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Transition Metal Catalyzed Ring-Opening Polymerization (ROP) of Silicon-Bridged [1]Ferrocenophanes: Facile Molecular Weight Control and the Remarkably Convenient Synthesis of Poly(ferrocenes) with Regioregular, Comb, Star, and Block Architectures

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Abstract: Transition metal (Pt^{II} or Pt^0) catalyzed ring-opening polymerization (ROP) of silicon-bridged [1]-ferrocenophanes has been found to permit simple and convenient control of the regiostructure, molecular weight, and architecture of poly(ferrocenes). Whereas thermal ROP of the unsymmetrical silicon-bridged [1]-ferrocenophane $Fe(\eta\text{-}C_5H_4)(\eta\text{-}C_5Me_4)SiMe_2$ (**3**) at 150 °C proceeds via a nonselective cleavage of the $Si-Cp^H$ and $Si-Cp^{Me}$ bonds ($Cp^H = \eta\text{-}C_5H_4$, $Cp^{Me} = \eta\text{-}C_5Me_4$) to yield an amorphous, regioirregular poly(ferrocenylsilane), the Pt-catalyzed ROP of **3** in solution at 25 °C involves selective cleavage of the $Si-Cp^H$ bond to afford a crystalline poly(ferrocenylsilane) **5** with a regioregular microstructure. Regioselective ROP of **3** was also detected during the Pt-catalyzed copolymerization of **3** with benzosilacyclobutane (**7**). The presence of Et_3SiH during the Pt-catalyzed ROP of the [1]silaferrocenophane $Fe(\eta\text{-}C_5H_4)_2SiMe_2$ (**1**) permits molecular weight control and the formation of poly(ferrocenylsilanes) capped by Et_3Si and $Si-H$ groups, $Et_3Si-[Fe(\eta\text{-}C_5H_4)_2SiMe_2]_n-H$ (**11**) with $M_n = 2000-45\,000$ and PDIs of 1.1−2.3. The use of siloxane-based materials with Si−H groups such as the random copolymer $[MeHSiO\text{-}/\text{-}Me_2SiO]_n$ or the cyclotetrasiloxane $[MeHSiO]_4$ in place of Et_3SiH allowed the preparation of comb-shaped polysiloxane-poly(ferrocenylsilane) graft copolymers (**12**) and star-shaped polymers (**16**) with a cyclic siloxane core, respectively. In addition, the use of Si−H terminated poly(dimethylsiloxane)s in place of Et_3SiH provided facile access to poly(ferrocene)-poly(siloxane)-poly(ferrocene) triblock copolymers (**18**).

Introduction

Polymers containing skeletal transition metal atoms are attracting increasing attention because of their physical properties and potential applications.[1−3] However, in general, synthetic routes to high molecular weight examples of these materials are poorly developed.[3] This is particularly the case for polymers with well-defined architectures (e.g. graft or multiblock structures), although in the past few years access to interesting metal-containing dendritic structures using iterative synthetic procedures has been achieved.[4−7] The discovery that strained, ring-tilted metallocenophanes such as the silicon-bridged [1]ferrocenophane (**1**) undergo thermal ring-opening polymerization (ROP) to afford high molecular weight poly(metallocenes), such as the poly(ferrocenylsilane) (**2**), has provided access to a range of new transition metal-based polymers with intriguing properties.[8] Recent work in this area has focused on the extension of this ROP route to other strained metallocenophanes[9−12] as well as on detailed studies of the physical properties of the resulting ring-opened polymeric materials.[9,13−19] The morphological

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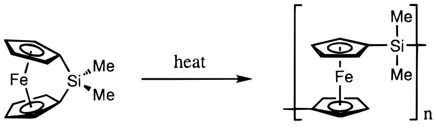
characteristics and the unusual electrochemical behavior of these polymers, which is a consequence of intrachain spacer-mediated metal−metal interactions, have attracted particular attention.[17,20−22] In addition, oxidized polymers have been investigated because of their cooperative magnetic properties,[19,23] and recently, pyrolysis to magnetic nanostructures[13] and the preparation of liquid crystalline poly(ferrocenylsilanes) have been reported.[24]



1 **2**

We have also previously reported that the silicon-bridged [1]-ferrocenophane **1** undergoes living anionic ROP under mild conditions (in solution at room temperature) in the presence of anionic initiators.[25,26] This has allowed access to polymers with controlled chain length and architectures, such as block copolymers. The latter are of interest with respect to the formation of phase-separated redox active domains in the solid state and novel micellar aggregates in solution.[26,27] However, a significant practical drawback with anionic ROP lies in the fact that very stringent experimental conditions involving scrupulously pure monomer and solvents are required for this method to be successful. With this in mind, the recent discovery that a variety of Rh^I, Pt^0, Pd^0, Pd^{II}, and Pt^{II} complexes will conveniently catalyze the ROP of [1]ferrocenophanes in solution at room temperature to yield high molecular weight poly(ferrocenes) is of particular significance.[28−30] However, apart from the convenient formation of random copolymers via the transition metal catalyzed ROP of **1** with other [1]ferrocenophanes or cyclic carbosilanes,[29,31,32] the use of transition metal catalyzed ROP in the controlled synthesis of poly(metallocenes) is unexplored. As a follow up to our communication,[33] we now report full details on our studies that have shown that transition metal catalyzed ROP of silicon-bridged [1]ferrocenophanes permits considerable control over the architecture of the resulting poly(ferrocenylsilanes) under experimentally convenient conditions.

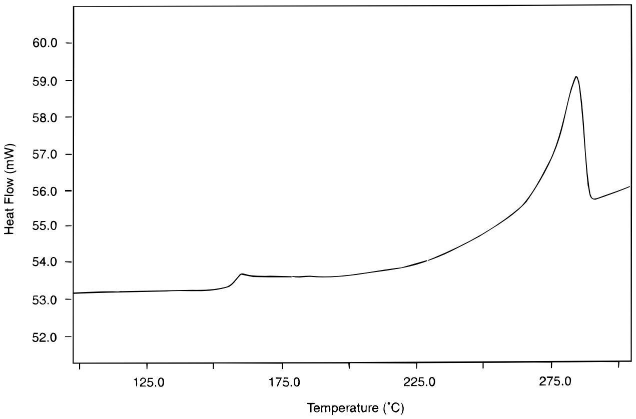
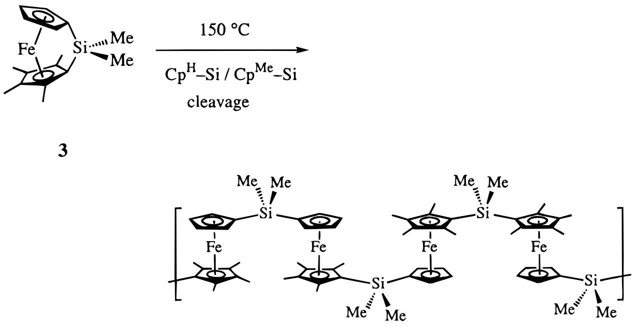


Figure 1. DSC trace of polymer **5**.

Results and Discussion

1. Transition Metal Catalyzed ROP of the Unsymmetrical [1]Ferrocenophane $Fe(\eta\text{-}C_5H_4)(\eta\text{-}C_5Me_4)SiMe_2$ (3). Synthesis of Regioregular Poly(ferrocenylsilanes). We have previously shown that the thermal ROP of **3** proceeds via a nonselective cleavage of the $Si-Cp^H$ and $Si-Cp^{Me}$ bonds.[34,35] The resulting polymeric product (**4**), which is completely soluble in THF, contains three different silicon environments ($Cp^H-Si-Cp^H$, $Cp^H-Si-Cp^{Me}$, and $Cp^{Me}-Si-Cp^{Me}$) but only a single iron environment ($Cp^H-Fe-Cp^{Me}$). Consistent with the lack of regioregularity, samples of poly(ferrocenylsilane) **4** are amorphous.



