Hydrophilic and Water-Soluble Poly(ferrocenylsilanes)

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ABSTRACT: The synthesis of a series of novel hydrophilic and water-soluble neutral and cationic high molecular weight poly(ferrocenylsilanes) is reported. The dichlorosilyl-bridged [1]ferrocenophane Fe(η-C_5H_4)$_2$SiCl$_2$ (**3**) was reacted with various polyether alcohols in the presence of Et_3N as an HCl acceptor to afford the monomers Fe(η-C_5H_4)$_2$Si(OR)$_2$ (**4**: R = $CH_2CH_2OCH_3$; **5**: R = $CH_2CH_2OCH_2CH_2OCH_3$). Using ambient temperature transition-metal catalyzed ring-opening polymerization of these monomers, hydrophilic poly(ferrocenylsilanes) were obtained. Transition-metal catalyzed ring-opening polymerization of the silicon-bridged [1]ferrocenophane Fe(η-C_5H_4)$_2$SiMeCl (**8**) afforded the corresponding polymer [Fe(η-C_5H_4)$_2$SiMeCl]$_n$ (**9**). Replacement of the chlorine substituents of **9** was achieved using (a) poly(ethylene glycol) methyl ether, M_n = 350, in the presence of Et_3N to afford the poly(ferrocenylsilane) [Fe(η-C_5H_4)$_2$SiMe(OCH_2CH_2)$_x$$OCH_3$]$_n$ ($x \sim 8$: **10a**: $M_n \sim 56\,000$; **10b**: $M_n \sim 189\,000$) and (b) *N*,*N*-dimethylethanolamine to afford [Fe(η-C_5H_4)$_2$SiMe($OCH_2CH_2NMe_2$)]$_n$ (**11**). Quaternization of polymer **11** with MeI or HCl afforded the polyelectrolytes [Fe(η-C_5H_4)$_2$SiMe($OCH_2CH_2NMe_3I$)]$_n$ (**12**) and [Fe(η-C_5H_4)$_2$SiMe($OCH_2CH_2NMe_2HCl$)]$_n$ (**13**). Poly(ferrocene) **10b** dissolved in water to give a clear solution whereas **10a**, **12**, and **13** afford slightly cloudy solutions. Lower critical solution temperatures (LCST) for **10a** and **10b** were determined to be 38 and 46 °C, respectively. Investigations by dynamic light scattering and centrifugation experiments indicated the presence of aggregates. In the case of **12** the larger aggregates could be partially broken up using mild ultrasonication but re-form over time. Clear solutions of the polymers **10a**, **12**, and **13** in water can be easily prepared by microfiltration techniques.

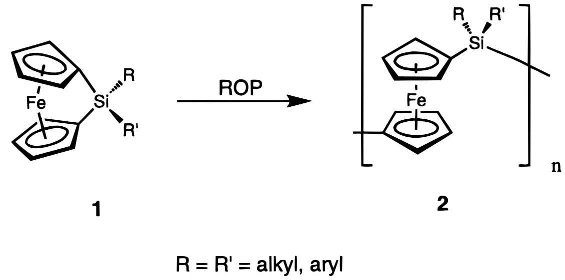
Introduction

Water-soluble polymers encompass a wide variety of macromolecules, from biopolymers to synthetic polymers, that are of great industrial and commercial importance.[1] Although water-soluble organic polymers have been widely studied, their inorganic counterparts have been largely left unexplored.[2] Poly[bis(methoxyethoxyethoxy)phosphazene] represents the most well-known polymer of this class.[3] Several examples of water-soluble poly(silanes) and poly(siloxanes) have also been reported.[4] However, water-soluble polymers with transition elements in the main chain are rare. To our knowledge, the only previous report of a water-soluble ferrocene-based polymer is that from Neuse et al., in which low molecular weight (ca. M_n = 2400) poly(ferrocenium) salts were studied.[5]

Thermal ring-opening polymerization (ROP) of silicon-bridged [1]ferrocenophanes **1** provides a convenient route to high molecular weight ($M_n > 10^5$) poly(ferrocenes) **2** (Scheme 1).[6] Ambient temperature transition-metal catalyzed and anionic ROP routes to these materials have subsequently been reported.[7,8] Initially, the substituents attached to silicon were limited to aryl and alkyl groups. More recently, we described a general route to polymerizable silicon-bridged [1]ferrocenophanes with amino, alkoxy, and aryloxy substituents at silicon.[9] The resulting poly(ferrocenylsilanes) are redox-active and possess interacting metal atoms in the main chain. Interest has also focused on their pyrolytic conversion to magnetic ceramic materials (including nanostructures) and their semiconductive properties.[6]

To further diversify the properties accessible with poly(ferrocenylsilanes), in this paper we report the introduction of polyether or ionic substituents that can impart hydrophilicity or water solubility to the resultant organometallic polymer. These poly(ferrocenylsilanes) are of potential interest as electrode materials and as redox-active polymeric electrolytes, in which the ionic conductivity might be switched by oxidation of the iron centers.[10] Such materials are also of interest for multilayer self-assembly applications and for the preparation of micellar aggregates as preliminary results indicate that ferrocene-based surfactants could potentially be used as redox-active drug delivery agents.[11] Moreover, various water-soluble ferrocenium salts have been shown to display anticancer activity.[12]

