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Notes

Synthesis and Characterization of Anionic and Cationic Poly(ferrocenylsilane) Polyelectrolytes

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Introduction

Macromolecules containing inorganic elements or organometallic units in the main chain combine potentially useful chemical, electrochemical, optical, and other interesting characteristics with the properties and processability of polymers.[1] Poly(ferrocenylsilanes), composed of alternating ferrocene and alkylsilane units in the main chain, belong to this class of organometallic polymers. With the discovery of the anionic ring-opening polymerization of silicon-bridged ferrocenophanes,[1] well-defined poly(ferrocenylsilanes) and block copolymers featuring corresponding organometallic blocks have become accessible.[2]

As we found poly(ferrocenyldimethylsilane) to be an effective resist in reactive ion etching processes,[3] it became of interest to employ this polymer in surface patterning of silicon substrates, which is relevant to the fabrication of for example electrooptical and magnetic storage devices and sensors. Patterns on the (sub)micrometer scale can be introduced by soft lithography, using poly(ferrocenylsilanes) as ink.[4] Block copolymers featuring poly(ferrocenylsilane) blocks form nanoperiodic microdomain structures upon phase separation.[5] Thin films of such block copolymers, e.g., poly(ferrocenyldimethylsilane-*block*-isoprene), can serve as self-assembling templates, enabling nanometer-sized patterns to be transferred directly into silicon or silicon nitride substrates by reactive ion etching.[6] Ferrocenylsilane−styrene block copolymer thin films were successfully used as templates in the fabrication of arrays of nanometer-sized cobalt magnetic dots.[7]

Water-soluble poly(ferrocenylsilane) polycations, belonging to the rare class of main-chain organometallic polyelectrolytes, have recently been reported by us and others.[8−11] Such materials are of interest as they can be processed in aqueous media to multilayer films, using the electrostatic self-assembly process.[12,13] In this process, a substrate is immersed alternatingly in polyanion and polycation solutions, leading to the assembly of a multilayer thin film with controlled thickness and composition. Aqueous processing enables synthetic as well as natural polyelectrolytes to be assembled to thin films for a variety of applications, ranging from light-emitting devices[14] to biomimetic surfaces.[15] We recently reported the synthesis of the first poly(ferrocenylsilane) polyanion.[16,17] This development enabled the fabrication of all-organometallic multilayers,[18,19] which are of interest for example due to their redox activity.[20] In addition to forming continuous organometallic multilayer thin films, we explored the layer-by-layer deposition of poly(ferrocenylsilane) polyions onto hydrophilically/hydrophobically modified substrates with the aim of building two-dimensionally patterned organometallic multilayers.[18] Such films may be of interest as ultrathin resists in reactive ion etch processes. The poly(ferrocenylsilane) polyanion and polycation employed in this study are weak polyelectrolytes,[21] whose linear charge density varies with solution pH. Here we report a generic route for the synthesis of weak and strong anionic and cationic poly(ferrocenylsilane) polyelectrolytes. The strong anionic polyelectrolyte constitutes the first example of an organometallic polyanion with a pH-independent charge density.

Results and Discussion

Polyelectrolyte Synthesis. Any route to high molar mass poly(ferrocenylsilanes) incorporates a ring-opening polymerization step of a strained silicon-bridged ferrocenophane.[1] Such ferrocenophanes are obtained by treating 1,1′-dilithioferrocene with a dichlorosilane. Many functionalities, however, do not tolerate the highly basic dilithioferrocene or the reactive chlorosilane moieties, are incompatible with the reactive strained monomer itself, or hinder monomer purification. Side-group modification following polymerization is therefore a viable approach if polar or even ionic moieties are to be introduced.

We employ a poly(ferrocenylsilane) featuring chloropropylmethylsilane repeat units as an organometallic main chain which already has reactive pendant groups in place for further functionalization[11] (Scheme 1). Poly(ferrocenyl(3-chloropropyl)methylsilane), **2**, was readily accessible by transition-metal-catalyzed ring-opening polymerization[22] of the corresponding (3-chloropropyl)methylsilyl[1]ferrocenophane, **1**.[11] By means of halogen exchange,[23] **2** can be converted quantitatively into its iodopropyl (**3**) or bromopropyl analogues (**4**), which are particularly suitable for functionalization by nucleophilic substitution. The characteristics of the poly(ferrocenyl(3-halopropyl)methylsilanes) are summarized in Table 1.