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4

(a) Transition Metal Catalyzed ROP of 3: Synthesis of the Regioregular Poly(ferrocenylsilane) 5. In contrast to the thermal ROP of **3**, the transition metal catalyzed ROP of **3** with $PtCl_2$ (ca. 1 mol %) in toluene yielded an insoluble orange precipitate. All attempts to dissolve the material in different organic solvents such as CH_2Cl_2, benzene, aniline, or DMF were unsuccessful, even at elevated temperatures. The new insoluble polymer **5** was analytically identical to **4** but was found to be crystalline as indicated by the presence of a melt transition (T_m = 285 °C) in the DSC trace (Figure 1). The wide-angle X-ray scattering pattern of **5** was also consistent with the presence of crystallinity and showed several sharp peaks superimposed on an amorphous halo (Figure 2). The most intense peak was found at a 2θ angle of 12.06° and corresponds to an average d spacing

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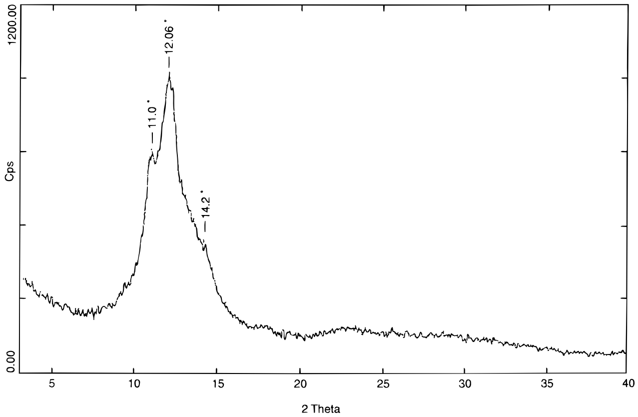


Figure 2. Wide angle X-ray scattering pattern of polymer **5**.

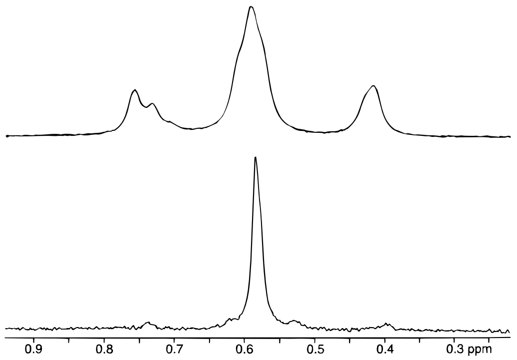


Figure 3. Expansion of ^{1}H NMR (200 MHz, CDCl$_3$) spectrum in the Si−Me region for polymer **4** (top) and soluble fraction of polymer **5** (bottom).

of ca. 7.3 Å. This value is similar to that obtained for the analogous thermally ring-opened polymer **4** ($2\theta = 12.26°$, d spacing = 7.2 Å), but in the latter case the peak is much less intense and is much broader. These results are consistent with the presence of a more regular microstructure in **5** than in the amorphous poly(ferrocenylsilane) **4**. Analysis of the small quantity (ca. 10%) of THF-soluble extract by GPC revealed this fraction to be of low molecular weight (M_n = 1,100, PDI = 2.02). The ^{1}H NMR (CDCl$_3$) spectrum of the soluble extract revealed only one signal corresponding to the methyl substituents at silicon (at 0.59 ppm), whereas the ^{1}H NMR spectrum of the soluble polymer **4** obtained by thermal ROP revealed three resonances (at 0.38, 0.59, and 0.81 ppm) in a 1:2:1 ratio (Figure 3).[36] Taking into account the observation that the permethylated silicon-bridged [1]ferrocenophane Fe(η-C$_5$Me$_4$)$_2$-SiMe$_2$ was unreactive toward Pt ROP catalysts, these results are consistent with selective Si−Cp^H bond cleavage in **3** to yield a regioregular poly(ferrocenylsilane) **5**.

As the majority of **5** was insoluble, CP-MAS ^{13}C and ^{29}Si NMR spectra were recorded to further substantiate the proposed structure. These data, although consistent with the assigned structure, were unsuccessful in distinguishing **5** from **4** as the solid-state NMR techniques did not provide sufficient spectral resolution. For example, the ^{29}Si NMR spectra of both **5** and **4** possessed a single broad singlet resonance despite the fact that the solution spectrum of the latter consisted of three peaks. Pyrolysis mass spectrometry analysis was carried out on a sample of **5** which was heated from 25 °C to 500 °C. Ion fragments were observed with intense peaks at m/z = 299, 596, 894, and 1192 corresponding to oligomers [Fe(η-C$_5$H$_4$)(η-C$_5$-Me$_4$)SiMe$_2$]$_x$ where x = 1−4. Nevertheless, distinction of **5** from **4** was once again unsuccessful as a similar fragmentation pattern was obtained for **4**. Thermogravimetric analysis (TGA) provided information on the thermal stabilities of **5** and **4** to weight loss (heating rate of 10 °C/min) and revealed some differences. Although the onset of weight loss for each material was similar (temperatures for 10% weight loss T_{10} = 370 °C for **5** and 380 °C for **4**) and the ceramic yields at 900 °C nearly identical (ca. 40%), it was found that polymer **5** decomposed more slowly in the 400−750 °C region than did polymer **4**. For example, the temperature for 50% weight loss, T_{50}, was 710 °C for **5**, whereas the value for **4** was 445 °C (Figure 4). The more rapid weight loss for the regioirregular polymer **4** might be attributed to the presence of more sterically encumbered, and hence less thermally stable, Cp^{Me}−Si−Cp^{Me} linkages which are absent in the regioregular analogue **5**. The glass transition temperature for **5** detected by DSC (158 °C) (Figure 1) was also found to be significantly higher than that found for the corresponding polymer **4** (T_g = 116 °C). A possible explanation arises from the fact that **5** possesses a more regular backbone arrangement than **4** and may therefore possess less free volume and more restricted skeletal conformational motions.[37]

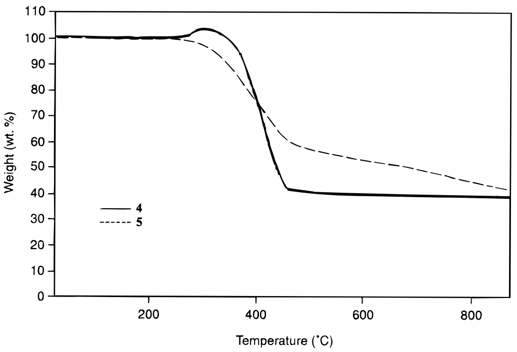
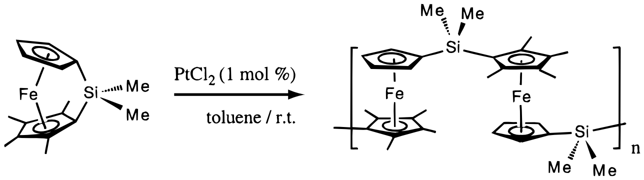


Figure 4. TGA trace of the regioirregular poly(ferrocenylsilane) **4** (amorphous) and the regioregular polymer **5** (crystalline).



3 **5**

(b) Transition Metal Catalyzed Copolymerization of 3 with Silacyclobutanes: Synthesis of Random Copolymers with Regioregular Ferrocenylsilane Segments. To provide further evidence for the regioselective ROP of **3** using transition metal catalysts we attempted to form a more soluble polymer which could be more easily characterized. We have previously shown that the [1]ferrocenophane **1** undergoes Pt-catalyzed copolymerization with silacyclobutanes.[32] We therefore investigated the copolymerization of **3** with the disilacyclobutane **6** and the benzosilacyclobutane **7**. In addition, we hoped that the study of the copolymerization reaction of **3** and **7** might provide further support for the selective Si−Cp^H bond cleavage believed to be operating in the transition metal catalyzed ROP of **3**. As Si−Ar bond cleavage has been established for the ROP of **7** we reasoned that if the ROP of **3** proceeded through the cleavage

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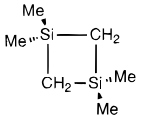
[36] The random cleavage of Si−Cp^{Me} and Si−Cp^H bonds results in the statistical distribution of bridging Si environments in **4**. See refs 34 and 35.

