Synthesis of a Polyanionic Water-Soluble Poly(ferrocenylsilane)

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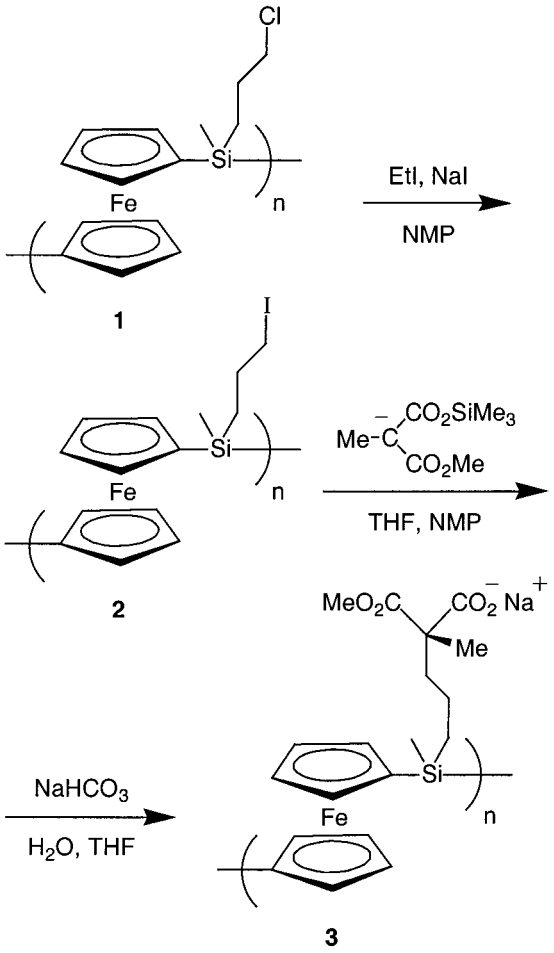
Macromolecules containing inorganic elements or organometallic units in the main chain are of considerable interest as they may combine potentially useful chemical, electrochemical, optical, and other interesting characteristics with the processability of polymers.[1] Poly(ferrocenylsilanes), consisting of alternating ferrocenyl units and silicon atoms in the main chain, are among this class of materials. With the discovery of the anionic ring-opening polymerization (ROP) of silicon-bridged ferrocenophanes,[2] well-defined poly(ferrocenylsilanes) and block copolymers featuring corresponding organometallic blocks have become accessible.[1] As poly(ferrocenyldimethylsilane) was an effective resist in reactive ion etching processes,[3] it became of interest to employ this polymer in surface patterning of for example silicon (or other) substrates, which has relevance in the fabrication of for example electrical and electrooptical devices, sensors, etc. A line pattern of this polymer, deposited on silicon substrates using a MIMIC microcontact printing technique, could be transferred into the substrate by removing uncovered silicon areas in an O_2/CF_4 plasma.[3] Block copolymers featuring poly(ferrocenylsilane) blocks form nanoperiodic microdomain structures upon phase separation.[4] In thin films of such block copolymers, e.g., poly(ferrocenyldimethylsilane-*block*-isoprene), the high resistance of the organometallic phase to reactive ion etching compared to the organic phase was used to form nanopatterned surfaces in a one-step etching process and subsequently transfer these patterns into silicon substrates.[5] The utility of ferrocenylsilane block copolymers in surface patterning was further demonstrated by the use of ferrocenylsilane−styrene block copolymers as templates in the fabrication of arrays of nanometer-sized cobalt magnetic dots.[6]

Water-soluble poly(ferrocenylsilane) polycations, belonging to the rare class of main-chain organometallic polyelectrolytes,[7−10] have recently been reported by us and others. These compounds are of interest because they combine the unusual properties of poly(ferrocenylsilanes) with the processability of polyelectrolytes, for example, enabling one to make use of ionic interactions to deposit these polymers onto substrates. Polyelectrolytes can be employed in layer-by-layer self-assembly processes to form multilayer thin films.[11] The method is based on electrostatic intermolecular forces and involves the sequential adsorption of polyanions and polycations from the corresponding aqueous electrolyte solutions, forming (multi)layered supramolecular nanostructures with controlled thicknesses and composition.[12]

While few examples of cationic organometallic polyelectrolytes exist in the literature, organometallic polyanions have not been described to our knowledge. This paper reports on the synthesis of a water-soluble poly(ferrocenylsilane) polyanion. We aim to employ this polyelectrolyte with cationic poly(ferrocenylsilanes) to form fully organometallic multilayer thin films. Such electroactive multilayer thin films are of potential interest in for example electrode modification, electrocatalysis, and electrochromism.[12] Furthermore, selective deposition of poly(ferrocenylsilane) polyions onto for example hydrophilic/hydrophobically modified substrates would enable the growth of two-dimensionally patterned organometallic multilayers. These patterns can then be transferred into for example silicon or silicon nitride substrates, due to the high plasma etch resistance of poly(ferrocenylsilanes).