Scheme 1



Results and Discussion

Synthesis and NMR Characterization of the Silicon-Bridged [1]Ferrocenophanes (4, 5). The starting material, Fe(η-C_5H_4)$_2$SiCl$_2$ (**3**), was prepared by the method of Wrighton et al.[13] The monomer was synthesized in high yield (77%) as a moisture-sensitive, red crystalline solid and was purified by vacuum sublimation. Ferrocenophane **3** reacts under mild conditions (25 °C, Et_2O, 1.5−24 h) with various polyether alcohols via nucleophilic substitution of the chlorine substituents at silicon (Scheme 2). We have shown that triethylamine must be present as a base in this reaction in order to remove the liberated HCl which would

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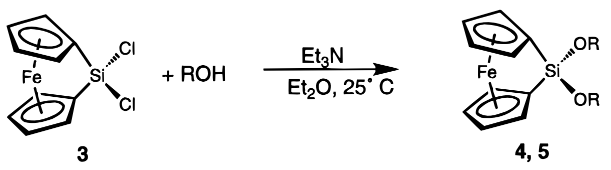
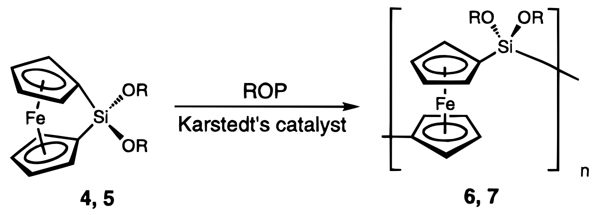
Scheme 2



4: R = $CH_2CH_2OCH_3$, 5: R = $CH_2CH_2OCH_2CH_2OCH_3$

Scheme 3



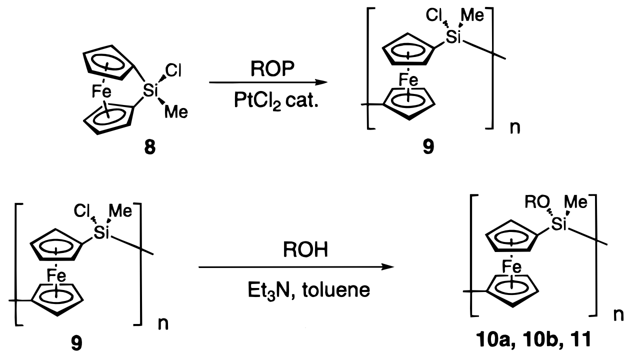
4, 6: R = $CH_2CH_2OCH_3$ 5, 7: R = $CH_2CH_2OCH_2CH_2OCH_3$

otherwise add across the strained C−Si bond.[9] The new polyether-substituted [1]ferrocenophanes, **4** and **5**, were obtained as dark red, viscous liquids.

The monomers were characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. The ^1H NMR spectra of **4** and **5** showed two sets of resonances for the cyclopentadienyl rings with correct integration ratios relative to the CH_2 groups for the polyether substituents. The ^{13}C NMR spectra showed upfield shifts of the ipso carbons of the cyclopentadienyl rings in the region of 40.0 ppm. This is expected as analogous alkoxy-substituted [1]ferrocenophanes have been previously reported in which the ipso carbons of the cyclopentadienyl rings were observed in the region of 34−41 ppm.[9] These values are consistent with the strain that has been shown to exist in silicon-bridged [1]ferrocenophanes possessing alkyl and aryl substituents.[14] The ^{29}Si NMR spectra showed a single resonance for monomers **4** and **5** at −34.1 and −34.0 ppm, respectively. These values are consistent with analogues such as $Fe(\eta\text{-}C_5H_4)_2Si(OCH_2CH_3)_2$ which possesses a corresponding resonance at −34.8 ppm.[9]

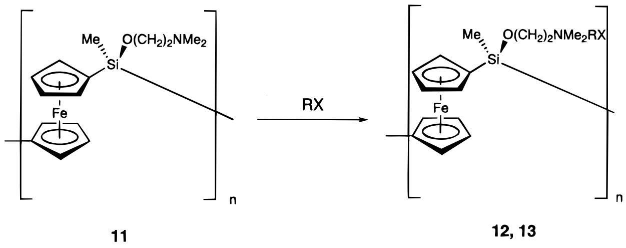
Transition-Metal Catalyzed ROP of the Silicon-Bridged [1]Ferrocenophanes (4 and 5) and Characterization of the Poly(ferrocenylsilanes) 6 and 7. The cyclic monomers **4** and **5** were dissolved in THF, and Karstedt's catalyst (a platinum(0) complex) was added. After 24 h at 25 °C, the monomers had undergone ROP to give viscous dark amber THF solutions of the corresponding polymers **6** and **7** (Scheme 3). Precipitation into methanol (for **6**) or hexanes (**7**) afforded the corresponding poly(ferrocenylsilanes) **6** and **7** in good yields (71−86%). The polymers obtained by transition-metal catalyzed ROP were characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. Polymer **6** possessed a number-average molecular weight (M_n) of 235 400 and a polydispersity index of 2.62 by gel-permeation chromatography. The corresponding values for polymer **7** were M_n = 101 800 and PDI = 2.57. The ^{29}Si resonances for **6** and **7** were detected at −19.4 and −20.8 ppm, repectively, which are similar to the value of −20.9 ppm for their analogue, $[Fe(\eta\text{-}C_5H_4)_2Si(OCH_2CH_3)_2]_n$.[9] Both the ^1H and ^{13}C NMR data for **6** and **7** were consistent with the assigned structure.