[37] Young, R. J.; Lovell, P. A. In *Introduction to Polymers*; Chapman and Hall: New York, 1992; p 294.

of the Si−Cp^H bond, peaks for crossover regions corresponding to Cp^{Me}−Si−Ar and Cp^H−Si−CH_2 environments should be detected by ^{29}Si NMR. In addition, no resonances attributable to Cp^H−Si−Ar or Cp^{Me}−Si−CH_2 environments would be expected. In the case of Si−Cp^{Me} cleavage the opposite situation would be anticipated.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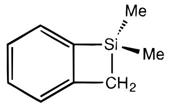
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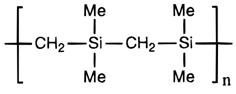
i. Attempted Copolymerizations of 3 with the Disilacyclobutane 6. Due to the marked difference in polymerization rates for the ferrocenophane **3** and the disilacyclobutane **6**, it proved impossible to obtain a copolymer in which both are incorporated in the same proportions as the initial monomer ratio. Thus, as the ferrocenophane **3** polymerizes faster than the carbosilane **6**, a mixture of these two monomers in a 1:2 ratio in the presence of $PtCl_2$ (1 mol %) gave insoluble polymer **5** as an orange precipitate in 80% yield (based on **3**). The ^{1}H NMR spectrum of the polymeric material isolated from the filtrate showed peaks corresponding to poly(carbosilane) and very small peaks attributed to poly(ferrocenylsilane) fragments. However, the GPC trace of this material revealed a broad bimodal molecular weight distribution. When the ratio of **3** to **6** was increased to 1:15, precipitation of **5** was not observed. ^{1}H NMR analysis of the resulting material confirmed the presence of repeat units derived from each monomer; however, the GPC trace once again revealed a bimodal molecular weight distribution. We believe that the most likely explanation for the bimodal molecular weight distribution involves the formation of a mixture of poly(carbosilane) homopolymer **8** (large GPC peak) and a poly(carbosilane-ferrocenylsilane) copolymer **9** (small GPC peak). It is likely that the latter forms initially, and, once **3** is completely consumed, this is followed by homopolymerization of **6** to **8**.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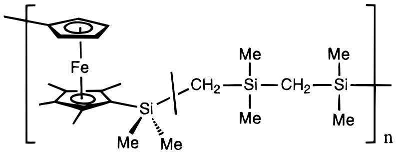
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ii. Copolymerization of 3 with the Benzosilacyclobutane 7. In contrast, in the presence of $PtCl_2$ or Pt(1,5-cod)$_2$ (ca. 1 mol %) a 1:1 mole ratio of **3** and the benzosilacyclobutane **7** afforded a pale orange, toluene-, and THF-soluble poly(ferrocenylsilane)-poly(carbosilane) random copolymer (**10**) which possessed a monomodal molecular weight distribution ($M_n = 2.4 \times 10^4$, PDI = 2.3). The ^{1}H and ^{29}Si NMR spectra of **10** were consistent with a random copolymer structure and showed the presence of characteristic switching groups between the poly(ferrocenylsilane) and poly(carbosilane) segments. Thus, the ^{1}H NMR spectrum of **10** showed a single resonance at 0.81 ppm corresponding to $SiMe_2$ groups in only a Cp^H−Si−Cp^{Me} environment. The ^{29}Si NMR of **10** (Figure 5) showed signals due to poly(ferrocenylsilane) segments centered at −6.45 ppm (Cp^H−Si−Cp^{Me}) and poly(benzosilacyclobutane) segments at −3.69 ppm (CH_2−Si−Ar) as well as others associated with the switching groups centered at −2.23 and −5.81 ppm. The latter were assigned to Cp^H−Si−CH_2 and Cp^{Me}−Si−Ar environments, respectively, by comparison with data for the previously synthesized copolymer containing segments derived from the symmetrical ferrocenophane **1** and the benzosilacyclobutane **7**.[32] As no signals corresponding to a Cp^H−Si−Ar environment (δ = ca. −7.55 ppm) were detected, the results of this experiment clearly indicate that the transition metal catalyzed ROP of **3** proceeds via selective Si−Cp^H bond cleavage.

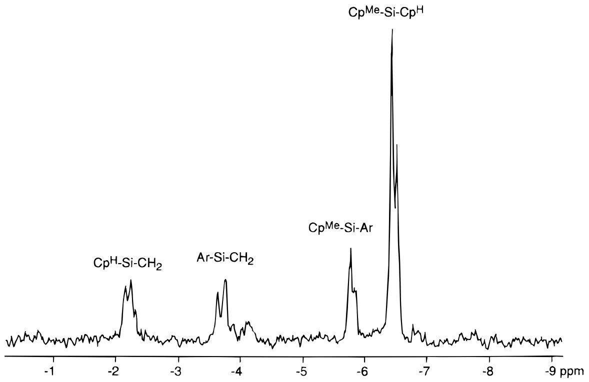
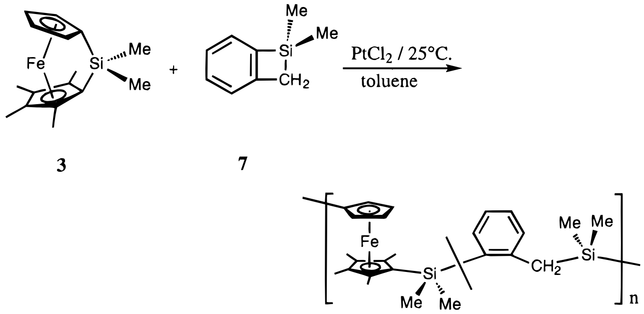


Figure 5. ^{29}Si NMR (C_6D_6, 79.5 MHz) for copolymer **10**.



3 **7**

10

The thermal behavior of the copolymer **10** was studied by DSC. Analysis of the DSC trace showed two glass transitions at T_g = 66 and 147 °C with small heat capacity changes and no evidence for melt transitions. The T_g values for homopolymers derived from **7** and **3** are 48 °C[38] and 158 °C, respectively. It is well-known that block copolymers generally possess multiple glass transition temperatures with values close to those found for the corresponding homopolymers, while random copolymers typically possess a single T_g with a value intermediate to those of the homopolymers.[39] In the case of copolymer **10**, the blocks are distributed randomly but are long enough to show independent glass transitions. The influence of the other segment leads to differences in the T_g values observed relative to the homopolymers. The random introduction of regioregular and sterically encumbered ferrocenylsilane segments increases the T_g relative to that of the more flexible homopolymeric benzocarbosilane chains, whereas the presence of the carbosilane chains leads to a T_g reduction for the ferrocenylsilane segments relative to **3**. Although each homopolymer is crystalline (T_m = 285 °C for polymer **5** and 204 °C for the poly(benzocarbosilane)) the absence of a melt transition for **10** was expected as the more irregular structure of the copolymer should disrupt effective packing of the polymer chains and would result in a completely amorphous material.

2. Transition Metal Catalyzed ROP of the Ferrocenophane 1 in the Presence of Et_3SiH: Molecular Weight Control. Previous work has demonstrated that the molecular

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(38) Theuring, M.; Sargeant, S. S.; Manuel, G.; Weber, W. P. *Macromolecules* **1992**, *25*, 5, 3834.