Poly(ferrocenyl(3-chloropropyl)methylsilane) (**1**) was used as the starting organometallic main chain, as its chloropropyl moieties in principle allow one to introduce functional groups via nucleophilic substitution reactions. Polymer **1** was readily accessible by transition-metal-catalyzed ring-opening polymerization[1] of the corresponding (3-chloropropyl)methylsilyl[1]ferrocenophane.[10] By means of halogen exchange,[13] **1** was converted quantitatively into its bromopropyl or iodopropyl analogues,[14] which are particularly suitable for functionalization by nucleophilic substitution. Reaction of poly(ferrocenyl(3-iodopropyl)methylsilane) (**2**) with malonic ester enolates such as dimethyl methylmalonate anion or dibenzyl methylmalonate anion smoothly produced the corresponding polyesters with quantitative conversions, but subsequent base-catalyzed saponification to form the desired organometallic polyanion required

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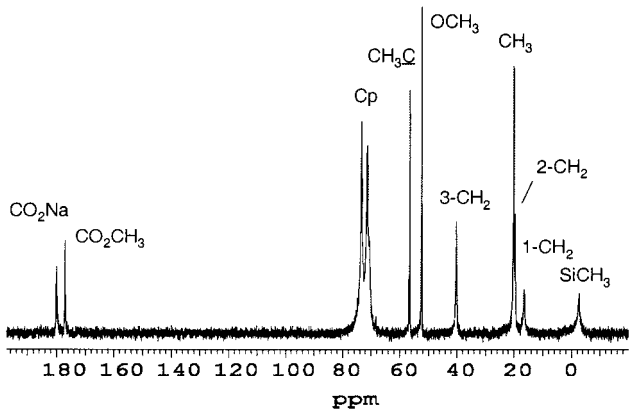

Figure 1. ^{13}C NMR spectrum of the poly(ferrocenylsilane) polyanion **3** in D_2O.

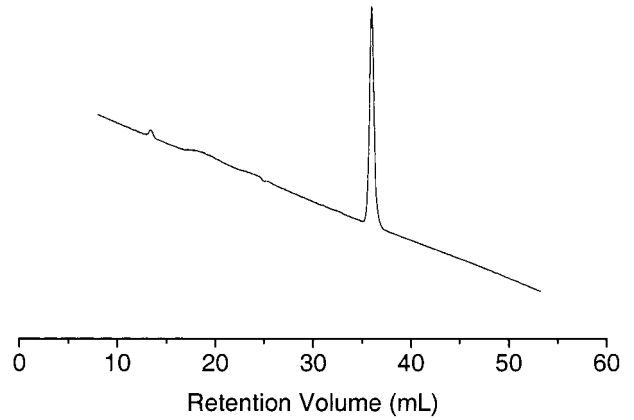

Figure 2. GPC trace of the poly(ferrocenylsilane) polyanion **3** in water.

prolonged reaction times due to the sensitivity of the main chain to strongly acidic or basic conditions. Use of the methyltrimethylsilyl methylmalonate anion,[15] however, enabled us to introduce labile trimethylsilyl ester side groups, which were readily hydrolyzed to carboxylate salts under mild conditions,[16] producing polyanion **3**. The material is highly water-soluble: it could be dissolved to concentrations exceeding 100 mg/mL. It must be noted that the solubility of the polyanion, which is a weak polyelectrolyte, decreases below pH 6.[17]

^1H and ^{13}C NMR spectroscopy supported the high efficiency of the side-group modifications. As an example, the ^{13}C NMR spectrum of **3** is shown in Figure 1. No signals associated with residual iodopropyl moieties could be identified in this spectrum. In addition, elemental analysis of all polymers had excellent agreement between the expected and measured compositions. Polymers **1** and **2** were characterized using gel permeation chromatography (GPC) in THF, using polystyrene standards, to ensure that no molar mass decline had occurred during the halogen exchange reaction. Based on GPC, poly(ferrocenylsilanes) **1** and **2** have a degree of polymerization $DP_n = 80$ and a polydispersity of $M_w/M_n = 1.8-1.9$. GPC measurements on polyanion **3** had to be carried out in water, precluding a direct comparison with its precursors, but the GPC trace (Figure 2) showed a single maximum, indicating that the organometallic main chain had remained intact during deprotection of the silyl ester groups.