Scheme 4



10a, 10b: R = $(CH_2CH_2O)_xOCH_3$, x ~ 8
11: R = $CH_2CH_2NMe_2$

Scheme 5



12: R = Me, X = I
13: R = H, X = Cl

Synthesis of the Water-Soluble Poly(ferrocenylsilane)s 10a, 10b, 12, and 13. The silicon-bridged [1]-ferrocenophane **8** with methyl and chlorine substituents at silicon has been previously reported.[15] The monomer (**8**) was obtained in high yield (82%) as a crystalline red solid after vacuum sublimation of the crude product. A sample of the monomer was dissolved in toluene, to which were added catalytic amounts of $PtCl_2$, to initiate ROP of the monomer. The resulting polymer was isolated by precipitation into hexanes.

Previously, substitution reactions were performed on **9** with organolithium reagents such as MeLi, PhLi, and $LiC{\equiv}C(CH_2)_4H$.[15] In all cases, complete substitution of the chlorine substituents of the polymer was observed by ^{29}Si NMR after stirring for 24 h at 25 °C. In this study, a convenient methodology for the substitution of the chlorine substituents on **9** was discovered which involved treatment with a polyether alcohol or ethanolamine in the presence of triethylamine to afford **10a,b** and **11**, respectively (Scheme 4). The substituted polymer **10a** was isolated as an extremely viscous amber fluid material, whereas **10b**, the higher molecular weight analogue (vide infra), was a gum. Both **10a** and **10b** were found to be readily soluble in solvents such as water, methanol, THF, and benzene. Similarly, poly(ferrocenylsilane) **11** was isolated as an orange gum. This species was dissolved in CH_2Cl_2 to which was added 1 equiv of MeI as an alkylating agent. The solution was then heated to reflux to afford the water-soluble polyelectrolyte **12** (Scheme 5). Poly(ferrocenylsilane) **11** was also dissolved in THF to which was added 1 equiv of a 1.0 M solution of HCl in Et_2O to obtain the protonated polymer **13**. Polymer **13** was also found to dissolve in water.

Characterization of the Poly(ferrocenylsilane)s 10a, b, 11, 12, and 13. Polymers **10a**, **10b,** and **11** were characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy as well as by gel-permeation chromatography using polystyrene standards for column calibration. The polymer **10a** possessed a number-average molecular weight

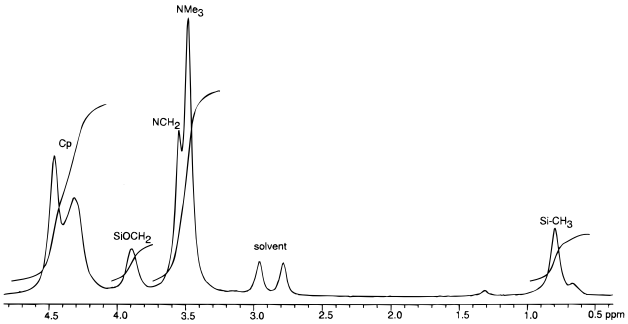


Figure 1. ^{1}H NMR spectrum of **12** in d_7-DMF.

of 56 000, with a polydispersity of 2.29. The higher molecular weight analogue of **10a**, polymer **10b**, possessed a number-average molecular weight of 189 700 and polydispersity of 2.17. The ^{29}Si NMR for each material showed one resonance at 3.7 ppm. This value is consistent with its structural analogue, $[Fe(\eta\text{-}C_5H_4)_2SiMe(OCH_3)]_n$, which possesses a resonance at 4.6 ppm.[16] The ^{13}C Si−Me resonances for $[Fe(\eta\text{-}C_5H_4)_2SiMeCl]_n$ (**9**) and $[Fe(\eta\text{-}C_5H_4)_2SiMe(OMe)]_n$ are found at 2.5 and −2.2 ppm, respectively, compared to −1.7 ppm for **10a**.[15,16] The ^{1}H NMR spectra of **10a** and **10b** in C_6D_6 were consistent with the assigned structure and showed the expected integration ratios.

The cationic poly(ferrocenylsilane) **12** was found to be insoluble in most common organic solvents but was only readily soluble in water and DMF and slightly soluble in THF. ^{1}H NMR spectra were obtained for **12** in D_2O; however, only the resonances corresponding to the protons of the NMe_3 and methylene groups were visible. This suggested the presence of aggregates in solution in which the poly(ferrocene) main chain was rigidified. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were thus recorded in d_7-DMF in order to observe the ferrocene region of the polymer. In the ^{1}H NMR spectrum (Figure 1), the Si−Me protons were visible at 0.78 ppm. A singlet was observed at 3.45 ppm for the NMe_3 groups and broad multiplets for the two CH_2 groups at 3.52 and 3.89 ppm, respectively. The ferrocene region was broad, spanning from 4.15 to 4.52 ppm. The ^{1}H NMR spectrum of **13** was also recorded in d_7-DMF and was analogous to that observed for **12**, though most notably, the resonances corresponding to the NMe_2 and $N{-}CH_2$ protons were shifted upfield; the NMe_2 and methylene protons appear at 2.91 and 3.30 ppm, respectively. In comparison to **12** and **13**, the protons of the unquaternized NMe_2 group of **11** appeared at 2.31 ppm whereas the protons of the $N{-}CH_2$ group were observed at 2.58 ppm. Because of the absence of the NMe_2 resonance at 2.31 ppm in the proton NMR spectra of **12** and **13**, we concluded that approximately 100% quaternization had taken place. The ^{29}Si NMR data showed one peak at 5.6 ppm for **12**, compared to 0.9 ppm for **13**. The ^{13}C NMR spectra of **12** and **13** are consistent with the proposed structures. The ^{1}H, ^{13}C, and ^{29}Si CP-MAS NMR spectra of **12** were also recorded and supported the solution NMR data. GPC data were not obtained for **12** and **13** due to their limited solubilities in THF.