(39) Young, R. J.; Lovell, P. A. In *Introduction to Polymers*; Chapman and Hall: New York, 1992; p 297.

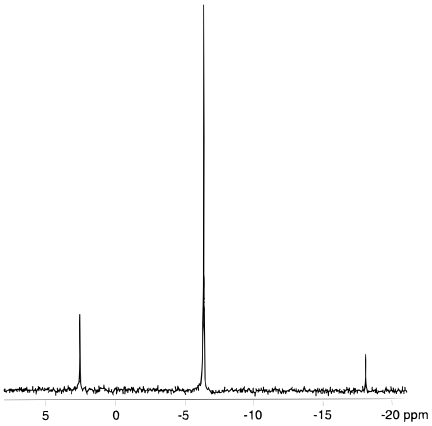
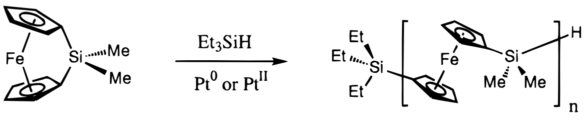


Figure 6. $^{29}Si\{^1H\}$ NMR (79.5 MHz, C_6D_6, DEPT $J = 51$ Hz) for polymer **11** with $M_n = 2100$ (PDI = 1.1).

weights of oligo(carbosilanes) derived from the transition metal (Pt^{II}) catalyzed ROP of silacyclobutanes can be controlled in the range $M_n = 540-4800$ at elevated temperatures (100 °C) by the addition of Et_3SiH.[40] We therefore explored whether such a methodology would allow convenient molecular weight control for poly(ferrocenylsilanes) prepared by transition metal-catalyzed ROP at room temperature.

Mixtures of [1]ferrocenophane **1** and Et_3SiH in different ratios were dissolved in toluene and treated with Karstedt's catalyst (a (divinyltetramethyldisiloxane)platinum(0) complex in xylenes) or $PtCl_2$ at room temperature. Under these conditions a rapid increase in solution viscosity was noticed. After ca. 2 h analysis by ^1H NMR of the reaction mixture confirmed complete conversion of **1**.

The resulting polymers were isolated by precipitation into methanol as orange powders and were isolated in 70−90% yields. Analysis of the ^1H NMR, ^{29}Si NMR, and IR spectra confirmed the nature of the end groups for low molecular weight **11** ($M_n = 2100$, PDI = 1.1) formed from the Pt^0-catalyzed ROP of **1** in the presence of relatively large amounts of Et_3SiH. The ^1H NMR spectrum showed a small, broad resonance at 4.68 ppm, assigned to an Si−H group present at one chain end as well as a triplet at 1.06 ppm and a quartet at 0.74 ppm corresponding to the Et_3Si group present at the other end. These signals are shifted downfield with respect to Et_3SiH which is consistent with being attached to the poly(ferrocenylsilane) chain. The ^{29}Si NMR (DEPT, $J_{Si-H} = 51$ Hz) spectrum of this low molecular weight sample of **11** consisted of three resonances at 2.5, −6.4, and −18.2 ppm assigned to Et_3Si-Cp, Cp−Si−Cp, and $Cp-SiMe_2H$ environments, respectively (Figure 6). Additionally, the IR spectrum revealed a Si−H stretching frequency at ca. 2114 cm^{-1}.



1 **11**

Significantly, excellent control of molecular weight was possible as shown by a plot of the values of M_w and M_n as a function of the ferrocenophane **1** to Et_3SiH ratio (Figure 7) for the Pt^0 catalyst. Control was demonstrated over the range $M_n = 2000-45\,000$ (PDI = 1.1−2.3), and the data were reproducible as similar molecular weight distributions were obtained for the same ratios in different experiments.

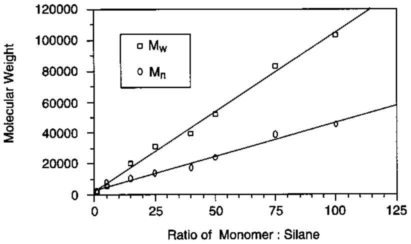


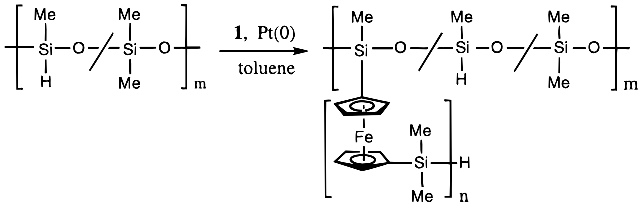
Figure 7. Plot of the M_w (□) and M_w (○) values the mole ratio of monomer:silane for the synthesis of poly(ferrocenylsilane), **11**.

It was found that the observed values of M_n for **11** are higher than those calculated based on the ratio of **1** to Et_3SiH used. This suggests that **1** is more reactive at the catalytic center. Based on recent mechanistic considerations for the transition metal catalyzed ROP of silicon-bridged [1]ferrocenophanes,[41−43] it is likely that oxidative addition of the Si−H group of the silane at the catalytic center competes with that of the strained Si−C bond in **1** and that reductive elimination reactions lead to the observed Et_3Si-Cp and Si−H end groups. In a separate experiment, in the absence of triethylsilane, high molecular weight poly(ferrocenylsilane) was obtained ($M_n = 1.2 \times 10^5$, PDI = 1.7).

Significantly, attempts to control the molecular weight by analogous thermal ROP procedures were unsuccessful. It was found that, when heated at 150 °C, a mixture of **1** and triethylsilane in a 5:1 molar ratio yielded only high molecular weight poly(ferrocenylsilane) **2** ($M_n = 2.7 \times 10^5$, PDI = 1.4).

3. Synthesis of Poly(ferrocenylsilanes) with Graft, Star, and Block Architectures. The facile use of Et_3SiH to end-cap poly(ferrocenylsilanes) and allow molecular weight control suggested that other species containing Si−H bonds might behave in a similar manner. In particular the possible use of this type of methodology to prepare graft, star, and block copolymers appeared very attractive and was therefore investigated.

(a) Synthesis and Characterization of the Polysiloxane-Poly(ferrocenylsilane) Comb Copolymer 12. Reaction of a 2:1 mole ratio of **1** with the commercially available poly(methylhydrosiloxane-dimethylsiloxane) copolymer (50−55% methylhydrosiloxane units) as the Si−H source in the presence of Karstedt's catalyst (1 mol %) yielded a poly(dimethylsiloxane)-*graft*-poly(ferrocenylsilane) copolymer (**12**) with a comb architecture. The polymer was isolated as an orange gum and possessed a monomodal molecular weight distribution ($M_n = 8.2 \times 10^3$, PDI = 1.7) which was significantly higher than that of the polysiloxane starting material ($M_n \approx 10^3$).



12

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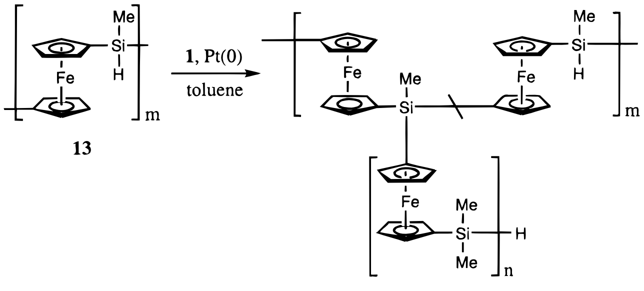
(41) Manners, I. *Polyhedron* **1996**, *15*, 4311.

(42) Sheridan, J. B.; Lough, A. J.; Manners, I. *Organometallics* **1996**, *15*, 2195.

(43) Sheridan, J. B.; Temple, K.; Lough, A. J.; Manners, I. *J. Chem. Soc., Dalton Commun.* **1997**, 711.