Polymer **3** was furthermore studied by viscometry in ultrapure water, in the absence of salt. Values of the reduced viscosity, η_{sp}/C, plotted against polymer concentration C increased strongly with decreasing polymer concentrations, exhibiting a pronounced concave-upward relationship (η_{sp} is the specific viscosity); see Figure 3. This behavior is typical of polyelectrolytes.[18]

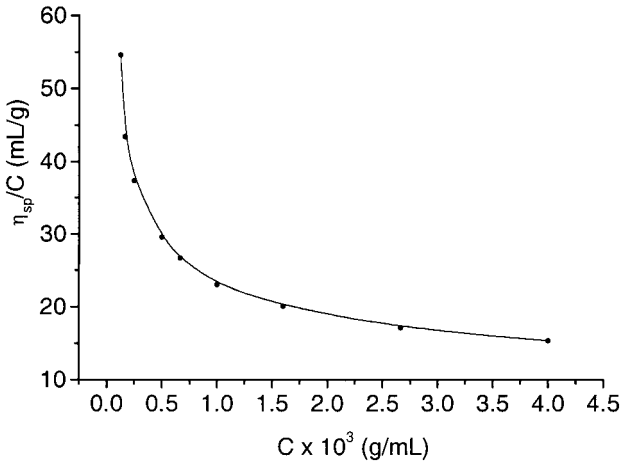

Figure 3. Reduced viscosity η_{sp}/C as a function of the concentration of polyanion **3** in salt-free water.

In summary, a universal route to functionalized poly(ferrocenylsilanes), using nucleophilic substitution reactions, enabled us to produce a water-soluble poly(ferrocenylsilane) polyanion. To our knowledge, no materials belonging to the class of anionic organometallic polyelectrolytes have been reported to date. We are using poly(ferrocenylsilane) polyanions and polycations in the fabrication of all-organometallic multilayer thin films by means of the layer-by-layer deposition process. Such films have potential applications as electroactive interface materials for electrode modifications. When patterned, they are of interest as reactive ion etch barriers in nano- and microlithographic applications.

Acknowledgment. The authors thank the University of Twente for financial support.

References and Notes

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(14) A round-bottomed flask fitted with a reflux condenser was charged with polymer **1** (5.00 g, 16.4 mmol repeat units),[10] NMP (30 mL), NaI (0.3 g, 2.0 mmol), and EtI (15 mL, ca. 50 mmol), and the mixture was stirred at 40 °C. Aliquots of

EtI (2 mL) were added every 48 h. After 144 h, the mixture was precipitated in cold MeOH (300 mL) and dried under vacuum. Yield 6.2 g (95%). ^{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 + 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. GPC (using polystyrene standards in THF): M_w 2.71 × 10^4 g/mol, M_n 1.37 × 10^4 g/mol, M_w/M_n 1.9.

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(16) A solution of methyltrimethylsilyl methylmalonate (0.70 g, 3.43 mmol) in dry THF (5 mL) was added dropwise at −80 °C to LDA (3.2 mmol, prepared from *n*-BuLi and DA in THF) under argon. After stirring for 3 h, the temperature had risen to −50 °C. The solution was frozen and degassed, and the solvents were removed under vacuum. The solid LiCMe-(CO_2Me)(CO_2SiMe_3) was dissolved in dry NMP (2 mL), and a solution of **2** (0.40 g, 1.01 mmol repeat units) in THF (5 mL) was added to the malonate anion. Stirring was continued for 48 h at room temperature under dry nitrogen. The reaction mixture was cooled in ice, a degassed aqueous $NaHCO_3$ solution (1.0 g/10 mL) was added, and THF was evaporated. Polyanion **3** was purified by means of dialysis against Milli-Q water, using Spectra/Por 4 membranes with a cutoff MW of 12 000−14 000 g/mol. Anal. Calcd for $C_{19}H_{23}O_4FeNaSi$: C, 54.04; H, 5.49. Found: C, 54.39; H, 5.64.^{1}H 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); 71.51 + 73.54 (Cp); 177.20 (O=C−OCH_3); 180.12 (O=C−ONa).

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