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Anionic Ring-Opening Oligomerization and Polymerization of Silicon-Bridged [1]Ferrocenophanes: Characterization of Short-Chain Models for Poly(ferrocenylsilane) High Polymers

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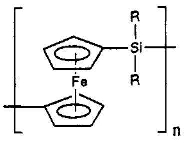
Polymers with skeletal transition-metal atoms are attractive materials as a result of their novel electrical, optical, magnetic, and chemical characteristics.[1,2] We have previously reported the preparation of the first examples of high molecular weight poly(ferrocenylsilanes) **1** via the thermal ring-opening polymerization (ROP) of strained, ring-tilted, silicon-bridged [1]ferrocenophanes such as **2** at elevated temperatures.[3] These polymers display novel electrochemical properties which are indicative that the iron atoms interact with one another, and several show evidence for the formation of ordered structures in the solid state.[4-7] Studies of well-defined short-chain oligomers would be expected to provide additional understanding of the characteristics of these unusual polymers, but such species are often very difficult to prepare and crystallize for X-ray diffraction studies.



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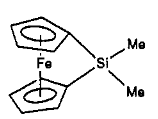

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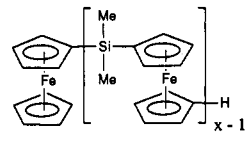

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To develop nonthermal ROP methods for [1]ferrocenophanes which operate under milder conditions, we have explored the reactions of anionic initiators with **2**.[8] In this paper we report studies of the reaction of ferrocenyllithium, FcLi (Fc = Fe(η-C_5H_4)(η-C_5H_5)), with **2**, which yields either oligomeric or polymeric products depending on the mole ratio of the reactants.[9]

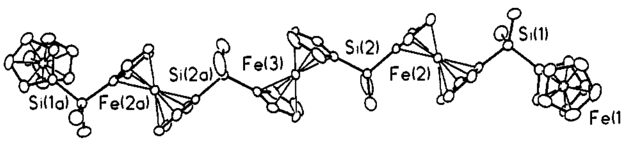

Figure 1. Molecular structure of **3** (x = 5).

Reaction of FcLi[10] with **2** (ca. 0.5–1:1, THF, 10 min, 0 °C) followed by warming to room temperature and a hydrolytic workup yielded a mixture of proton-terminated oligomeric products **3** (x = 2–8). These were each successfully isolated after column chromatography on alumina as amber powders and were characterized by ^{29}Si and ^{1}H NMR and mass spectrometry.[11] Significantly, the correct integration ratio was observed for the resonances arising from the silicon atoms (in the ^{29}Si NMR) and the $SiMe_2$ and the cyclopentadienyl groups (in the ^{1}H NMR) associated with the repeat units at the chain termini compared to those in the chain interior. In addition, the mass spectrum of each oligomer showed peaks assigned to a molecular ion and logical fragmentation products.[11]

We have been able to obtain crystals of the pentamer **3** (x = 5) for X-ray diffraction studies.[12] The molecular structure is shown in Figure 1 and provides intriguing insight into the probable conformations of polymer chains in ordered samples of the high polymer **1** (R = Me). The interior ferrocenylsilane repeat units possess a trans planar, zigzag conformation with the adjacent ferrocenyl groups oriented at ca. 110° relative to one another. Interestingly, the ferrocenyl end groups are twisted in opposite directions perpendicular to the plane of the interior. The sets of two methyl groups at silicon on adjacent repeat units are oriented in opposite directions (ca. 180°) from one another, whereas the iron atoms in the interior are approximately collinear and are separated by 6.913(5) Å.