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra for **12** revealed characteristic resonances for both polymer segments as well as the switching and terminal groups characteristic of the graft nature of this material. The ^{29}Si NMR spectrum revealed, for example, a resonance at -29.1 ppm, corresponding to the silicon atom which binds the poly(ferrocenylsilane) to the polysiloxane chain, and a resonance at -18.2 ppm that corresponds to the $SiMe_2H$ end group for the poly(ferrocenylsilane) graft. The latter resonance occurs at an identical chemical shift to that of the analogous end group present in **11**. The length of the ferrocenyl grafts was determined to be five repeat units, on average, by ^{1}H NMR integration of the Si−Me resonances. Also an approximate grafting efficiency of 50% was determined by IR which showed two ν(Si−H) absorptions at 2150 cm^{-1} (unreacted poly(hydrosiloxane)) and 2114 cm^{-1} (terminal fcSi−H). The relatively low grafting efficiency is almost certainly a consequence of steric effects as the siloxane Si−H bonds are generally very reactive toward catalytic reactions.

(b) Attempted Preparation of the Poly(ferrocenylsilane)−Graft- Poly(ferrocenylsilane) Copolymer 14. To explore the scope of the grafting reactions we also investigated the grafting of poly(ferrocenyldimethylsilane) onto a poly(ferrocenylsilane) by using poly(ferrocenylhydromethylsilane) **13** as the Si−H source. This Si−H functionality in **13** has previously been shown to be active in hydrosilylation reactions in the presence of Karstedt's catalyst.[24]



13

14

Polymer **13** ($M_n = 6.5 \times 10^4$, PDI = 1.8) was stirred with **1** in a 1:4 ratio in the presence of Karstedt's catalyst (1 mol %). The reaction was followed by ^{1}H NMR which showed a shift downfield in the signal corresponding to the methyl groups in **13** from 0.65 to 0.89 ppm as well as formation of poly(ferrocenyldimethylsilane) segments. After 24 h the polymer product was isolated as an orange material, but the GPC trace in THF showed a broad bimodal molecular weight distribution comprising two overlapping peaks centered at $M_n = 2.5 \times 10^5$ (PDI > 3). The ^{1}H NMR showed a grafting efficiency of ca. 90% via integration of the signals corresponding to the Si−H groups at 5.25 (for the unreacted Si−H groups in environments similar to that in **13**) and 4.74 ppm (for the terminal Si−H in the grafted fragment). The average length of ferrocenyldimethylsilane fragments was established to be approximately four repeat units by integration of the Si−Me ^{1}H NMR resonances. The presence of a bimodal molecular weight distribution suggests that in addition to the formation of **14** some homopolymerization of **1** to yield **2** may occur. This is consistent with the rather sluggish reactivity of the poly(ferrocenylmethylhydrosilane) Si−H bonds toward catalytic reactions.[24]

(c) Synthesis and Characterization of Star Poly(ferrocene) Architectures (16) with a Cyclotetrasiloxane Core. Star-shaped polymers constitute another interesting architecture that we have investigated.[44] To this end we reacted monomer **1** with hydromethylcyclotetrasiloxane (**15**) in the presence of Karstedt's catalyst. After all of **1** had been consumed more of this monomer was added to the solution as ^{1}H NMR showed the presence of unreacted Si−H units derived from **15**. After the additional monomer was consumed ^{1}H NMR showed derivatization of **15** to be complete. An orange gum with a molecular weight $M_n = 5.8 \times 10^3$ (PDI = 1.26) was isolated by precipitation into hexanes.

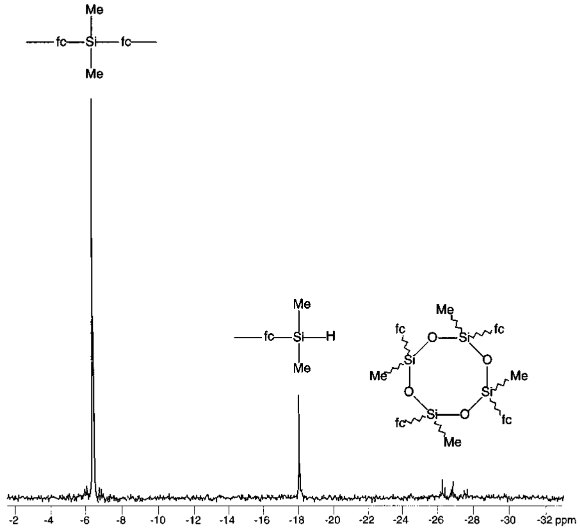
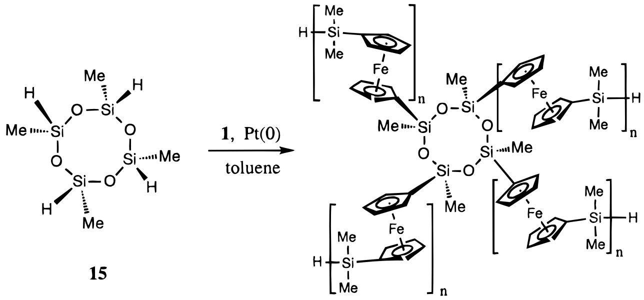


Figure 8. ^{29}Si NMR (C_6D_6, 79.5 MHz) of star copolymer **16**.



15

16

The ^{1}H NMR spectrum of the product was consistent with the structure **16** and revealed a multiplet at 4.69 ppm corresponding to the terminal Si−H groups in the poly(ferrocene) arms which is significantly shifted upfield relative to the hydride present in **15**. Integration of the methyl signals for both the poly(ferrocenylsilane) and the siloxane segments indicated that the poly(ferrocenylsilane) branches were, on average, 5 repeat units long. In addition, the ^{29}Si NMR spectrum of the product (Figure 8) showed three resonances at -6.4, -18.1, and ca. -27 ppm assigned to the three different fc-$SiMe_2$-fc, fcMe_2-Si−H, and O−SiMefc-O environments, respectively. The latter environment was observed as several resonances due to the different stereoisomers present for the cyclosiloxane ring. The IR spectrum of **16** showed only a single absorption in the Si−H region at 2114 cm^{-1} which is identical in frequency to that detected for the same terminal group in polymers **11**, **12**, and **14**.

(d) Synthesis and Characterization of Poly(ferrocene)-Poly(dimethylsiloxane)-Poly(ferrocene) Triblock Copolymers. In previous papers our group has described the synthesis of poly(ferrocenylsilane)-polysiloxane diblock copolymers via

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[44] Interesting network structures with cyclosiloxane cores joined by ferrocene units have previously been prepared by Cuadrado and co-workers using a hydrosilylation strategy. See ref 4b.

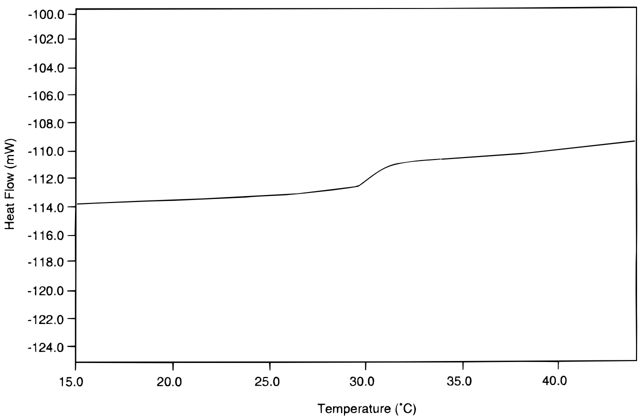
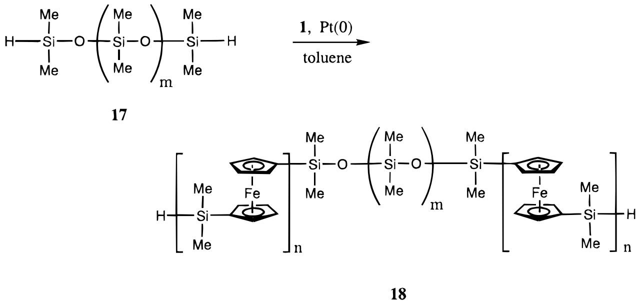


Figure 9. DSC trace of triblock copolymer **18**.

the living anionic ROP of strained cyclosiloxanes initiated with living, anionically ring-opened poly(ferrocenylsilanes).[25−27] Although other multiblock structures might be envisaged, these interesting materials are structurally limited by the need to polymerize the [1]ferrocenophane first, as living polysiloxanes do not initiate the ROP of [1]ferrocenophanes efficiently. Based on the aforementioned results described in this paper we attempted to prepare a novel poly(ferrocene)-poly(siloxane)-poly(ferrocene) triblock copolymer which would be synthetically innaccessible via sequential anionic polymerization routes.

