J. Am. Chem. Soc. 1994, 116, 12121−12122

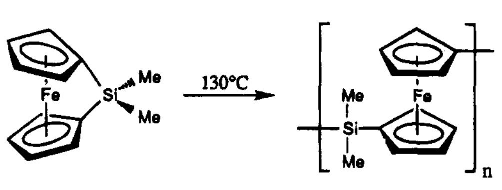
Living Anionic Ring-Opening Polymerization of Silicon-Bridged [1]Ferrocenophanes: Synthesis and Characterization of Poly(ferrocenylsilane)−Polysiloxane Block Copolymers

Ron Rulkens, Yizeng Ni, and Ian Manners*

Department of Chemistry, University of Toronto
80 St. George Street, Toronto, Ontario M5S 1A1, Canada

Received September 12, 1994

Soluble, high molecular weight polymers with skeletal transition metal atoms are of considerable interest because of their novel properties and potential applications.[1–3] However, in general, synthetic routes to these materials are poorly developed, and, in contrast to the situation with organic polymers,[4] means of controlling factors such as chain length and preparing complex architectures (e.g., multiblock structures) are virtually nonexistent. In 1992, we reported the discovery that strained, ring-tilted, silicon-bridged [1]ferrocenophanes such as **1** undergo thermal ring-opening polymerization (ROP) to yield high molecular weight poly(ferrocenylsilanes) (e.g., **2**).[5]



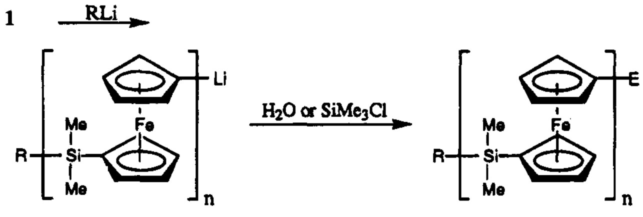
1 **2**

Subsequent papers have detailed the interesting electrochemical, preceramic, morphological, and (when oxidized) magnetic properties that these polymers possess[6–9] and have also described the extension of the thermal ROP route to other strained [1]- and [2]metallocenophanes.[7,10] We have also reported that **1** undergoes anionic ring-opening oligomerization when treated with 0.5−1.0 equiv of ferrocenyllithium, FcLi (Fc = $Fe(\eta\text{-}C_5H_4)(\eta\text{-}C_5H_5)$), in THF to afford linear oligo(ferrocenylsilanes) which function as models for the corresponding high polymers with respect to conformational and electrochemical properties.[8] We also briefly noted that when lower concentrations of initiator were used, poly(ferrocenylsilanes) were formed.[8,11] In this paper we report the results of our very recent studies which have demonstrated that the living anionic ROP of **1** can be achieved. This permits molecular weight control, end-group control, and the formation of novel transition metal-containing block copolymers.

Table 1. Synthesis of Poly(ferrocenylsilanes) **3** (E = H) via the Living Anionic ROP of **1**[a]

run	initiator RLi	mole ratio RLi:1	M_n calcd	M_n found[b]	M_w/M_n[b]
1	FcLi	1:20	4.9×10^3	4.0×10^3	1.02
2	FcLi	1:35	8.6×10^3	7.9×10^3	1.11
3	FcLi	1:50	1.2×10^4	1.3×10^4	1.26
4	PhLi	1:52	1.3×10^4	1.8×10^4	1.25
5	PhLi	1:91	2.2×10^4	3.4×10^4	1.19
6	*n*-BuLi	1:47	1.1×10^4	1.2×10^4	1.15
7	*n*-BuLi	1:99	2.4×10^4	2.3×10^4	1.14
8	**3** from run 6	1:48	2.3×10^4	2.7×10^4	1.15
9	PhLi	1:50	1.2×10^4	1.6×10^4	1.20
10	**3** from run 9	1:57	2.6×10^4	2.7×10^4	1.47

[a] Polymerizations were run in dry THF at 25 °C under N_2. The polymers **4** (E = H) were isolated after termination via the addition of H_2O and precipitation into methanol. [b] See footnote 12.