Properties of Aqueous Solutions of Polymers 10a, 10b, 12, and 13. The poly(ferrocenylsilanes) **10a** and **10b** both dissolved readily in water and remain stable in this solvent as observed by ^{1}H NMR over a period of months. Polymer **12** dissolves slowly in water over a period of hours. However, solutions of **10a** and **12** in water appear slightly cloudy, with a similar appearance to micellar solutions, whereas a solution of **10b** in water is clear. Some water-soluble polymers, such as poly(ethylene oxide) and poly(*N*-isopropylacrylamide), undergo a reversible phase separation above a particular temperature, known as the lower critical solution temperature (LCST). In particular, poly(ethylene oxide) displays a LCST near the boiling point of water.[2b] Solutions of **10a** and **10b** in water also display lower critical solution temperatures due to the presence of the oligo(ethylene glycol) side chains. LCST values were determined by heating samples of **10a** and **10b** in a controlled temperature oil bath until they began to precipitate from solution. This occurred at 38 and 46 °C, respectively. Previously, an aqueous solution of a polysilane with methyl and oligo(oxyethylene) groups displayed a LCST at 46 °C.[4e] The ^{1}H NMR spectrum of **10a** in D_2O (Figure 2) showed only the resonances corresponding to the D_2O-soluble oligo(ethylene glycol) side group, as does the analogous spectrum for **10b**. When centrifuged, a solution of **10a** in water becomes clear amber while an orange precipitate settles out of solution, whereas **10b** remains entirely soluble in water. In the case of **10a**, analysis by ^{1}H NMR showed that both the resultant solute and precipitate after centrifugation are the oligo(ethylene glycol)-substituted polymer, therefore suggesting the formation of aggregates of **10a** in water. A clear solution of **10a** in water can also be obtained by microfiltration (using a 0.2 μm pore filter).

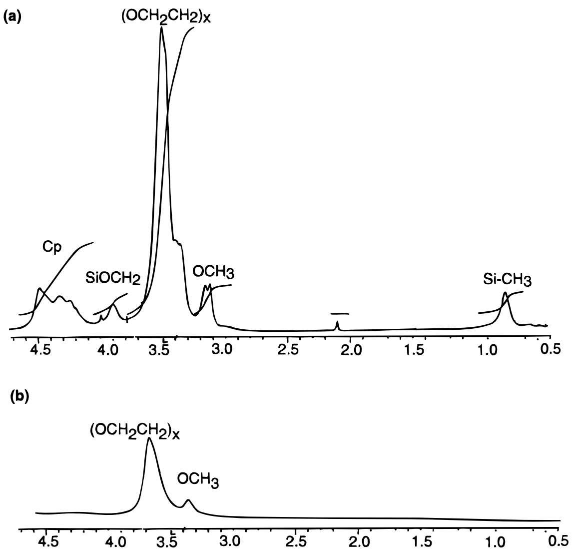


Figure 2. ^{1}H NMR spectrum of polymer **10a** in (a) C_6D_6 and (b) D_2O.

To further characterize aqueous solutions of the poly(ferrocenylsilanes) **10a**, **10b**, **12**, and **13**, dynamic light scattering studies were performed. Samples of both **10a** and **10b** in water were studied. In each case, the broad size distribution was monitored. However, polymer **10a** possessed an average hydrodynamic diameter (D_H) of 290 nm whereas **10b** possessed a D_H = 170 nm. Thus, polymer **10a** appears to aggregate to a larger extent than polymer **10b**.

The aggregation behavior of a sample of **12** in water was also studied. Dynamic light scattering data showed that aggregates form with D_H = 400 nm. However, the size distribution was bimodal with the smaller fraction with D_H = 50−100 nm. It was speculated that this fraction might represent single polymer chains in solu-