Reaction of the commercially available Si−H terminated polysiloxane **17** ($M_n \approx 600$) with [1]silaferrocenophane **1** in toluene in the presence of Karstedt's catalyst (Pt^0) produced an orange triblock copolymer (**18**) which was determined by GPC to possess a monomodal molecular weight distribution with $M_n = 5.1 \times 10^3$ (PDI = 1.7). The molecular weight was, as expected, considerably higher than that of the starting polysiloxane ($M_n \approx 600$). The ^{1}H NMR spectrum showed a new but typical resonance at 4.69 ppm corresponding to the terminal fcSiMe$_2$H group which was also detected by IR (ν(Si−H) = 2116 cm^{-1}). Integration of the ^{1}H NMR resonances revealed an average of 10 ferrocenylsilane repeat units on each side of a siloxane block with ca. 8 Me$_2$SiO repeat units. The ^{29}Si NMR spectrum of **18** provided further characterization of this novel block copolymer. In addition to resonances corresponding to the interiors of the poly(ferrocenyldimethylsilane) and polysiloxane blocks, small resonances were also detected at −18.2 ppm, which was assigned to the terminal fc*Si*Me$_2$H group, and at 0.7 ppm, which was assigned to the fc*Si*Me$_2$O switching groups. DSC analysis of **18** (Figure 9) revealed a T_g at ca. 30 °C, which is similar to that previously measured for the ferrocenylsilane homopolymer.[9] While the DSC analysis was carried out from −150 to 150 °C, no T_g was observed for the siloxane block. This is presumably due to the very short (ca. 8 repeat unit) length for the polysiloxane block in **18**.



17

18

Summary

Transition metal catalyzed ROP of silicon-bridged [1]ferrocenophanes represents a mild methodology for the synthesis of poly(ferrocenes). Compared to anionic polymerizations for which painstakingly rigorous reactant purity and care is necessary, transition metal catalyzed ROP is very convenient. In addition, the mild reaction conditions permit control over the regiostructure of the resulting polymers and molecular weight control is also facile via the addition of Et$_3$SiH. Furthermore, the use of commercially available sources of the Si−H functionality allows remarkably facile, "one pot" access to novel poly(ferrocenes) with graft, star, and block architectures. Further extensions of the versatile synthetic methodologies described in this paper are in progress together with detailed studies of the properties of the resulting transition metal-based polymeric materials.

Experimental Section

Materials. All reactions were performed under an inert atmosphere (prepurified N$_2$) using either standard Schlenk techniques or a Vacuum Atmospheres glovebox, except for the polymers for which manipulations were carried out in air. The polymerization reactions were monitored by ^{1}H NMR using D$_2$O in a sealed capillary tube as lock signal.

Solvents were dried by standard procedures and distilled immediately prior to use. PtCl$_2$, Karstedt's catalyst, Et$_3$SiH, poly(methylhydrosiloxane-dimethylsiloxane) copolymer (50−55% methylhydrosiloxane units), hydride terminated poly(dimethylsiloxane), and methylhydrocyclotetrasiloxane were purchased from Genessee Inc. and were used as received. Silicon-bridged [1]ferrocenophanes **1**[26] and **3**,[45] disila- (**6**) and benzosilacyclobutane (**7**),[46] and poly(ferrocenylmethylhydrosilane) (**13**)[47] were synthesized as described in the literature.

Equipment. Mass spectra were obtained with the use of a VG 70−250S instrument operating in electron impact (EI) mode. Pyrolysis mass spectrometry experiments were carried out by heating the sample probe to 500 °C. Solution NMR spectra were recorded on Varian Gemini 200 or Varian XL 400 instruments. ^{1}H NMR spectra were referenced to residual protonated CDCl$_3$ at 7.24 ppm or C$_6$D$_6$ at 7.14 ppm, and ^{13}C NMR spectra were referenced to the C$_6$D$_6$ signal at 128.0 ppm. ^{29}Si NMR spectra were recorded on a Varian Gemini 400 instrument utilizing a proton-decoupled DEPT ($J_{Si-H} = 6.7$ Hz) pulse sequence and were referenced externally to TMS. Solid state ^{13}C and ^{29}Si spectra (CPMAS) were obtained using a Chemagnetics CMX 300 spectrometer equipped with a Chemagnetics magic angle spinning probe doubly tuned to the resonance frequencies of ^{13}C (75.3 MHz) and ^{29}Si (59.5 MHz). The sample was spun in a 7.5 mm o.d. zirconium rotor at a spinning rate of 6000 Hz. A single-contact cross-polarization technique was employed with a contact time of 5 ms and a proton decoupling during the signal acquisition period. The proton radio frequency field strength was 50 kHz. Spectra were acquired using a sweep width of 100 kHz, a data size of 2 Hz, and a recycle delay of 5 s. All chemical shifts were referenced to external TMS. Wide-angle X-ray diffraction data were obtained at 25 °C using a Siemens D5000 diffractometer employing Ni-filter Cu Kα ($\lambda = 1.541\ 78$ Å) radiation. Samples were scanned at step widths of 0.02° with 1.0 s per step in the Bragg angle range 3−40° 2θ. Samples were prepared by spreading finely ground polymer on grooved glass slides. DSC analyses were performed at a heating rate of 10 °C/min under prepurified N$_2$ using a Perkin-Elmer DSC 7 differential scanning calorimeter. Thermogravimetric analyses were performed at a heating rate of 10 °C/min under prepurified N$_2$ using a Perkin-Elmer TGA & thermogravimetric analyzer. Molecular weight distributions were analyzed by gel

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[45] Pudelski, J. K.; Foucher, D. A.; Honeyman, C. H.; Lough, A. J.; Manners, I.; Barlow, S.; O'Hare, D. *Organometallics* **1995**, *14*, 2470.

[46] (a) Kriner, W. A. *J. Org. Chem.* **1964**, *29*, 1601. (b) Eaborn, C.; Walton, D. R. M.; Chan, M. *J. Organomet. Chem.* **1967**, *9*, 251.

[47] Foucher, D.; Ziembinski, R.; Petersen, R.; Pudelski, J.; Edwards, M.; Ni, Y.; Massey, J.; Jaeger, C. R.; Vancso, G. J.; Manners, I. *Macromolecules* **1994**, *27*, 3992.

permeation chromatography using a Waters Associates liquid chromatograph equipped with a 510 HPLC pump, U6K injector, Ultrastyragel columns with a pore size between 10^3 and 10^5 Å, and a Waters 410 differential refractrometer. A flow rate of 1.0 mL/min was used, and samples were dissolved in a THF solution of 0.1% tetra-*n*-butylammonium bromide. Polystyrene standards purchased from American Polymer Standards were used for calibration purposes.