The availability of **2**−**4** enables one to access a wide range of functional poly(ferrocenylsilanes). As an example, reaction of **2** with alkali metal amides, such as potassium 1,1,3,3-tetramethyldisilazide[24] in THF, in the presence of dicyclohexano-18-crown-6, afforded a *N*,*N*-bis(dimethylsilyl)-protected poly(ferrocenyl(3-aminopropyl)methylsilane), which was hydrolyzed to the desired

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Scheme 1. Synthesis of Poly(ferrocenyl(3-halopropyl)methylsilanes) by Halogen Exchange

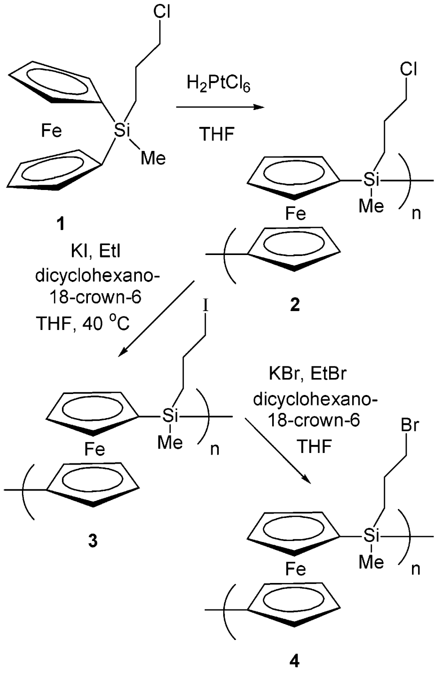
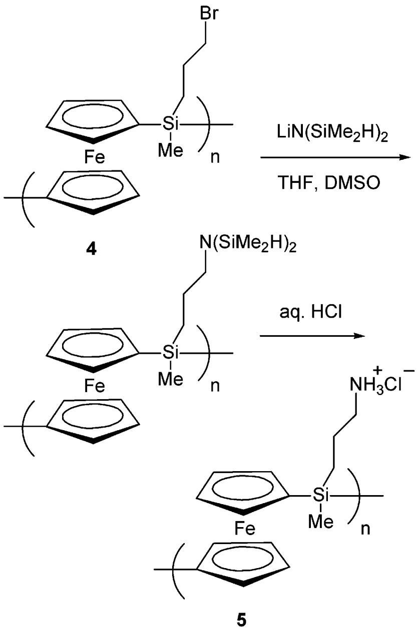


Table 1. Characteristics of the Poly(ferrocenylsilanes)

polymer, side group	M_n (g/mol)	M_w (g/mol)	M_w/M_n	T_g (°C)[d]
2 $-(CH_2)_3-Cl$	1.92×10^5 [a]	3.11×10^5	1.62	38
3 $-(CH_2)_3-I$	1.37×10^4 [a]	2.71×10^4	1.97	
	1.88×10^5 [a]	3.05×10^5	1.62	45
4 $-(CH_2)_3-Br$	1.35×10^4 [a]	2.56×10^4	1.90	
	1.49×10^5 [a]	2.87×10^5	1.93	41
5 $-(CH_2)_3-NH_3Cl$	1.24×10^4 [b]	2.36×10^4	1.90	
7 $-(CH_2)_3-NEtMe_2Cl$	1.31×10^4 [c]	2.59×10^4	1.97	
	1.79×10^5 [c]	2.91×10^5	1.62	
8 $-(CH_2)_3-CO_2Na$	1.47×10^4 [c]	2.89×10^4	1.97	
9 $-(CH_2)_3-SO_3i\mathrm{Bu}$	1.31×10^4 [a]	2.59×10^4	1.98	
10 $-(CH_2)_3-SO_3Na$	1.34×10^4 [c]	2.65×10^4	1.97	

[a] Obtained by GPC in THF, relative to polystyrene standards. [b] Calculated from the corresponding molar mass values of **4**. [c] Calculated from the corresponding molar mass values of **3**. [d] Midpoint.

Scheme 2. Synthesis of Polycation 5



polycation **5** in aqueous acid (Scheme 2). The disilazide reagent converts reactive alkyl halides such as benzyl and allyl chlorides and alkyl bromides into primary amines.[24] Poly(ferrocenyl(3-bromopropyl)methylsilane), **4**, was converted quantitatively into polycation **5** using lithium 1,1,3,3-tetramethyldisilazide in the presence of dimethyl sulfoxide.[25] The lithium disilazide reagent was readily obtained by treating 1,1,3,3-tetramethyldisilazane with lithium diisopropylamide (LDA), which has handling advantages over the earlier employed potassium hydride. In contrast with alkyl bromides and chlorides, alkyl iodides show elimination as a side reaction when treated with these alkali metal amides, due to the basicity of the reagent.