The oligomers **3** (x = 2–8) also provide excellent models for the high polymer **1** (R = Me) with respect to electrochemical properties.[13] Cyclic voltammograms (CVs) of **1** (R = Me) show

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(1) See, for example: (a) Wright, M. E.; Sigman, M. S. *Macromolecules* **1992**, *25*, 6055. (b) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188. (c) Roesky, H. W.; Lūcke, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 493. (d) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187. (e) Tenhaeff, S. C.; Tyler, D. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1459. (f) Neuse, E. W.; Bednarik, L. *Macromolecules* **1979**, *12*, 187. (g) Sturge, K. C.; Hunter, A. D.; McDonald, R.; Santarsiero, B. D. *Organometallics* **1992**, *11*, 3056. (h) Pollagi, T. P.; Stoner, T. C.; Dallinger, R. F.; Gilbert, T. M.; Hopkins, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 703. (i) Bayer, R.; Pohlmann, T.; Nuyken, O. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 359. (j) Gonsalves, K.; Zhanru, L.; Rausch, M. V. *J. Am. Chem. Soc.* **1984**, *106*, 3862. (k) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926. (l) Nugent, H. M.; Rosenblum, M.; Klemarczyk, P. *J. Am. Chem. Soc.* **1993**, *115*, 3848. (m) Nelson, J. M.; Rengel, H.; Manners, I. *J. Am. Chem. Soc.* **1993**, *115*, 7035.

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(5) (a) Foucher, D. A.; Petersen, R.; Tang, B. Z.; Ziembinski, R.; Coombs, N.; MacDonald, P. M.; Sodhi, R. N. S.; Massey, J.; Vancso, J. G.; Manners, I. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1993**, *34*(1), 328. (b) Manners, I. *J. Inorg. Organomet. Polym.* **1993**, *3*, 185. (c) Foucher, D. A.; Honeyman, C.; Nelson, J. M.; Tang, B. Z.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1709. (d) Manners, I. *Adv. Mater.* **1994**, *6*, 62.

(6) For the work of other groups on poly(ferrocenylsilanes) and related polymers, see: (a) Rosenberg, H. U.S. Patent 3,426,053, 1969. (b) Tanaka, M.; Háyashi, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 334. (c) Nguyen, M. T.; Diaz, A. F.; Dement'ev, V. V.; Pannell, K. H. *Chem. Mater.* **1993**, *5*, 1389.

(7) The morphology of the poly(ferrocenylsilane) **1** (R = Me) is dependent on sample thermal history, and, after (and for some samples without) annealing, a T_m is observed at 122 °C. See refs 5b and 5d.

(8) Anionic ROP is known for a variety of organosilicon rings. See, for example: (a) Cypryk, M.; Gupta, Y.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1991**, *113*, 1046. (b) Sargeant, S. J.; Zhou, S. Q.; Manuel, G.; Weber, W. P. *Macromolecules* **1992**, *25*, 2832. (c) West, R.; Hayase, S.; Iwahara, T. *J. Inorg. Organomet. Polym.* **1991**, *1*, 545. (d) Suzuki, M.; Obayashi, T.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1993**, 717.

(9) Seyferth and co-workers have reported that phosphorus-bridged [1]-ferrocenophane [Fe(η-C_5H_4)$_2$PPh] yields short-chain oligomers H[Fe(η-C_5H_4)$_2$PPh]$_x$Ph (x = 2–5) when treated with [Fe(η-C_5H_4Li)(η-$C_5H_4PPh_2$)]. However, ROP was not detected. See: Withers, H. P.; Seyferth, D.; Fellmann, J. D.; Garrou, P.; Martin, S. *Organometallics* **1982**, *1*, 1283.

(10) FcLi was generated in situ via the reaction of ferrocene with 0.75 equiv of *t*-BuLi in THF over 10 min at 0 °C. See: Rebiere, F.; Samuel, O.; Kagan, H. B. *Tetrahedron Lett.* **1990**, *31*, 3121.

(11) ^{29}Si and ^{1}H NMR and mass spectral data are given in the supplementary material.

(12) Crystal structure data for **3** (x = 5): crystals from cyclohexane over 5 days, formula = $C_{58}H_{66}Fe_5Si_4$, FW = 1154.7, triclinic, space group $P\bar{1}$, a = 11.764(4), b = 11.850(2), and c = 12.514(2) Å, α = 94.85(2)°, β = 114.15(2)°, γ = 117.66(2)°, V = 1326.1(8) Å^3, Z = 1, d = 1.446 g cm^{-3}, T = 294 K. Anisotropic refinement of all non-hydrogen (H-riding model refined with isotropic thermal parameters, 305 variables) atoms using 3268 unique reflections with $F > 6.0\sigma(F)$) from 4353 unique data (5723 collected) gave R = 0.0466, R_w = 0.0621.