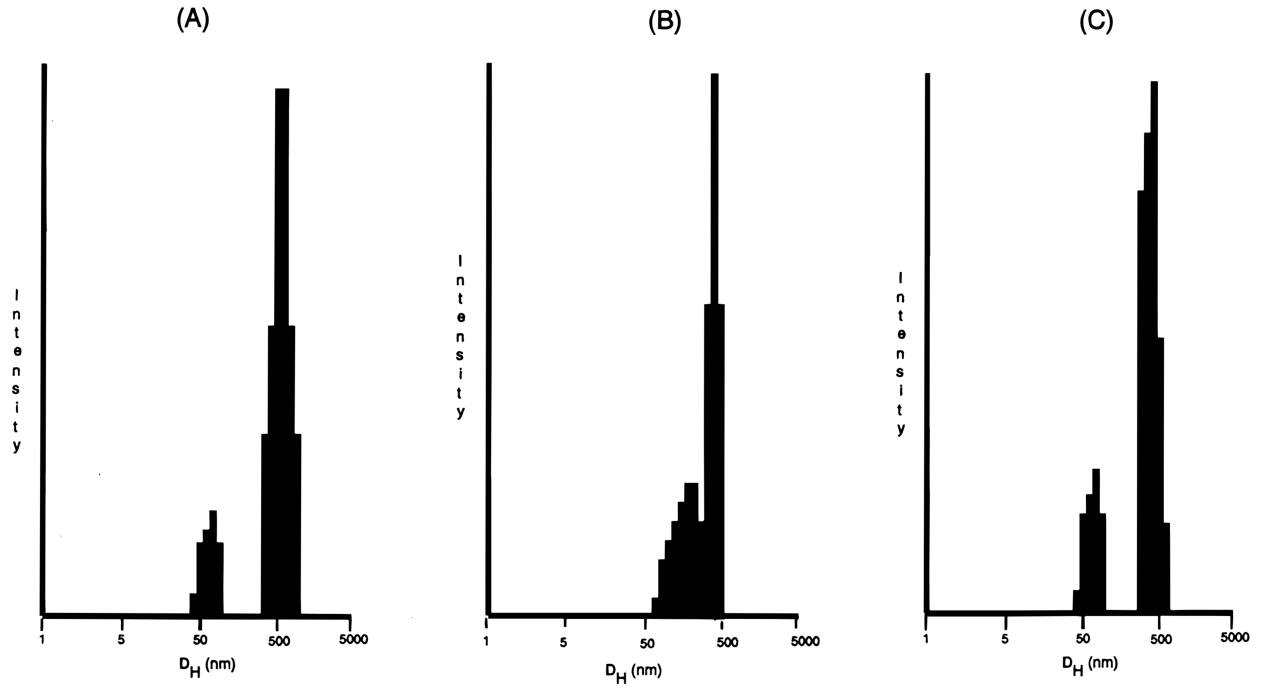


Figure 3. Dynamic light scattering analysis of **12**: (A) original size distribution of a sample of **12** in H_2O; (B) 15 min after sonication; (C) 30 min after sonication.

tion, as this is a reasonable estimate of the hydrodynamic diameter of **12**. A sample of **12** was sonicated for an hour in a 60 W sonication bath to investigate whether it would be possible to break up the larger aggregates and produce mainly single polymer chains in solution. After mild sonication for 1 h it was found that the size distribution more heavily favored the proposed single chain fraction, but over time (ca. 30 min), the majority of polymer chains recombined to again form aggregates (Figure 3). An aqueous solution of poly(ferrocenylsilane) **13** was also studied by dynamic light scattering, which showed that the polymer formed aggregates with $D_H = 150$ nm.

Thermal Transition Behavior and Thermal Stability of Poly(ferrocenylsilanes) 6, 7, 10a, 10b, 11, and 12. The poly(ferrocenylsilanes) **6**, **7**, **10a**, and **10b** were investigated by differential scanning calorimetry (DSC) in order to investigate their thermal transition behavior. We previously found that for poly(ferrocenyldialkylsilanes) possessing methyl or ethyl substituents (**2:** R = R′ = Me, R = R′ = Et) the T_g values were 33 and 22 °C, respectively.[6b,17] Incorporation of an oxygen spacer into the side chain leads to lower T_g values; poly(ferrocenylalkoxysilanes) with methoxy and ethoxy substituents possess T_g values of 19 and 0 °C, respectively.[9] Therefore, the presence of the Si−O−C spacer increases free volume, resulting in lower T_g values. It would thus be expected that T_g values would continue to decrease significantly as a function of the number of ether linkages in the side chains. By DSC, polymers **10a** and **10b** possess T_g values of ca. −70 °C. This is the lowest known T_g value for a substituted poly(ferrocenylsilane), with the lowest previous value of −51 °C for the polymer $[Fe(\eta\text{-}C_5H_4)_2Si(OHex)_2]_n$.[9] No other thermal transitions were observed for **10a** or **10b**. The DSC data for polymers **6**, **7**, **10a**, and **10b** are summarized in Table 1. Thermogravimetric analysis (TGA) was also performed on the poly(ferrocenylsilanes) at a heating rate of 10 °C/min under N_2, and the data are listed in Table 2. The polymers **6, 7**, and **11** underwent similar weight loss whereas **10a** and **10b** appear slightly less thermally stable. Poly(ferrocenylsilane)s **12**, **10a**, and **10b** are the least thermally stable of the polymers, with T_{10} at 240, 250, and 280 °C, respectively. All other polymers possess a T_{10} greater than 300 °C.

Table 1. DSC Analysis for the Homopolymers (Scan Rate 10 °C/min)

sample	T_g (°C)
6	−31
7	−53
10a	−69
10b	−72

Table 2. TGA Data for Poly(ferrocenylsilanes) 6, 7, 10a, 10b, 11, and 12 (Scan Rate 10 °C/min) under N_2

sample	T_{10}[a] (°C)	T_{50}[b] (°C)	ceramic yield (%) at 900 °C
6	375	475	40
7	300	525	35
10a	250	425	18
10b	280	425	28
11	325	575	48
12	240	325	14

[a] Temperature at which the polymer sample has lost 10% of its original mass. [b] Temperature at which the polymer sample has lost 50% of its initial mass.

Summary

A series of novel hydrophilic and water-soluble poly(ferrocenylsilanes) have been synthesized. Ring-opening polymerization of monomers with hydrophilic side groups and facile substitution of the chlorine substituents on poly(ferrocene) **9** with organic water-soluble moieties were used to prepare these materials. Both neutral and cationic water-soluble poly(ferrocenylsilanes) were thus studied and were shown to form aggregates in water by dynamic light scattering methods. The type of substitution method demonstrated for polymer **9** should provide access to a wide range of functionalized poly(ferrocenylsilanes), and further work aimed at exploring these possibilities and applications of the materials is in progress and will be reported subsequently.