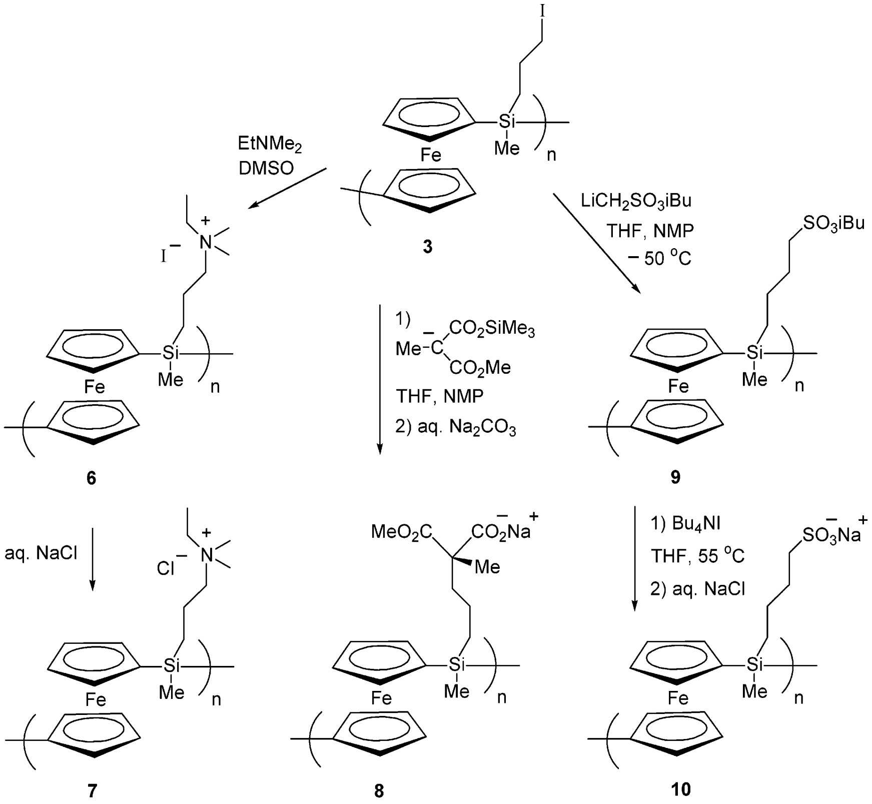
Polycation **5** is a weak polyelectrolyte, of which the linear charge density depends on solution pH. In the fabrication of multilayer films by the electrostatic self-assembly process, pH control is a powerful tool, enabling one to control multilayer thickness.[26] The linear charge density in strong polyelectrolytes is independent of pH, which limits processing options, but also ensures that the surface charge density of the deposited multilayer is not influenced by the pH of the electrolyte solutions in use, which may vary in the case of weak polyelectrolytes. We were therefore interested in also forming strong poly(ferrocenylsilane) polyelectrolytes.

A corresponding organometallic polycation was obtained by amination of the iodopropyl-functional poly(ferrocenylsilane) **3** in DMSO, using a tertiary amine as the nucleophile. After stirring for a few days at room temperature, complete conversion was achieved, both for low and high molar mass **3**. The resulting polycation **6**, featuring iodide counterions, dissolved well in DMSO but was not soluble in water. Exchange of the iodide ions to chloride counterions, however, produced the highly water-soluble polycation **7**. The counterion identity strongly influences polyelectrolyte solubility.[27]

The reactive poly(ferrocenyl(3-iodopropyl)methylsilane), **3**, is also a suitable starting material for functionalization by carbon nucleophiles. Malonic ester anions such as dimethyl methylmalonate anion or dibenzyl methylmalonate anion smoothly react to produce the corresponding polyesters with quantitative conversions, as was evident from ^{1}H and ^{13}C NMR spectrometry. By using hydrolytically labile ester enolates, such as methyltrimethylsilyl methylmalonate anion,[28] one can easily convert the corresponding pendant ester groups into carboxylate salts, thus forming polyanion **8**[16] (Scheme 3). This polyanion is, to our knowledge, the first reported organometallic polyanion. The material is highly water-soluble: it could be dissolved in Milli-Q water to concentrations exceeding 100 mg/mL.[29]

For the synthesis of a strong anionic polyelectrolyte we employed α-lithioisobutylmethanesulfonate[30] as a carbon nucleophile. Sulfonate ester carbanions are of interest as nucleophiles, as they enable the introduction of alkanesulfonate ester moieties which, after deprotection, are turned into alkanesulfonate functionalities. Alkylalkanesulfonates are conveniently α-metalated by *n*-butyllithium and can subsequently be alkylated by alkyl halides.[31] Alkylations are especially efficient when alkyl iodides are employed.[31] Reaction of poly(ferrocenyl(3-iodopropyl)methylsilane), **3**, with α-lithioisobutylmethanesulfonate led to the formation of polymer **9** with quantitative conversion (Scheme 3). The isobutyl pro-

Scheme 3. Synthesis of Poly(ferrocenylsilane) Polyions



tecting groups were removed by heating polymer **9** with tetrabutylammonium iodide in THF.[30] Exchange of the tetrabutylammonium counterions with sodium ions by dialysis against an excess of 0.1 M NaCl produced polyanion **10**.

