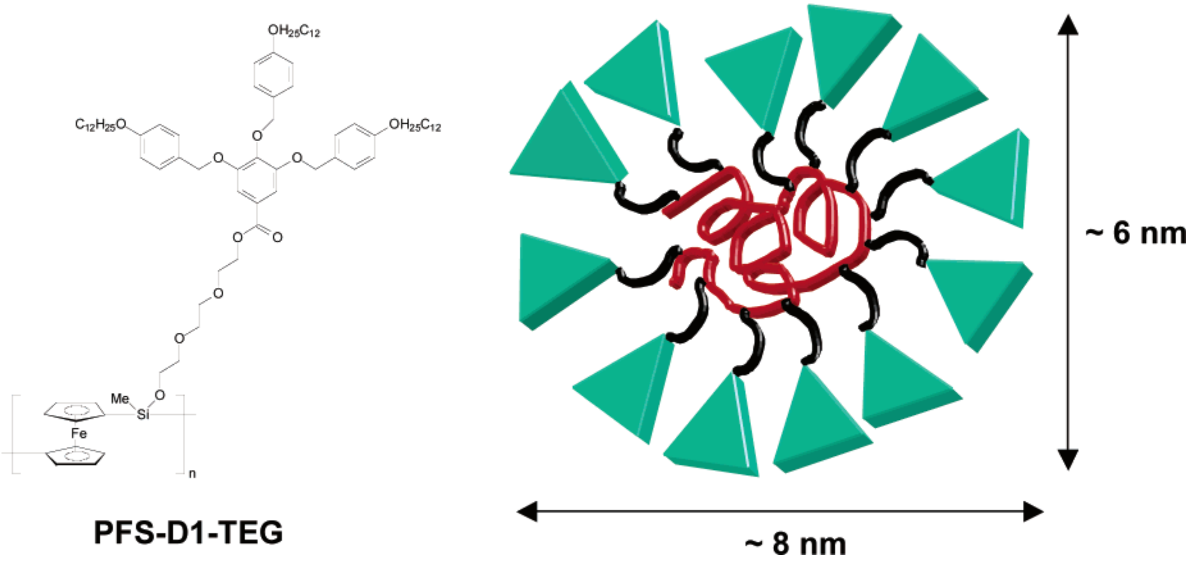


Figure 6. Chemical structure of **PFS-D1-TEG** and the proposed cocoon structure of the single chain **PFS-D1-TEG** in cyclohexane.

experiments due probably to low concentration of polymer solutions used for the sample preparation and the lack of the rigidity of the conformation of dendronized PFSs indicated by weak liquid crystal formation.

The redox activity of **PFS-D1** and **PFS-D1-TEG** was studied by cyclic voltammetry. **PFS-D1** and **PFS-D1-TEG** showed two broad waves characteristic of oxidation of ferrocene units affecting the redox potential of nearest neighbors (Figure 7).[19] The steric bulkiness around the ferrocene redox centers in the backbone of dendronized PFSs could be the reason for broad waves observed by CV experiments as slow electron transfer would be anticipated. Nevertheless, the demonstrated redox activity

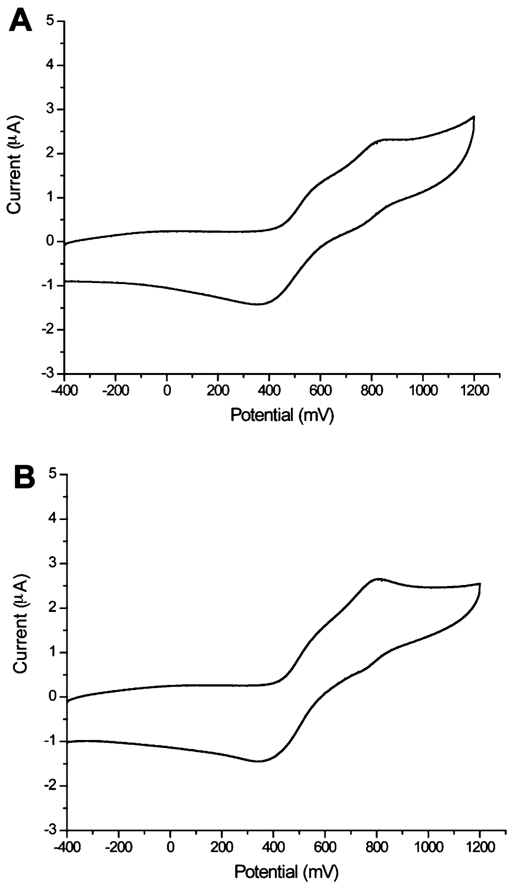


Figure 7. Cyclic voltamograms of in CH$_2$Cl$_2$ solutions (concentration of 5 × 10^{-3} M and 0.1 M in [NBu$_4$][PF$_6$]) of **PFS-D1** (A) and **PFS-D1-TEG** (B) obtained at a scan rate of 100 mV/s and referenced to the ferrocene/ferrocenium ion couple at E = 0.00 V.

suggests that these materials are realistic substrates for the templated growth of metal nanoparticles using redox chemistry.[14]

Summary and Conclusions

Dendronized polymers with a polyferrocenylsilane metallopolymer backbone have been synthesized by the macromolecular reaction of reactive **PFS-Cl** and the dendrons with a focal hydroxy group. The dendronized PFSs were characterized by NMR, GPC, and DSC. AFM studies of the dendronized PFS revealed that the single chain of **PFS-D1-TEG** possess a spherical shape in solution, and the cocoon of the single chain of **PFS-D1-TEG** probably has an outer layer of the dendrons and an iron-rich inner core of the PFS main chain. An analogy can be made between the cocoon of the single chain of the dendronized PFS and the unimolecular micelles of dendrimers and linear−dendritic block copolymers. The PFS core of the single chain cocoon could be interesting as a metal-rich, redox-active array isolated by the layer of the dendrons for future purposes such as catalysis and encapsulation.

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