Experimental Section

Materials. Tetrachlorosilane and trichloromethylsilane were purchased from Aldrich, distilled, and stored over Linde 4 Å molecular sieves. Diethylene glycol methyl ether, 2-methoxyethanol, tetramethylethylenediamine (TMEDA), triethylamine, *N*,*N*-dimethylethanolamine, and poly(ethylene glycol) methyl ether ($M_n = 350$) were purchased from Aldrich and dried over sodium. All compounds except for poly(ethylene glycol) methyl ether were distilled and stored over Linde 4 Å molecular sieves. MeI was purchased from Pfaltz and Bauer Inc. and was reacted with $Na_2S_2O_3$ until colorless. Dilithioferrocene·TMEDA was synthesized following the method of Bishop et al.[18] A solution of HCl in Et_2O (1.0 M) was purchased from Aldrich and used as received. Karstedt's catalyst, a (divinyltetramethyldisiloxane)platinum(0) complex in vinyl-terminated poly(dimethylsiloxane), was purchased from Gelest Inc. and was diluted with toluene prior to use.

Equipment. All reactions and manipulations were carried out in either an inert-atmosphere glovebox or under an atmosphere of prepurified nitrogen using Schlenk techniques. ^1H NMR spectra were recorded using Varian Gemini 200 and 300 MHz instruments. ^{13}C NMR were recorded on a Varian Unity 300 and a 400 MHz Varian Unity 400 spectrometer. ^{29}Si NMR (79.5 MHz) were also recorded on the Varian Unity 400 spectrometer in a proton decoupled mode using DEPT pulse sequence with $^2J_{Si-H} = 6.7$ Hz. ^1H NMR spectra were referenced to residual protonated solvents, and ^{13}C spectra were referenced to the C_6D_6 signal at 128.0 ppm unless otherwise noted. Solid-state ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker DSX 200 spectrometer. ^1H NMR spectra were obtained with a spinning rate of 9.5 MHz and a recycle delay of 3 s. ^{13}C NMR spectra were recorded with a spinning rate of 5.5 MHz, a recycle delay of 4 s, and a typical contact time of 2 ms. Solid-state ^{29}Si NMR were recorded using a recycle delay of 10 s, a contact time of 5 ms, and a spinning rate of 4 MHz. Molecular weight estimates were obtained via gel-permeation chromatography (GPC) using a Waters Associates 2690 separations module equipped with a column heater, Ultrastyragel columns with pore sizes of 10^3-10^5 Å, in-line degasser, and a differential refractometer. A flow rate of 1.0 mL/min was used, and the eluent was a solution of 0.1% tetra-*n*-butylammonium bromide in THF. Polystyrene standards purchased from American Polymer Standards were used for calibration purposes. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ. Mass spectra data were obtained with a VG 70-250S mass spectrometer operating in electron impact mode (EI, 70 eV). The thermal behavior of polymers **6**, **7**, **10a**, **10b**, and **12** was studied using a Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a TAC 7 instrument controller. The melting transitions for indium and cyclohexane were used as references for calibration and were obtained at a heating rate of 10 °C/min under nitrogen. T_g values are accurate within ±5 °C. Thermogravimetric analyses were performed at a heating rate of 10 °C/min under N_2 using a Perkin-Elmer TGA and thermogravimetric analyzer. Dynamic light scattering measurements were performed on a wide angle light scattering photometer from Brookhaven Instruments, using a 5 mW vertically polarized He−Ne laser (633 nm, Spectra Physics model) as the light source. Solutions of various concentrations (2 g/L, 4 g/L) were prepared at room temperature in distilled water. The distilled water was filtered with 0.2 μm Gelman PTFE filters. The cells were placed into the BI-200SM goniometer (Brookhaven Instruments) and sat in a vat of thermostated toluene which matched the refractive index of the glass cell. The scattered light was monitored at an angle of 90° using a Brookhaven photomultiplier unit and a BI-2030 AT digital correlator with 136 data channels. Six delay channels were used for establishing a baseline (correlation function at infinite time). Before analysis, data sets were checked for interference from dust by comparing the measured and calculated baselines. For differences greater than 0.2%, the data were discarded. The software used to analyze the data was provided by Brookhaven Instruments Corp. Ultrasonication was performed using a 60 W bath, and samples were sonicated for 1 h.

Synthesis of $Fe(\eta\text{-}C_5H_4)_2SiCl_2$ (3). This compound was synthesized following the method of Wrighton et al.[13] Yield: 15.2 g (77%).

Synthesis of $Fe(\eta\text{-}C_5H_4)_2Si(OCH_2CH_2OCH_3)_2$ (4). A 2.11 mL (26.7 mmol) aliquot of $CH_3OCH_2CH_2OH$ was added to a solution containing **3** (3.78 g, 13.4 mmol) and Et_3N (18.7 mL, 134 mmol) in 400 mL of Et_2O under N_2. The reaction was allowed to proceed with stirring for 1 h and filtered, and the solvent was removed in vacuo to afford a dark red liquid (2.91 g, 60% yield). ^1H NMR (C_6D_6, 300 MHz): $\delta = 3.16$ (s, 6H, OCH_3), 3.42 (t, 4H, CH_2O), 4.14 (t, 4H, $SiOCH_2$), 4.31 (m, 4H, Cp), 4.44 (m, 4H, Cp). ^{13}C NMR (C_6D_6, 400 MHz): $\delta = 41.0$ (*ipso*-Cp), 58.6 ($SiOCH_2$), 62.2 (OCH_3), 73.9 (OCH_2), 75.8 (Cp), 78.0 (Cp). ^{29}Si NMR (C_6D_6, 400 MHz): $\delta = -34.1$. Anal. Calcd for $C_{16}H_{22}FeO_4Si$: C, 53.0; H, 6.1. Found: C, 53.1; H, 6.0. MS (EI, 70 eV): $m/z = 362$ (M^+, 100%).