Polymer Characterization. The poly(ferrocenyl(3-halopropyl)methylsilanes) **2**, **3**, **4**, and **9** were characterized by ^1H NMR and ^{13}C NMR spectrometry, elemental analysis, and gel permeation chromatography (GPC) in THF, using polystyrene standards. On the basis of the corresponding results, we conclude that the halogen-exchange reactions and the alkylation leading to **9** proceeded with quantitative conversions and that the organometallic main chains remained intact. If chain scission or cross-linking reactions in the following steps are excluded, then the molar mass characteristics of polyions **7**, **8**, and **10** can be calculated from **3**. High and low molar mass polymers **3** ($M_w = 3.05 \times 10^5$ g/mol, $M_w/M_n = 1.62$; $M_w = 2.71 \times 10^4$ g/mol, $M_w/M_n = 1.97$) were converted into corresponding polycations **6** and **7**, which were characterized by ^1H and ^{13}C NMR spectrometry. The ^{13}C NMR spectrum of **7** in D_2O is shown in Figure 1. Polyions **5**, **7**, **8**, and **10** were further characterized by elemental analysis, showing excellent agreement between the expected and measured elemental compositions.

An attempt was made to characterize the low and high molar mass polycations **7** as well as polyanions **8** and **10** by gel permeation chromatography. GPC experiments on polyelectrolytes[32] are often complicated by polyelectrolyte adsorption to the stationary phase, which may be observed as tailing, or by aggregation of the charged macromolecules, leading to multimodal molar mass distributions. Indeed, experiments with low and high molar mass polycations **7** on microstyragel columns, using DMSO as eluent at elevated temperature (50 °C) to reduce solvent viscosity, produced multimodal GPC traces with significant high molar mass fractions. Upon addition of lithium chloride, however, the multimodal molar mass distribution disappeared (Figure 2). Low molar mass electrolytes disrupt inter- and intramolecular electrostatic interactions in polyelectrolytes and

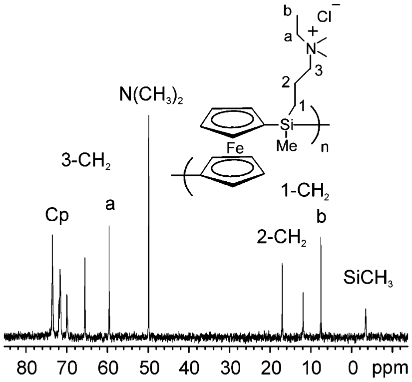


Figure 1. ^{13}C NMR spectrum of the poly(ferrocenylsilane) polycation **7** in D_2O.

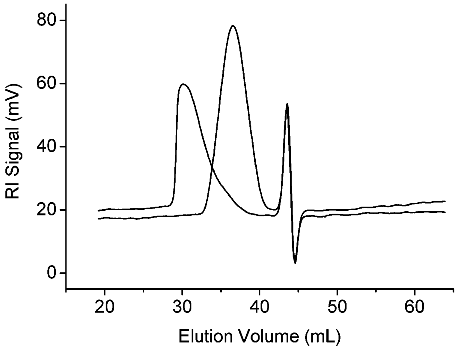


Figure 2. GPC traces of high and low molar mass polycations **7** in DMSO with LiCl (0.12 M).

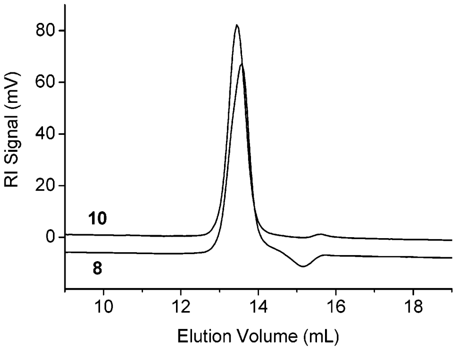


Figure 3. GPC traces of polyanions **8** and **10** in aqueous sodium phosphate (0.1 M, pH 9).

are therefore commonly used in the GPC analysis of polyions.[33] The anticipated high molar mass polycation **7** was eluted faster from the column set than the low molar mass **7**, and despite some tailing of high molar mass **7**, the polymer peaks are well-separated and monomodal, demonstrating that the organometallic chains did not undergo any molar mass decline. The sharp signal, present in both traces at an elution volume of 43.5 mL, appeared when LiCl was added to the eluent and can thus be ascribed to salt exclusion effects.

Polyanions **8** and **10**, which are insoluble in DMSO, were analyzed by gel permeation chromatography in aqueous sodium phosphate at pH 9. Polyanion **8** is fully ionized at this pH. The polyanions, which were both synthesized from the same low molar mass **3**, give very similar traces (Figure 3) and unimodal distributions, showing that also in these cases the main chains remained intact.

Conclusion

Poly(ferrocenylsilane) polyanions and polycations were synthesized by treating poly(ferrocenyl(3-halopropyl)-methylsilanes) with a variety of nucleophiles, ranging from alkali metal amides and neutral amines to ester enolate anions. Highly water-soluble weak and strong organometallic polyelectrolytes were obtained. Analysis of the polyelectrolytes by GPC demonstrated that the organometallic polymers did not undergo chain scission under the employed reaction conditions.