(13) Cyclic voltammetric data for **3** (x = 2–8), 0.5 g L^{-1} in CH_2Cl_2/CH_3CN (1:1) relative to ferrocene $E_{1/2}$ = 0.00 V using 0.1 M [NBu_4][PF_6] as supporting electrolyte. For **3** (x = 2): $E_{1/2}$ = –0.01, 0.14 V (ratio 1:1). For **3** (x = 3): $E_{1/2}$ = –0.03, 0.23 V (2:1). For **3** (x = 4): $E_{1/2}$ = –0.01, 0.14, 0.26 V (2:1:1). For **3** (x = 5): $E_{1/2}$ = 0.01, 0.24 (3:2). For **3** (x = 6): $E_{1/2}$ = –0.01, 0.14, 0.25 V (3:1:2). For **3** (x = 7): $E_{1/2}$ = –0.01, 0.23 (4:3). For **3** (x = 8): $E_{1/2}$ = –0.01, 0.13, 0.23 V (4:1:3). The redox couples were reversible (as judged by equal cathodic and anodic peak currents) over the range of scan rates studied (25–1000 mV s^{-1}). The stoichiometries of the redox processes are given by the relative areas of the waves which were established by integration. For details of the electrochemical equipment, see ref 5c.

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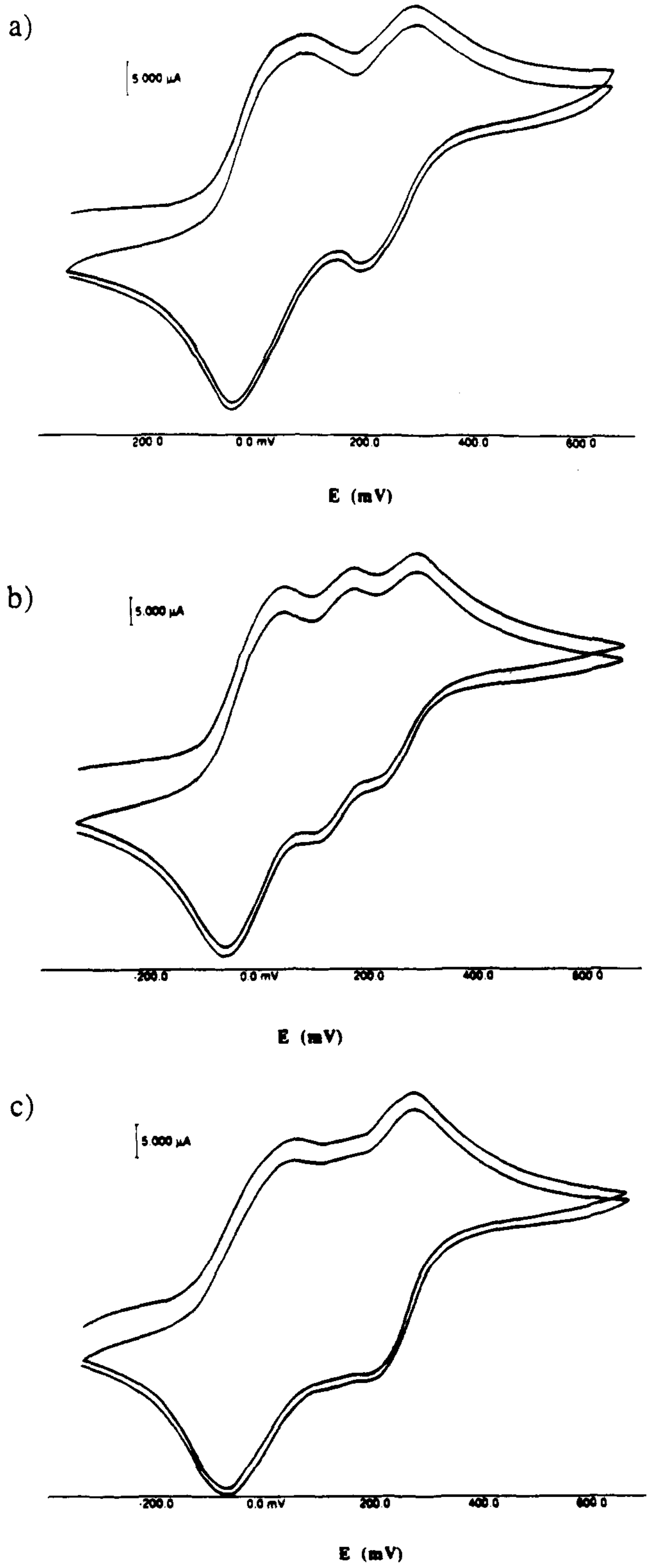