Synthesis of $Fe(\eta\text{-}C_5H_4)_2Si(OCH_2CH_2OCH_2CH_2OCH_3)_2$ (5). The alcohol $HOCH_2CH_2OCH_2CH_2OCH_3$ (0.84 mL, 7.1 mmol) was added to a solution of Et_3N (4.92 mL, 35.3 mmol), **3** (1.00 g, 3.54 mmol), and 300 mL of Et_2O under N_2. The solution was stirred for 2 h and filtered, and the solvent was removed under vacuo to afford **5** as a viscous red material (1.25 g, 79% yield). ^1H NMR (C_6D_6, 300 MHz): $\delta = 3.22$ (s, 6H, OCH_3), 3.48 (t, 4H, OCH_2), 3.50 (t, 4H, OCH_2), 3.56 (t, 4H, OCH_2), 3.78 (t, 4H, $SiOCH_2$), 4.37 (m, 4H, Cp), 4.46 (m, 4H, Cp). ^{13}C NMR (C_6D_6, 300 MHz): $\delta = 38.8$ (*ipso*-Cp), 56.5 ($SiOCH_2$), 60.2 (OCH_3), 68.6, 70.1, and 70.4 (OCH_2), 73.6 (Cp), 75.7 (Cp). ^{29}Si NMR (C_6D_6, 400 MHz): $\delta = -34.0$. MS (EI, eV): $m/z = 450$ (M^+, 100%).

General Synthesis of Poly(ferrocenylsilanes) 6 and 7. Polymers **6** and **7** were prepared analogously from monomers **4** and **5**, respectively. Therefore, the general synthesis is illustrated by that of **6**.

Immediately following the synthesis of **4**, (2.00 g, 5.43 mmol) 10 mL of THF was added as well as Karstedt's catalyst (0.20 mL, 0.0010 wt %). The polymerization reaction was left stirring at room temperature overnight and the polymer then precipitated into methanol. The solution was decanted and the polymer dried in vacuo to afford **6** as an adhesive dark amber gum (1.42 g, 71%). ^1H NMR (C_6D_6, 300 MHz): $\delta = 3.22$ (s, 6H, OCH_3), 3.49 (t, 4H, CH_2O), 4.15 (t, 4H, $SiOCH_2$), 4.53 (m, 4H, Cp), 4.69 (m, 4H, Cp). ^{13}C NMR (C_6D_6, 300 MHz): $\delta = 58.9$ ($SiOCH_2$), 62.9 (OCH_3), 66.5 (*ipso*-Cp), 73.2 (Cp), 74.4 (CH_2O), 74.8 (Cp). ^{29}Si NMR (C_6D_6, 400 MHz): $\delta = -19.4$. Anal. Calcd for $C_{16}H_{22}FeO_4Si$: C, 53.0; H, 6.1. Found: C, 53.0; H, 6.2. GPC: $M_n = 235\,400$, $M_w = 616\,500$, PDI = 2.62.

For **7**, an adhesive dark amber gum: yield, 1.07 g, 86%. ^1H NMR (C_6D_6, 300 MHz): $\delta = 3.20$ (s, 6H, OCH_3), 3.46 (t, 4H, OCH_2), 3.62 (m, 8H, OCH_2), 4.18 (t, 4H, $SiOCH_2$), 4.54 (m, 4H, Cp), 4.70 (m, 4H, Cp). ^{13}C NMR (C_6D_6, 400 MHz): $\delta = 58.9$ ($SiOCH_2$), 63.0 (OCH_3), 66.4 (*ipso*-Cp), 70.9, 72.5, and 73.1 (OCH_2), 73.2 (Cp), 74.7 (Cp). ^{29}Si NMR (C_6D_6, 400 MHz): $\delta = -20.8$. GPC: $M_n = 101\,800$ $M_w = 261\,500$. PDI = 2.57.

Synthesis of $[Fe(\eta\text{-}C_5H_4)_2SiMeCl]$ (8). The monomer, **8**, was synthesized following the previously reported method.[15] Yield: 14.7 g (82%).

Synthesis of $[Fe(\eta\text{-}C_5H_4)_2SiMeCl]_n$ (9). To a solution of $Fe(\eta\text{-}C_5H_4)_2SiMeCl$ (1.00 g, 3.82 mmol) in toluene (25 mL) was added a catalytic amount of $PtCl_2$ (2.0 mol %, 20 mg). This solution was allowed to stir overnight. The polymer was then precipitated into freshly distilled hexanes and dried in vacuo overnight to obtain $[Fe(\eta\text{-}C_5H_4)_2SiMeCl]_n$ as an orange powder.

Synthesis of $[Fe(\eta\text{-}C_5H_4)_2SiMe(OCH_2CH_2)_xOCH_3]_n$ (10). Synthesis of 10a. Polymer **9** (1.00 g, 3.82 mmol) was dissolved in toluene (100 mL), to which was added an excess of triethylamine (5.30 mL, 38.0 mmol) and poly(ethylene glycol) methyl ether, $M_n = 350$ (1.33 g, 3.80 mmol). The solution was stirred overnight and filtered, and excess triethylamine and toluene were removed in vacuo. The product was washed with hexanes and then ether to remove excess poly(ethylene glycol) methyl ether. The polymer **10a** was recovered as a dark amber, highly viscous material (1.85 g, 85% yield). ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 0.78$ (s, 3H, CH_3), 3.11 (s, 3H, OCH_3), 3.14−3.70 (br, 32H, OCH_2CH_2), 3.89 (br, 2H, $SiOCH_2$), 4.10−4.48 (br, 8H, Cp). ^{13}C NMR (C_6D_6, 400 MHz): $\delta = -1.7$ (Si−CH_3), 58.6−62.9 (OCH_2CH_2), 68.2 (*ipso*-Cp), 69.0−71.0 (OCH_2CH_2), 72.4−74.5 (OCH_2CH_2 and Cp). ^{29}Si NMR (C_6D_6, 400 MHz): $\delta = 3.7$. GPC: $M_n = 56\,000$, $M_w = 128\,100$, PDI = 2.29. The higher molecular weight analogue (**10b**) was prepared similarly and was isolated as an amber gum (1.21 g, 81%). ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 0.77$ (s, 3H, CH_3), 3.18 (s, 3H, OCH_3), 3.30−3.60 (br, 32H, OCH_2CH_2), 3.90 (br, 2H, $SiOCH_2$), 4.21−4.52 (br, 8H, Cp). GPC: $M_n = 189\,700$, $M_w = 411\,200$, PDI = 2.17.