Experimental Section

Materials. Ferrocene (98%), *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (99.5+%), *n*-butyllithium (1.6 M in hexanes), iodoethane (99%), bromoethane (99+%), *cis*-dicyclohexano-18-crown-6 (98%), potassium bromide (99+%), potassium iodide (99+%), hydrogen hexachloroplatinate(IV) hydrate (99.9+%), 1,1,3,3-tetramethyldisilazane (99%), diisopropylamine (99.5%), *N*,*N*-dimethylethylamine (99%), tetrabutylammonium iodide (98%), dimethyl methylmalonate (99%), methyl trimethylsilyl dimethylketene acetal (95%), dichloromethane (anhydrous, 99.8%), 1-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%), dimethyl sulfoxide (anhydrous, 99.9+%), dimethyl-d_6 sulfoxide (99.9 atom % D), and deuterium oxide (100 atom % D) were obtained from Aldrich and used as received. 3-Chloropropylmethyldichlorosilane was obtained from ABCR, Karlsruhe. *n*-Heptane (for synthesis) was purchased from Merck. Tetrahydrofuran (THF) was distilled from sodium benzophenone under argon. Isobutyl methanesulfonate was prepared according to ref 31. ^{13}C NMR ($CDCl_3$): δ 18.49 (CH_3); 28.10 (CH); 37.07 (CH_3SO_3); 75.73 (CH_2). Monomethyl methylmalonate: dimethyl methylmalonate (12.2 g, 83 mmol) was hydrolyzed to the monoacid (8.3 g, 75%) according to ref 34. ^{1}H NMR ($CDCl_3$): δ 1.46 (CH_3, d, 7.3 Hz, 3H); 3.49 (H, q, 7.3 Hz, 1H); 3.76 (OCH_3, s, 3H). ^{13}C NMR ($CDCl_3$): δ 13.33 (CH_3); 45.69 (OCH_3); 52.59 (CH); 170.22 (CO_2CH_3); 175.73 (CO_2H). The polyions were purified by dialysis (16−24 h), using Spectra/Por 4 dialysis tubing with a cutoff MW of 12 000−14 000 g/mol, while passing a slow stream of N_2 through the external solution.

Techniques. ^{1}H and ^{13}C NMR spectra of polymers **2**−**4** and **9** were recorded on a Varian Unity Inova (300 MHz) instrument at 300.3 and 75.5 MHz, respectively. Corresponding NMR spectra of the polyions were recorded on a Varian Unity 400 spectrometer at 399.9 and 100.6 MHz. The following solvent chemical shifts were used as a reference: ^{1}H NMR in D_2O, $\delta = 4.75$ ppm; ^{1}H and ^{13}C NMR in DMSO-d_6, $\delta = 2.50$ and 39.5 ppm, respectively. A Perkin-Elmer Pyris 1 differential scanning calorimeter was used for the determination of glass transition temperatures (T_g's) at a scan rate of 5 K/min. The midpoint of the change in heat capacity was taken as the T_g. Transition temperatures were calibrated using cyclohexane, gallium, and indium standards. GPC measurements on polymers **2**−**4** and **9** were carried out in THF (flow rate 2.0 mL/min) at 25 °C, using microstyragel columns (bead size 10 μm) with pore sizes of 10^5, 10^4, 10^3, and 10^6 Å (Waters) and a dual detection system consisting of a differential refractometer (Waters model 410) and a differential viscometer (Viscotek model H502). Molar masses were determined relative to polystyrene standards. GPC on polycations **7** (low and high molar mass) was performed in DMSO (Merck, for synthesis) containing LiCl (5.0 g/L, Merck, for analysis) at 50 °C with the same setup, using an identical set of microstyragel columns (Waters) and refractive index (RI) detection. A flow rate of 0.8 mL/min was maintained. Aqueous GPC on polyanions **8** and **10** was carried out using a 10 μm Suprema linear M column (Polymer Standards Service, Germany) at 25 °C, 0.1 M Na_2HPO_4/NaH_2PO_4 (0.5 mol/4 mmol in 5 L of Milli-Q, pH 9) as eluent (1.025 mL/min) and RI detection.

Synthesis of 2. In a glovebox under prepurified N_2, $H_2PtCl_6{\cdot}6H_2O$ (15 mg, 3×10^{-5} mol) was added to a solution of (3-chloropropyl)methylsilyl[1]ferrocenophane,[11] **1** (3.00 g, 9.85 mmol), in THF (30 mL), and stirring was continued for 6 h. Precipitation in MeOH afforded **2** (2.64 g, 88%) as an orange-yellow solid. ^{1}H NMR ($CDCl_3$): δ 0.48 ($SiCH_3$, s, 3H); 1.02 (1-CH_2, m, 2H); 1.83 (2-CH_2, m, 2H); 3.53 (3-CH_2, t, 6.6 Hz, 2H); 4.00 + 4.22 (Cp, m, 8H). ^{13}C NMR ($CDCl_3$): δ −3.27 ($SiCH_3$); 13.86 (1-CH_2); 27.79 (2-CH_2); 48.15 (3-CH_2); 70.00 (Cp−Si); 71.44 + 73.38 (Cp). Anal. Calcd for $C_{14}H_{17}FeClSi$: C, 55.26; H, 5.64; Cl, 11.50. Found: C, 55.07; H, 5.50; Cl, 11.15. $M_n = 1.92 \times 10^5$ g/mol, $M_w = 3.11 \times 10^5$ g/mol, $M_w/M_n = 1.62$.