Thermal ROP of 3. The thermal ROP of **3** was carried out via a minor modification of the previously described method.[35]

A sample of monomer **3** (450 mg, 1.51 mmol) was flame-sealed in an evacuated (0.01 mmHg) Pyrex tube and heated at 150 °C for 3 h. The tube content was dissolved in THF, filtered, and precipitated into methanol. The fibrous orange solid of **4** was filtered off, washed with methanol (3 × 5 mL), and dried under vacuum. Yield: 340 mg (75%). GPC: $M_w = 1.2 \times 10^5$, PDI = 1.8.

The characterization data matched that previously reported.[35]

Transition Metal-Catalyzed ROP of 3: Synthesis of the Regioregular Poly(ferrocenylsilane), 5. A solution of monomer **3** (350 mg, 1.17 mmol) in toluene (5 mL) was stirred for 12 h in the presence of $PtCl_2$ (1 mol %) as ROP catalyst. The precipitated solid was separated by filtration, washed with THF (3 × 5 mL) until the washings were colorless, and then washed with methanol (2 × 5 mL). The powder orange solid of **5** was then dried under vacuum. Yield: 310 mg (87%). Oligomeric **5** was obtained from THF mother liquors after evaporation. Yield: ca. 35 mg (ca. 10%).

For **5**: $^{29}Si\{^1H\}$ NMR (CPMAS, 59.5 MHz) δ −7.8 (s). $^{13}C\{^1H\}$ NMR (CPMAS, 73.5 MHz) δ = 2.6 (s, Si*Me*), 14.4 (s, $C_5\mathit{Me}_4$), 68.0 (s, *ipso-Cp*^{Me}), 77.0 (s, *Cp*^{H}), 86.9 (br, *Cp*^{Me}) ppm. DSC: T_g = 158 °C, T_m = 285 °C. Anal. Calcd for $C_{16}H_{22}FeSi$: C, 64.43; H, 7.43. Found: C, 63.77; H, 7.31.

For soluble oligomeric fractions of **5**: GPC: M_n = 1,100, PDI = 2.02. ^1H NMR ($CDCl_3$, 200 MHz) δ = 0.59 (s, 6H, Si*Me*), 1.65 (s, 6H, $C_5\mathit{Me}_4$), 1.83 (s, 6H, $C_5\mathit{Me}_4$), 3.74 (s, 2H, $C_5\mathit{H}_4$), 3.87 (s, 2H, $C_5\mathit{H}_4$) ppm.

Attempted Transition Metal Catalyzed ROP of the Permethylated Ferrocenophane, Fe(η-C_5Me_4)$_2$SiMe$_2$. A solution of [1]ferrocenophane Fe(η-C_5Me_4)$_2$SiMe$_2$ (20 mg, 0.06 mmol) in toluene (0.5 mL) was stirred with $PtCl_2$ (1 mol %) at room temperature. After 2 days, no polymerization was observed by ^1H NMR.

Attempted Copolymerizations of [1]Ferrocenophane 3 and Disilacyclobutane 6. (a) 1:2 Ratio. A mixture of **3** (15 mg, 0.05 mmol) and **6** (15 mg, 0.10 mmol) was stirred in toluene (1 mL) at room temperature in the presence of $PtCl_2$ (1 mol %); after 20 min a precipitate was formed, and the solution became more viscous. Analysis of the ^1H NMR spectra of the reaction solution over time showed a decrease in the intensity of signals corresponding to both monomers and an increase of peaks assigned to poly(carbosilane) **8**; after 36 h both monomers were consumed. The precipitate was filtered off, washed with toluene (2 × 2 mL), and dried yielding an orange solid (**5**). Yield: ca. 12 mg (80% relative to **3**).

Precipitation in methanol of the filtrate gave 14 mg of a sticky brown material (a mixture of **8** and **9**). GPC: bimodal distribution with a 9:1 ratio between peaks. For the larger peak: $M_n = 1.2 \times 10^6$, PDI = 2.3; for the smaller peak: $M_n = 1.3 \times 10^4$, PDI = 3.5.

(b) 1:15 ratio. A mixture of **3** (10 mg, 0.03 mmol) and **6** (72 mg, 0.5 mmol) was stirred in toluene (2 mL) at room temperature in the presence of $PtCl_2$ (1 mol %). After 24 h the solution was more viscous, and a ^1H NMR spectrum of the reaction solution showed that no monomers were left. The solution was filtered and precipitated into methanol yielding 70 mg of brown material (a mixture of **8** and **9**). GPC: bimodal distribution with a 3:1 ratio between peaks. For the larger peak: $M_n = 5.2 \times 10^5$, PDI = 2.5; for the smaller peak: $M_n = 8.9 \times 10^3$, PDI = 3.8. ^1H NMR (C_6D_6, 200 MHz) δ = −0.61 (s,CH_2−Si), 0.27 (s, CH_2−SiMe_2); 0.46, 0.56, 0.61, 0.82 (m, fc-SiMe_2); 1.84, 1.87, 1.93, 2.03 (m, $C_5\mathit{Me}_4$); 3.8−4.1 (m, $C_5\mathit{H}_4$) ppm.

Synthesis of Poly(ferrocene)-Poly(benzosilacyclobutane) Random Copolymer 10. A mixture of **3** (40 mg, 0.13 mmol) and **7** (20 mg, 0.13 mmol) was stirred in toluene (2 mL) at room temperature in the presence of $PtCl_2$ or Pt(1,5-cod)$_2$ (1 mol %) until all the reactive monomers were consumed (24 h). Over time the solution became more viscous. The solution was filtered and precipitated into methanol yielding copolymer **10** as an orange powder. Yield: 52 mg (87%).

GPC: monomodal distribution $M_n = 2.4 \times 10^4$, PDI = 2.3. ^1H NMR (C_6D_6, 200 MHz) δ = 0.23−0.36 (m, 6H, Ar−Si*Me*), 0.81 (br, 6H, fc-Si*Me*), 1.76−1.87 (m, 12H, $C_5\mathit{Me}_4$), 2.2−2.6 (m, 2H,CH_2), 3.8−4.1 (m, 4H, $C_5\mathit{H}_4$), 7.0−7.6 (m, 4H, *Ar*) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6, 79.5 MHz) δ = −6.5, −6.4 (Cp^{Me}−*Si*-Cp^H); −5.9 to −5.7 (m, Cp^{Me}−*Si*−Ar); −3.8 to −3.6 (m, CH_2−*Si*-Ar); −2.1 to −2.3 (m, Cp^H−Si−CH_2) ppm. DSC: T_g (Poly(carbosilane)) = 66 °C, T_g (Poly(ferrocene)) = 147 °C.

Synthesis of Polymer 11 with Molecular Weight Control. Similar procedures were used for the different monomer: Et_3SiH mole ratios. The following for a 1:1 ratio is typical.

A mixture of **1** (200 mg, 0.83 mmol) and Et_3SiH (132 μL, 0.83 mmol) was stirred in toluene (1.5 mL) at room temperature in the presence of Karstedt's catalyst (1 mol %). Over time the solution became more viscous, and after 2 h all the reactive monomer was consumed as shown by ^1H NMR. The solution was filtered, and the product isolated by precipitation into hexanes yielding 142 mg (71%) of polymer **11** as an orange powder.

GPC (THF, polystyrene standards): M_n = 2100; PDI = 1.1. ^1H NMR (C_6D_6, 200 MHz): δ = 0.26 (s, 6 H, SiMe_2H), 0.52 (s, 42 H, fcSi*Me*), 0.74 (q, 6 H, $^3J_{HH}$ = 7.7 Hz, $CH_3\mathit{CH}_2$), 1.06 (t, 9 H, $^3J_{HH}$ = 7.7 Hz, CH_3CH_2), 4.01−4.25 (m, 64 H, $C_5\mathit{H}_4$), 4.68 (m, 1 H, Si−*H*) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 50.3 MHz) δ = −0.4 (s, fc-SiMe_2), 1.4 (s, SiMe_2H), 5.2 (s, CH_3CH_2), 8.2 (s, $CH_3\mathit{CH}_2$), 71.5−74.0 (m, C_5H_4) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6, 79.5 MHz, DEPT *J* = 51 Hz) δ = −18.2 (s, *Si*−H) −6.4 (s, *Si*Me$_2$), 2.5 (s, Et$_3$*Si*) ppm. IR (Nujol, Si−H stretch): 2114 cm^{-1}.