3 **4**

R = Fc, Ph, or *n*Bu E = H or $SiMe_3$

Reaction of **1** with FcLi, PhLi, or *n*-BuLi in THF at 25 °C for 15 min followed by quenching of the living polymer **3** with either H_2O or $SiMe_3Cl$ yielded the H- or $SiMe_3$-capped poly(ferrocenylsilanes) **4** (E = H or $SiMe_3$). The molecular weights of **4** could be controlled from $M_n = 4.0 \times 10^3$−3.4×10^4 with narrow polydispersities ($M_w/M_n = 1.02$−1.26) by varying the initiator:monomer ratio from 1:20 to 1:99. Representative examples of our experiments are documented in Table 1.[12,13] The polymer products **4** gave ^{29}Si, ^1H, and ^{13}C NMR spectra

---

[1] See, for example: (a) Dembek, A. A.; Fagan, P. J.; Marsi, M. *Macromolecules* **1993**, *26*, 2992. (b) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188. (c) Allcock, H. R.; Dodge, J. A.; Manners, I.; Riding, G. H. *J. Am. Chem. Soc.* **1991**, *113*, 9596. (d) Wright, M. E.; Sigman, M. S. *Macromolecules* **1992**, *25*, 6055. (e) Roesky, H. W.; Lücke, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 493. (f) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187. (g) Tenhaeff, S. C.; Tyler, D. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1459. (h) Sturge, K. C.; Hunter, A. D.; McDonald, R.; Santarsiero, B. D. *Organometallics* **1992**, *11*, 3056. (i) Bayer, R.; Pöhlmann, T.; Nuyken, O. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 359.

[2] (a) Patterson, W. J.; McManus, S. P.; Pittman, C. U. *J. Polym. Sci. (A)* **1974**, *12*, 837. (b) Neuse, E. W.; Bednarik, L. *Macromolecules* **1979**, *12*, 187. (c) Gonsalves, K.; Zhanru, L.; Rausch, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3862. (d) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926.

[3] (a) Sheats, J. E.; Carraher, C. E.; Pittman, C. U. *Metal Containing Polymer Systems*; Plenum: New York, 1985. (b) Allcock, H. R. *Adv. Mater.* **1994**, *6*, 106. (c) Rosenblum, M. *Adv. Mater.* **1994**, *6*, 159.

[4] (a) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907. (b) Matyjaszewski, K. *Makromol. Chem. Macromol. Symp.* **1992**, *54/55*, 51.

[5] Foucher, D. A.; Tang, B. Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246.

[6] (a) Foucher, D. A.; Ziembinski, R.; Tang, B. Z.; Macdonald, P. M.; Massey, J.; Jaeger, R.; Vancso, G. J.; Manners, I. *Macromolecules* **1993**, *26*, 2878. (b) Foucher, D. A.; Honeyman, C.; Nelson, J. M.; Tang, B. Z.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1709. (c) Manners, I. *J. Inorg. Organomet. Polym.* **1993**, *3*, 185. (d) Finckh, W.; Tang, B. Z.; Foucher, D. A.; Zamble, D. B.; Ziembinski, R.; Lough, A.; Manners, I. *Organometallics* **1993**, *12*, 823. (e) Foucher, D. A.; Ziembinski, R.; Petersen, R.; Pudelski, J.; Edwards, M.; Ni, Y.; Massey, J.; Jaeger, R.; Vancso, G. J.; Manners, I. *Macromolecules* **1994**, *27*, 3992.

[7] Manners, I. *Adv. Mater.* **1994**, *6*, 68.

[8] Rulkens, R.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **1994**, *116*, 797.

[9] For the work of other groups on poly(ferrocenylsilanes) and related polymers, see: (a) H. Rosenberg, U.S. Patent 3,426,053, 1969. (b) Tanaka, M.; Hagashi, 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. (d) Hmyene, M.; Yasser, A.; Escorne, M.; Percheron-Guegan, A.; Garnier, F. *Adv. Mater.* **1994**, *6*, 564.