Synthesis of 3. A solution of **2** (0.924 g, 3.03 mmol repeat units), dicyclohexano-18-crown-6 (0.30 g, 0.80 mmol), KI (0.38 g, 2.3 mmol), and iodoethane (5.0 mL, 62 mmol) in THF (20 mL) was stirred at 40 °C for a week. The polymer was precipitated in MeOH, dried, and stirred with the same reagents for another 3 days at 40 °C to complete the halogen exchange. Precipitation in MeOH gave **3** (1.09 g, 91%). ^{1}H NMR ($CDCl_3$): δ 0.46 ($SiCH_3$, s, 3H); 1.00 (1-CH_2, m, 2H); 1.87 (2-CH_2, m, 2H); 3.22 (3-CH_2, m, 2H); 3.99 + 4.23 (Cp, m, 8H). ^{13}C NMR ($CDCl_3$): δ −3.12 ($SiCH_3$); 12.15 (1-CH_2); 18.16 (2-CH_2); 28.80 (3-CH_2); 69.97 (Cp−Si); 71.36 + 73.39 (Cp). Anal. Calcd for $C_{14}H_{17}FeISi$: C, 42.45; H, 4.33. Found: C, 42.62; H, 4.28. $M_n = 1.88 \times 10^5$ g/mol, $M_w = 3.05 \times 10^5$ g/mol, $M_w/M_n = 1.62$.

Synthesis of 4. Polymer **3** (0.31 g, 0.78 mmol r.u.), dicyclohexano-18-crown-6 (0.10 g, 0.27 mmol), KBr (62 mg, 0.52 mmol), and bromoethane (2.0 mL, 27 mmol) in THF (10 mL) was stirred at room temperature for a week. Precipitation in MeOH gave **4** (0.25 g, 92%). ^{1}H NMR ($CDCl_3$): δ 0.47 ($SiCH_3$, s, 3H); 1.01 (1-CH_2, m, 2H); 1.90 (2-CH_2, m, 2H); 3.41 (3-CH_2, m, 2H); 3.99 + 4.22 (Cp, m, 8H). ^{13}C NMR ($CDCl_3$): δ −3.22 ($SiCH_3$); 15.41 (1-CH_2); 28.01 (2-CH_2); 37.49 (3-CH_2); 69.97 (Cp−Si); 71.39 + 73.32 (Cp). Anal. Calcd for $C_{14}H_{17}FeBrSi$: C, 48.16; H, 4.91. Found: C, 48.41; H, 4.92. $M_n = 1.49 \times 10^5$ g/mol, $M_w = 2.87 \times 10^5$ g/mol, $M_w/M_n = 1.93$.

Synthesis of 5. To a solution of LDA (3.2 mmol) in dry THF (8 mL) at 0 °C, 1,1,3,3-tetramethyldisilazane (0.80 g, 6.0 mmol) was added under argon. The mixture was stirred in ice for 24 h and subsequently degassed in three freeze−pump−thaw cycles, and the solvents were removed by condensation under vacuum. To the solid $LiN(SiMe_2H)_2$, THF (2 mL) and DMSO (2 mL) were added, followed by a solution of **4** (0.37 g, 1.1 mmol r.u.) in THF (8 mL). The mixture was stirred in ice for 3 days. Degassed aqueous NH_4Cl (1 mL, 4.0 M) was added, and subsequent titration with dilute HCl yielded **5**. The polycation was dialyzed against 0.1 M NaCl in Milli-Q (3 × 1 L), followed by dialysis against Milli-Q to remove low-MW salts. The salt-free polyelectrolyte solution was concentrated and dried by a flow of N_2 and further dried under vacuum to produce polycation **5** as orange-brown flakes (0.30 g, 88%). ^1H NMR (D_2O): δ 0.58 ($SiCH_3$, s, 3H); 0.99 (1-CH_2, m, 2H); 1.73 (2-CH_2, m, 2H); 2.94 (3-CH_2, m, 2H); 4.05 + 4.28 (Cp, m, 8H). ^{13}C NMR (D_2O): δ −2.64 (CH_3), 13.11 (1-CH_2), 22.64 (2-CH_2), 42.96 (3-CH_2), 71.20 (Cp−Si); 72.36 + 74.38 (Cp). Anal. Calcd for $C_{14}H_{20}NFeClSi$: C, 52.27; H, 6.27. Found: C, 52.51; H, 6.16. $M_n = 1.24 \times 10^4$ g/mol, $M_w = 2.36 \times 10^4$ g/mol, $M_w/M_n = 1.90$.