Transition Metal-Catalyzed ROP of 1 in the Absence of Et$_3$SiH. A solution of **1** (200 mg, 0.83 mmol) in toluene (1.5 mL) was stirred in the presence of Karstedt's catalyst (1 mol %). After 3 h the monomer was consumed as shown by ^1H NMR, the solution was filtered, and the product was isolated by precipitation into methanol yielding 179 mg (90%) of poly(ferrocenylsilane) **2** as an orange fibrous material. NMR data were consistent with literature.[8]

GPC: $M_n = 1.2 \times 10^5$; PDI = 1.7.

Thermal ROP of 1 in the Presence of Triethylsilane. A mixture of **1** (200 mg, 0.83 mmol) and triethylsilane (26.5 μL, 0.17 mmol) was flame-sealed in an evacuated (0.01 mmHg) Pyrex tube and heated first for 2 h at 80 °C (melt temperature for **1**) in order to obtain an homogeneous mixture and then for 3 h at 150 °C. The product was dissolved in THF, and the polymer **2** was isolated by precipitation into hexanes. This afforded 152 mg (76%) of an orange fibrous material (**2**).

GPC (THF): $M_n = 2.7 \times 10^5$; PDI = 1.4. NMR data were consistent with that reported in the literature.[8]

Synthesis of Poly(dimethylsiloxane)-Poly(ferrocene) Graft Copolymer 12. A mixture of **1** (232 mg, 0.96 mmol) and poly(methylhydrosiloxane-dimethylsiloxane) (50−55% methylhydrosiloxane units) copolymer (70 mg, 0.52 mmol) was stirred in toluene (1.5 mL) at room temperature in the presence of Karstedt's catalyst (1 mol %). After 3 h all the reactive monomer was consumed, and the solution was filtered and precipitated into hexanes yielding polymer **12** as an orange gum. Yield: 270 mg (89%).

GPC: $M_n = 8.2 \times 10^3$, PDI = 1.7. ^1H NMR (C_6D_6, 200 MHz) δ = 0.20−0.36 (m, 20H, OSi*Me*, SiMe_2H), 0.53 (s, 24H, fc-SiMe_2), 4.09−4.53 (m, 32H, $C_5\mathit{H}_4$), 4.69 (br, 1H, CpSi−*H*), 5.10 (br, 1H, OSi−*H*) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz) δ = −2.8 (br, *Me*HSiO), −1.3 (br, *Me*SiO-fc), −0.5 (s, fcMe_2Si), 1.7 (s, Me_2SiO), 71.8−74.0 (m, C_5H_4) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6, 79.5 MHz, DEPT *J* = 51 Hz) δ = −36.9 (br, MeH*Si*O), −29.1 (br, Me*Si*O-fc), −21.0 (Me$_2$*Si*O), −18.2 (s, fc*Si*H), −6.4 (s, fc−*Si*Me$_2$), 11.2 (s, Me$_3$*Si*O terminal) ppm. IR (Nujol, Si−H stretch): 2150 cm^{-1} (OSi−H), 2114 cm^{-1} (fcSi−H). DSC: $T_g(1)$ = − 120 °C, $T_g(2)$ = −87 °C.

Synthesis of Poly(ferrocene)-Poly(ferrocene) Graft Copolymer 14. A mixture of **1** (100 mg, 0.41 mmol) and poly(ferrocenylhydromethylsilane), **13**, (51 mg, 0.23 mmol) was stirred in toluene (1.5 mL) at room temperature in the presence of Karstedt's catalyst (1 mol %). After 24 h **14** was isolated as an orange powder by precipitation into hexanes (−78 °C). Yield: 100 mg (66%). GPC: Bimodal molecular weight distribution centered on $M_n = 2.5 \times 10^5$, PDI > ca. 3. ^{1}H NMR (C_6D_6, 200 MHz) $\delta = 0.34$ (s, fc-Si*Me*$_2$−H), 0.59 (fc-Si*Me*$_2$), 0.90 (fc-Si*Me*-Cp), 4.08−4.30 (m, C_5H_4), 4.74 (br, fc-SiMe$_2$*H*), 5.25 (br, fc-SiMe*H*) ppm.

Synthesis of Poly(ferrocene) Star Copolymer 16. A mixture of **1** (335 mg, 1.38 mmol) and **15** (20 μL, 0.083 mmol) was stirred in toluene (3 mL) at room temperature in the presence of Karstedt's catalyst (1 mol %). The reaction was followed by ^{1}H NMR. After 2 h there was no **1** left, but Si−H units remained unreacted. Additional **1** (100 mg, 0.41 mmol) was added to the solution that was stirred for 3 h. ^{1}H NMR showed no reagents left, and the product was isolated by precipitation into cold hexanes as an orange gum. Yield = 312 mg (69%).

GPC: $M_n = 5.8 \times 10^3$, PDI = 1.26. ^{1}H NMR (C_6D_6, 200 MHz) $\delta = 0.26$ (s, OSi*Me*), 0.28 (s, fc-Si*Me*$_2$H), 0.53 (s, fc-Si*Me*$_2$), 4.09−4.4 (m, C_5H_4), 4.69 (m, fcSi−*H*) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz) $\delta = -2.7$ (br, fc*Me*SiO), −0.4 (s, fc*Me*$_2$Si, fcSi*Me*$_2$H), 71.8−74.0 (m, C_5H_4) ppm. ^{29}Si{^{1}H} NMR (C_6D_6, 79.5 MHz, DEPT $J = 51$ Hz) $\delta = -26.9$ to −26.2 (m, fcMe*Si*O), −18.1 (s, fc*Si*Me$_2$H), −6.4 (s, fc−*Si*Me$_2$) ppm. IR (Nujol, Si−H stretch): 2114 cm^{-1}(fcSi−H).

Synthesis of Poly(ferrocene)-Poly(dimethylsiloxane)-Poly(ferrocene) Triblock Copolymer 18. To a solution of **1** (335 mg, 1.38 mmol) and hydride-terminated polysiloxane **17** (50 mg, 0.086 mmol) in toluene (3 mL) Karstedt's catalyst (1 mol %) was added. After stirring at 25 °C for 3 h the ^{1}H NMR spectrum showed that no monomer was left as no Si−H resonance was detected for the hydride end groups in the polysiloxane. The solution was then filtered and concentrated before precipitation into cold (− 78 °C) hexanes, which gave an orange solid. Yield: 380 mg (99%).

GPC: $M_n = 5.1 \times 10^3$, PDI = 1.7. ^{1}H NMR (C_6D_6, 200 MHz) $\delta = 0.19$−0.48 (m, OSi*Me*$_2$, *Me*$_2$SiO-fc, fc-Si*Me*$_2$H), 0.54 (s, fc-Si*Me*$_2$), 4.10−4.43(m, C_5H_4), 4.69 (m, fcSi−*H*) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz) $\delta = -0.4$ (s, *Me*$_2$Sifc), 1.4 (b, *Me*$_2$SiO), 71.7−73.6 (m, C_5H_4) ppm. ^{29}Si{^{1}H} NMR (C_6D_6, 79.5 MHz, DEPT $J = 51$ Hz) $\delta = -21.5$ to −20.8 (m, Me$_2$*Si*O), −18.2 (s, fc*Si*Me$_2$H), −6.4 (s, fc−*Si*Me$_2$), 0.7 (s, Me$_2$*Si*O-fc) ppm. IR (Nujol, Si−H stretch): 2116 cm^{-1}(fcSi−H).

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