[10] (a) Nelson, J. M.; Rengel, H.; Manners, I. *J. Am. Chem. Soc.* **1993**, *115*, 7035. (b) Nelson, J. M.; Lough, A. J.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 989.

[11] Anionically induced ROP has been previously established for a range 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.

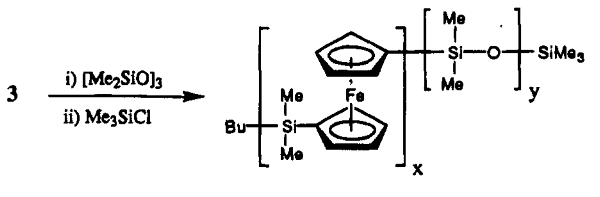
[12] Polymer molecular weights were determined by gel permeation chromatography in THF using polystyrene standards for column calibration.

[13] *n*-BuLi appeared to be the most successful initiator for the living anionic ROP of **1**. However, attempts to produce polymers with $M_n \gg$ ca. 30 000 lead to a significant broadening of the molecular weight distribution, probably due to chain transfer reactions. For example, reaction of BuLi with **1** in a 1:200 mole ratio followed by hydrolytic workup yielded a polymer **4** (E = H) with $M_w = 7.4 \times 10^4$, $M_n = 4.9 \times 10^4$, and $M_w/M_n = 1.51$.

0002-7863/94/1516-12121$04.50/0

which were identical to those previously reported[5] for **2** formed by thermal ROP except that for the lower molecular weight products, end groups were detected.[14] Treatment of the intermediate polymer **3** with additional monomer **1** before quenching with H_2O led to polymers **4** which showed the expected increase in molecular weight characteristic of a living process (Table 1, runs 8 and 10).[13]

In order to demonstrate that the living anionic ROP of **1** can be exploited to prepare novel, well-defined polymer structures, we have synthesized poly(ferrocenylsilane)–poly(dimethylsiloxane) block copolymers **5**.[15] Thus, the living polymer **3** (R = *n*-Bu) was reacted (THF, 25 °C) with the strained cyclotrisiloxane $[Me_2SiO]_3$ for 20 min. Following the addition of Me_3SiCl, the yellow copolymers **5a** or **5b** were isolated by precipitation into methanol.[16] The block copolymers **5a** and **5b**, which in contrast to the poly(ferrocenylsilane) **2** are soluble in hexanes,[17] were structurally characterized by ^1H, ^{13}C, and ^{29}Si NMR and by elemental analysis.[18] The ^1H NMR spectrum of **5a** and **5b** (Figure 1) showed resonances at 4.10, 4.26, and 0.54 ppm which were assigned to the ferrocenyldimethylsilane block and a silicon methyl resonance at 0.28 ppm which was assigned to the dimethylsiloxane block. Significantly, the ^{29}Si NMR spectra of these copolymers showed not only two very intense resonances for the poly(ferrocenylsilane) (at −6.4 ppm) and the polysiloxane segments (at −21.4 ppm) but, in addition, small peaks arising from groups located at the start ($BuSiMe_2$) and end ($OSiMe_3$) of the polymer chains together with crossover groups ($FcSiMe_2O$) between the ferrocenylsilane and polysiloxane segments. The molecular weights of the block copolymers **5a** and **5b** were estimated to be $M_n = 7.7 \times 10^3$, $M_w/M_n = 1.15$ and $M_n = 2.1 \times 10^4$, $M_w/M_n = 1.13$, respectively, and analytical data were consistent with the assigned structures.