Synthesis of 6. Polymer **3** (0.51 g, 1.3 mmol r.u.) was dissolved in THF (9 mL), and DMSO (4.5 mL) was added, followed by Me_2NEt (2.5 mL, 23 mmol). Within 24 h, the polymer had precipitated. THF was evaporated, DMSO (3 mL) and Me_2NEt (2.0 mL, 18 mmol) were added, and stirring was continued for 1 week. A ^1H NMR spectrum of a sample taken after 4 days already showed complete conversion. Polycation **6** was precipitated by adding diethyl ether, washed by replacing ether several times, and finally dried under vacuum. Yield 0.60 g, product contained traces of DMSO. ^1H NMR (DMSO-d_6): δ 0.54 ($SiCH_3$, s, 3H); 0.87 (1-CH_2, m, 2H); 1.22 ($N-CH_2CH_3$, t, 7.0 Hz, 3H); 1.72 (2-CH_2, m, 2H); 3.01 ($N-CH_3$, s, 6H); 3.34 (3-CH_2 + $N-CH_2CH_3$, m, 4H); 4.05 + 4.24 (Cp, m, 8H). ^{13}C NMR (DMSO-d_6): δ −3.42 ($SiCH_3$); 7.77 ($N-CH_2CH_3$); 11.67 (1-CH_2); 16.80 (2-CH_2); 49.24 ($N-CH_3$); 58.61 ($N-CH_2CH_3$); 65.06 (3-CH_2); 69.38 (Cp−Si); 71.01 + 72.88 (Cp).

Ion Exchange of 6 to 7. Polycation **6** (0.60 g) in DMSO (10 mL) was transferred to a Spectra/Por 4 dialysis hose and dialyzed against Milli-Q water (1.6 L), 0.1 M NaCl (3 × 1.6 L), and then against Milli-Q. Concentration of the salt-free polyelectrolyte solution by a flow of N_2 produced polycation **7** as orange-brown flakes (0.46 g, 95%). ^1H NMR (D_2O): δ 0.60 ($SiCH_3$, s, 3H); 0.96 (1-CH_2, m, 2H); 1.25 ($N-CH_2CH_3$, t, 6.4 Hz, 3H); 1.74 (2-CH_2, m, 2H); 2.94 ($N-CH_3$, s, 6H); 3.17 (3-CH_2, m, 2H); 3.27 ($N-CH_2CH_3$, m, 2H); 4.06−4.44 (Cp, m, 8H). ^{13}C NMR (D_2O): δ −3.42 ($SiCH_3$); 7.63 ($N-CH_2CH_3$); 11.96 (1-CH_2); 17.09 (2-CH_2); 49.94 ($N-CH_3$); 59.65 ($N-CH_2CH_3$); 65.61 (3-CH_2); 70.05 (Cp−Si); 71.68 + 73.60 (Cp). Anal. Calcd for $C_{18}H_{28}NFeClSi$: C, 57.22; H, 7.47; N, 3.71. Found: C, 56.39; H, 7.37; N, 3.67. $M_n = 1.79 \times 10^5$ g/mol, $M_w = 2.91 \times 10^5$ g/mol, $M_w/M_n = 1.62$.

Methyltrimethylsilyl Methylmalonate. In a glovebox under nitrogen, methyl trimethylsilyl dimethylketene acetal[35] (1.34 g, 7.6 mmol) was added dropwise to the dry monoacid (0.98 g, 7.4 mmol) in dry CH_2Cl_2 (5 mL). After stirring for 24 h, the solution was degassed in three freeze−pump−thaw cycles, and solvent and methyl isobutyrate were removed by condensation under vacuum, producing the desired trimethylsilyl malonate ester in quantitative yield. ^1H NMR ($CDCl_3$): δ 0.28 ($SiMe_3$, s, 9H); 1.39 (CH_3, d, 7.3 Hz, 3H); 3.41 (H, q, 7.3 Hz, 1H); 3.72 (OCH_3, s, 3H). ^{13}C NMR ($CDCl_3$): δ −0.53 ($SiMe_3$); 13.52 (CH_3); 47.36 (OCH_3); 52.18 (CH); 170.17 (CO_2CH_3); 170.76 (CO_2SiMe_3).