Synthesis of [Fe(η-C_5H_4)$_2$SiMe($OCH_2CH_2NMe_2$)]$_n$ (11). To a solution of **9** (0.50 g, 1.9 mmol) in 125 mL of toluene was added 2.67 mL of Et_3N (19.1 mmol) and 0.19 mL (1.9 mmol) of $HOCH_2CH_2NMe_2$. The solution was stirred overnight, and 7.7 μL (0.19 mmol) of MeOH was added to the reaction mixture to ensure full substitution of the chlorine atoms. The solution was then filtered, excess Et_3N and MeOH were removed in vacuo, and the product was washed with ethanol and hexanes to obtain **11** (0.45 g, 75%) as an orange gum. ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 0.46$ (s, 3H, Si−CH_3), 2.18 (s, 6H, $N(CH_3)_2$), 2.50 (br, 2H, N−CH_2), 3.89 (br, 2H, $SiOCH_2$), 4.22−4.48 (br, 8H, Cp). ^{1}H NMR (d_7-DMF, 200 MHz): $\delta = 0.68$ (s, 3H, Si−CH_3), 2.31 (s, 6H, $N(CH_3)_2$), 2.58 (m, 2H, NCH_2), 4.14−4.42 (10H, br, $SiOCH_2$ and Cp). ^{13}C NMR (C_6D_6, 300 MHz): $\delta = 0.0$ (Si−CH_3), 46.2 (NMe_2), 61.9, 62.1, 69.7 (OCH_2CH_2 and *ipso*-Cp), 72.4−74.5 (Cp). ^{29}Si NMR (d_7-DMF, 400 MHz): $\delta = 0.5$. GPC: $M_n = 22\,500$, $M_w = 41\,100$, PDI = 1.83. Anal. Calcd for $C_{15}H_{21}FeNOSi$: C, 57.2; H, 6.7; N, 4.5. Found: C, 57.0; H, 6.6; N, 4.4.

Synthesis of [Fe(η-C_5H_4)$_2$SiMe($OCH_2CH_2NMe_3I$)]$_n$ (12). Polymer **11** (0.20 g, 0.64 mmol) was dissolved in 15 mL of CH_2Cl_2. To this solution was added 40.0 μL (0.643 mmol) of MeI. The reaction mixture was then refluxed overnight while a yellow-orange polymer precipitated out of solution. The CH_2Cl_2 was evaporated in vacuo and the polymer washed with THF and CH_2Cl_2 to afford **12** (0.25 g, 85% yield). ^{1}H NMR (d_7-DMF, 200 MHz): $\delta = 0.78$ (s, 3H, Si−CH_3), 3.45 (s, 9H, $N(CH_3)_3$), 3.52 (s, 2H, N−CH_2), 3.89 (s, 2H, $SiOCH_2$), 4.15−4.52 (br, 8H, Cp). ^{13}C NMR (d_7-DMF, 400 MHz): $\delta = -3.2$ (Si−CH_3), 53.0 ($N(CH_3)_3$), 57.1, 66.5, and 67.6 (OCH_2CH_2 and *ipso*-Cp), 71.4−73.4 (Cp). ^{29}Si NMR (d_7-DMF, 400 MHz): $\delta = 5.6$. CP-MAS ^{13}C NMR: $\delta = -2.5$ (Si−CH_3), 53.0 ($N(CH_3)_3$), 57.0 (NCH_2), 67.0 (OCH_2 and Cp), 72.0 (Cp). Anal. Calcd for $C_{16}H_{24}FeNOSiI$: C, 41.9 H, 5.3; N, 3.1. Found: C, 41.3; H, 5.3; N, 2.6.

Synthesis of [Fe(η-C_5H_4)$_2$SiMe($OCH_2CH_2NMe_2HCl$)]$_n$ (13). Polymer **11** (0.20 g, 0.64 mmol) was dissolved in 15 mL of THF. To this solution was added 0.63 mL (0.63 mmol) of HCl in Et_2O (1.0 M). An orange precipitate immediately formed. The THF was decanted and the polymer washed with THF and hexanes to afford **13** (0.19 g, 86% yield). ^{1}H NMR (d_7-DMF, 200 MHz): $\delta = 0.70$ (br, 3H, Si−CH_3), 2.91 (br, 6H, $N(CH_3)_2$), 3.30 (br, 2H, NCH_2), 4.16−3.50 (br, 10H, $SiOCH_2$ and Cp). ^{13}C NMR (d_7-DMF, 400 MHz): $\delta = -3.0$ (Si−CH_3), 43.7 ($N(CH_3)_2H$), 57.3 (NCH_2), 60.8 (OCH_2), 68.3 (*ipso*-Cp), 71.5−74.6 (Cp). ^{29}Si NMR (d_7-DMF, 400 MHz): $\delta = 0.9$.

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