5

a x = 20, y = 40
b x = 50, y = 95

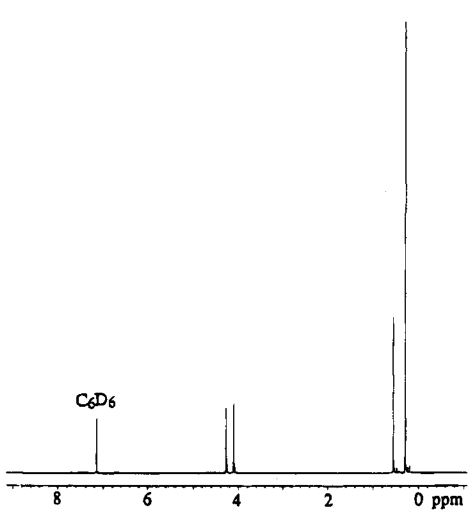


Figure 1. 400 MHz ^1H NMR spectrum of the block copolymer **5b** in C_6D_6.

These results demonstrate that the living anionic polymerization of **1** should allow access to a variety of transition metal-containing polymers with controlled structures and architectures.[4] Work aimed at the further development of this new area is in progress.

Acknowledgment. We thank the Institute for Chemical Science and Technology (ICST) for financial support of this work. We also acknowledge the University of Toronto for a Simcoe Fellowship for R.R. and a University of Toronto Open Fellowship for Y.N. In addition, I.M. is grateful to the Alfred P. Sloan Foundation for a Research Fellowship (1994–96).

Supplementary Material Available: Representative experimental procedures and ^{29}Si NMR spectra of a low molecular weight poly(ferrocenylsilane) **4** (E = $SiMe_3$) and the block copolymer **5b** (4 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.

---

(14) For low molecular weight, FcLi-initiated, $SiMe_3Cl$-capped species, ^{29}Si NMR resonances at −3.1 and −6.6 ppm were assigned to the terminal $SiMe_3$ and $FcSiMe_2$ groups, respectively (see supplementary material).

(15) Polymers containing ferrocene and siloxane units together with rigid organic spacers in the main chain have been previously prepared by Pittmann et al. by a condensation route: see ref 2a.

(16) For **5a**: mole ratio of BuLi:**1**:$[Me_2SiO]_3$ = 1:20:20. For **5b**: mole ratio of BuLi:**1**:$[Me_2SiO]_3$ = 1:50:50.

(17) A blend of the poly(ferrocenylsilane) **2** and poly(dimethylsiloxane) could be readily separated by precipitation from THF into hexanes, whereby the latter remained in solution.

(18) NMR data (δ, ppm) for copolymers **5a** and **5b**: ^{29}Si NMR (79.8 MHz, C_6D_6) −21.4 ($[Me_2\mathit{Si}O]_y$), −6.4 ($[(\eta\text{-}C_5H_4)_2Fe\mathit{Si}Me_2]_x$), −1.9 ($BuMe_2\mathit{Si}$), 0.7 ($(\eta\text{-}C_5H_4)_2Fe\mathit{Si}Me_2O$), 7.6 ($O\mathit{Si}Me_3$); ^1H NMR (400 MHz, C_6D_6) 0.28 ($[\mathit{Me}_2SiO]_y$), 0.54 ($[(\eta\text{-}C_5H_4)_2FeSi\mathit{Me}_2]_x$), 4.10, 4.26 ($[(\eta\text{-}C_5\mathit{H}_4)_2FeSiMe_2]_x$); ^{13}C NMR (50.3 MHz, C_6D_6) −0.5 ($[\mathit{Me}_2SiO]_y$), 1.4 ($[(\eta\text{-}C_5H_4)_2FeSi\mathit{Me}_2]_x$), 71.8, 73.7 ($[(\eta\text{-}\mathit{C}_5H_4)_2FeSiMe_2]_x$). ^1H NMR integration gave for **5a**, $x = 20$, $y = 40$, and for **5b**, $x = 50$, $y = 95$. Satisfactory C and H elemental analysis. GPC analysis (in THF vs polystyrene) for **5a** gave $M_n = 7.7 \times 10^3$, $M_w/M_n = 1.15$ and for **5b**, $M_n = 2.1 \times 10^4$, $M_w/M_n = 1.13$.