Synthesis of 8. A solution of methyltrimethylsilyl methylmalonate (0.70 g, 3.4 mmol) in dry THF (5 mL) was added dropwise at −80 °C to LDA (3.2 mmol, prepared from *n*-BuLi and diisopropylamine in THF) under argon. After stirring for 3 h, the temperature had risen to −50 °C. The solution was degassed in three freeze−pump−thaw cycles, and the solvents were removed by condensation under vacuum. The solid malonate salt was dissolved in dry NMP (2 mL), and a solution of **3** (0.4 g, 1.0 mmol r.u.) in THF (5 mL) was added. Stirring was continued for 48 h at room temperature under dry N_2. The reaction mixture was cooled in ice a degassed aqueous $NaHCO_3$ solution (1.0 g/10 mL) was added, and THF was evaporated. Purification by dialysis against Milli-Q, and concentration of the polyelectrolyte solution using N_2 gave **8** as orange-brown flakes (0.39 g, 92%). ^1H NMR (D_2O): δ 0.48 ($SiCH_3$, s, 3H); 0.95 (1-CH_2, m, 2H); 1.33 (CH_3, s, 3H); 1.79 (2-CH_2, m, 2H); 2.00 (3-CH_2, m, 2H); 3.67 (OCH_3, s, 3H); 4.04−4.23 (Cp, m, 8H). ^{13}C NMR (D_2O): δ −2.57 ($SiCH_3$); 16.49 (1-CH_2); 19.70 (2-CH_2); 20.26 (CH_3); 40.29 (3-CH_2); 52.50 (OCH_3); 56.70 (CH_3-C); 70.73 (Cp−Si); 71.51 + 73.54 (Cp); 177.20 ($O{=}C-OCH_3$); 180.12 ($O{=}C-ONa$). Anal. Calcd for $C_{19}H_{23}O_4FeNaSi$: C, 54.04; H, 5.49. Found: C, 54.39; H, 5.64. $M_n = 1.47 \times 10^4$ g/mol, $M_w = 2.89 \times 10^4$ g/mol, $M_w/M_n = 1.97$.

Synthesis of 9. A solution of isobutyl methanesulfonate (0.70 g, 4.6 mmol) in dry THF (5 mL) was cooled under argon to −80 °C, and *n*-BuLi (2.0 mL, 3.2 mmol) was added dropwise. After stirring for 20 min, a solution of **3** (0.40 g, 1.0 mmol r.u.) in THF (8 mL) and NMP (3 mL) was added dropwise. Stirring was continued at −50 °C for 8 h. The reaction was terminated at −50 °C by adding acetic acid (0.3 mL, 5 mmol) in THF (3 mL). Precipitation in MeOH (100 mL), followed by precipitation from THF in *n*-heptane, gave **9** (0.40 g, 94%) as an orange-brown solid. ^1H NMR ($CDCl_3$): δ 0.46 ($SiCH_3$, s, 3H); 0.90 (1-CH_2, m, 5.5 Hz, 2H); 0.97 (CH_3, d, 6.6 Hz, 6H); 1.47 (2-CH_2, m, 2H); 1.88 (3-CH_2, m, 2H); 2.01 (CH, m, 6.6 + 6.9 Hz, 1H); 3.06 (4-CH_2, t, 5.3 Hz, 2H); 3.95 (SO_3CH_2, d, 6.9 Hz, 2H); 3.96 + 4.19 (Cp, m, 8H). ^{13}C NMR ($CDCl_3$): δ −3.43 ($SiCH_3$); 15.97 (1-CH_2); 18.65 (CH_3); 23.01 (2-CH_2); 27.10 (3-CH_2); 28.26 (CH); 49.93 (4-CH_2); 69.97 (Cp−Si); 71.35 + 73.27 (Cp); 75.22 (CH_2). Anal. Calcd for $C_{19}H_{28}O_3SFeSi$: C, 54.28; H, 6.71; S, 7.63. Found: C, 54.59; H, 6.68; S, 7.32. $M_n = 1.31 \times 10^4$ g/mol, $M_w = 2.59 \times 10^4$ g/mol, $M_w/M_n = 1.98$.

Synthesis of 10. Polymer **9** (0.26 g, 0.62 mmol r.u.) and NBu_4I (0.50 g, 1.3 mmol) in THF (10 mL) were stirred at 55 °C for 6 h. By then, the polymer had precipitated. THF was evaporated, MeOH (10 mL) and NBu_4I (0.25 g) were added, and stirring was continued at 55 °C for 1 week. The solution was dialyzed against MeOH/Milli-Q (2 × 250/500 mL) to remove Bu_4NI. Further dialysis was performed against 0.1 M NaCl (3 × 800 mL) and Milli-Q (3 × 800 mL). Evaporation of Milli-Q, using a flow of N_2, gave polymer **10** as amber flakes (0.22 g, 92%). ^1H NMR (D_2O): δ 0.53 ($SiCH_3$, s, 3H); 0.98 (1-CH_2, m, 2H); 1.52 (2-CH_2, m, 2H); 1.81 (3-CH_2, m, 2H); 2.88 (4-CH_2, m, 2H); 4.07 + 4.28 (Cp, m, 8H). ^{13}C NMR (D_2O): δ −2.89 ($SiCH_3$); 15.83 (1-CH_2); 23.35 (2-CH_2); 28.30 (3-CH_2); 51.33 (4-CH_2); 71.31 (Cp−Si); 71.89 + 73.94 (Cp). Anal. Calcd for $C_{15}H_{19}O_3SFeNaSi$: C, 46.64; H, 4.96; S, 8.30. Found: C, 46.58; H, 5.22; S, 8.13. $M_n = 1.34 \times 10^4$ g/mol, $M_w = 2.65 \times 10^4$ g/mol, $M_w/M_n = 1.97$.

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