Figure 2. Cyclic voltammograms of **3** (a) x = 5, (b) x = 4, and (c) x = 8 in CH_2Cl_2/CH_3CN at 250 mV s^{-1}.

two oxidation waves separated by ca. 0.2 V, which has been attributed to the presence of cooperative interactions between the iron centers.[3,5] Thus, the first oxidation is believed to occur at alternating iron sites, and the subsequent oxidation at higher potentials involves the sites in between.[14] The electrochemistry of the oligomers **3** (x = 2–8) is fully consistent with this picture but differs significantly depending on whether the number of repeat units is odd or even. Considering **3** (x = odd) first, the CV of **3** (x = 3) showed two reversible oxidation waves of relative intensity 2:1, which are assigned to oxidation of the two ferrocenyl end groups followed by oxidation at the interior site. Under the same conditions, **3** (x = 5) showed two waves with a ratio of 3:2 assigned to oxidation of the iron atoms of two end groups and the middle repeat unit at the first potential and subsequent oxidation of the two remaining ferrocenyl groups in between at the second (Figure 2a). The "odd" oligomer **3** (x = 7) possessed a similar two-wave CV, and the ratio of the waves was 4:3 as expected on the basis of analogous arguments. The CV of the "even" oligomer **3** (x = 2) also showed two waves due to oxidation of one iron site and then the other as previously reported.[15] However, for **3** (x = 4), the initial oxidation of two alternating iron sites yields an oligomer which has two remaining sites which are inequivalent. This leads to three waves for **3** (x = 4) in a 2:1:1 ratio (Figure 2b). For similar reasons, three waves are detected for **3** (x = 6) in a ratio 3:1:2. As an even-numbered oligomer chain increases in length, the central wave (due to the end group next to a single oxidized ferrocene unit) decreases in intensity relative to the other two. In the case of **3** (x = 8), three waves of relative intensity 4:1:3 would be expected. However, the central wave is already virtually unresolvable at this chain length (Figure 2c). Clearly, in view of the electrochemical properties of both the odd and even oligomers, an infinite chain would be expected to possess two waves of equal intensity, which is observed for the high polymer **1** (R = Me).

The formation of higher molecular weight polymers from the reaction of FcLi with **2** might be anticipated at low initiator concentrations. Indeed, reaction of FcLi with **2** in a 1:10 mole ratio (THF, 1 h) followed by hydrolytic workup yielded a poly(ferrocenylsilane) as an amber powder with M_w = 9500 and M_n = 8000. This corresponds to the approximate formulation of **3** (x = ca. 29). These results indicate that polymers (albeit of moderate molecular weight) as well as oligomers can be generated by anionic ROP of **2**.[16] Further work is directed at investigating other properties of the oligomers in detail and the ROP of **2** using alternative anion-based initiator systems.

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Supplementary Material Available: ^1H, ^{29}Si, and mass spectral data for **3** (x = 2–8); experimental details for the crystal structure determination; tables of atomic coordinates, anisotropic thermal parameters, bond angles, and bond lengths for **3** (19 pages); listing of observed and calculated structure factors for **3** (x = 5) (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) Rauchfuss and Brandt have reported that polyferrocenylene persulfides, $[Fe(\eta^5\text{-}C_5H_3Bu)_2S_2]_n$, possess two reversible oxidation waves. The authors have proposed that the first oxidation occurs at alternating iron sites along the polymer chain; see ref 1k.

(15) Bocarsly, A. B.; Walton, E. G.; Bradley, M. G.; Wrighton, M. S. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *100*, 283.

(16) Preliminary studies indicate that ROP of **2** can be achieved using a variety of organolithium initiators including *n*-BuLi.