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Hyperbranched Poly(carbosilanes) from Silyl-Substituted Furans and Thiophenes

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ABSTRACT: The synthesis and characterization of new hyperbranched organosilicon polymers containing furan or thiophene are described. The air- and moisture-stable polymers were prepared in 78−98% yields by the platinum-catalyzed hydrosilylation polymerization of AB_2 and AB_3 silyl-substituted furans and thiophenes. Complete polymerization was achieved within several hours at room temperature. Number-average molecular weights of the products ranged from ∼2000 to 4000, as determined by both gel permeation chromatography and vapor pressure osmometry. The polymers were highly soluble in common solvents and possessed glass transition temperatures well below room temperature. ^{29}Si NMR spectroscopy confirmed the branched nature of the polymers.

Introduction

Many types of organosilicon dendrimers and hyperbranched polymers are now known.[1,2] Among the properties that make these materials attractive synthetic targets are ease of preparation, robustness, and excellent solubility and processability. Furthermore, since modifications of the end products are normally straightforward, materials of new properties and reactivity can be rapidly developed. When the significant role silicon-based materials have played in materials science is considered,[3] continued research in this field remains a practical goal.

Organosilicon hyperbranched polymers are commonly prepared in high yields via hydrosilylation[4] reactions. Hyperbranched poly(carbosilanes) have been prepared in this fashion, with the majority of examples being synthesized from simple alkyl silanes such as triallylsilane,[5] methyldivinylsilane,[5] and methyldiethynylsilane.[6] In view of potential applications, it is of interest to incorporate additional functionality that may impart different properties to the polymer. Numerous examples of siloxane-containing hyperbranched organosilicon polymers have been reported,[7−11] including a polymer incorporating both siloxane and phenyl groups.[12] Recently, we reported the synthesis of thermally stable hyperbranched poly(carbosilarylenes) consisting of phenyl groups in each repeat unit.[13] In this report, we report the synthesis of new hyperbranched poly(carbosilanes) containing thiophene or furan moieties. The presence of oxygen and sulfur atoms in the heteroaromatic groups may give these materials utility in host−guest or metal stabilization chemistry.[14−21]

Results and Discussion

Monomer Synthesis. The silyl-substituted monomers of this study (**1**−**8**) are shown in Figure 1. The precursors to these compounds, intermediates **A**−**D**, were synthesized as shown in Scheme 1. Converting **A**−**D** to the corresponding Grignard reagents followed by reaction with the appropriate chlorosilane led to monomers **1**−**8** (Scheme 2). Of particular note is that an excess of Grignard reagent should not be used for the synthesis of **5**, as this gives the tetrasubstituted silane (Scheme 3). In this case, attachment of the fourth furyl group to the silicon likely occurs with loss of lithium hydride. Reactions of organometallics with silyl hydrides in this manner have been reported as early as 1946.[22−26] However, an excess of the analogous Grignard reagent from **B** gave **6** without noticeable formation of the tetrasubstituted compound. All of these monomers are air- and moisture-stable, clear, colorless liquids and were characterized completely. Boiling points and elemental analysis data for **A**−**D** and **1**−**8** are given in

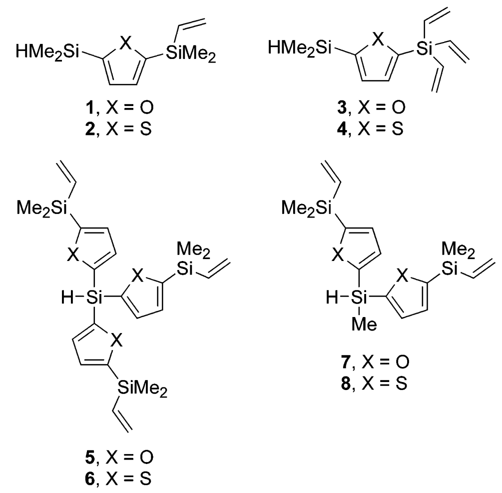
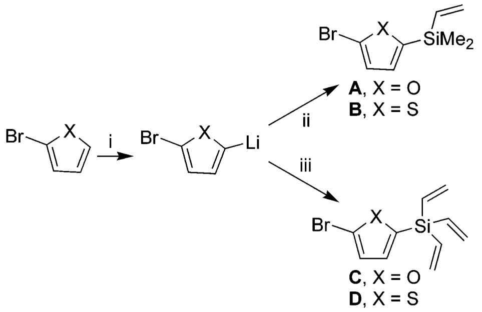


Figure 1. Monomers **1**−**8**.

Scheme 1. Synthesis of Intermediates A-D: (i) LDA; (ii) Chlorodimethylvinylsilane; (iii) Chlorotrivinylsilane



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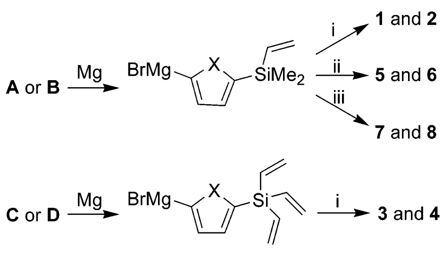
Scheme 2. Synthesis of 1-8 from A-D: (i) Chlorodimethylsilane; (ii) 0.33 equiv of Trichlorosilane; (iii) 0.5 equiv of Dichloromethylsilane



Scheme 3. Synthesis of Tetrasubstituted Silane

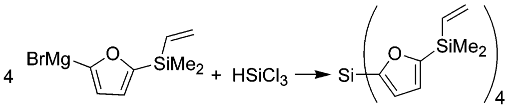


Table 1. Boiling Point and Analysis Data for A-D and 1-8

compound	bp (°C/mmHg)	elemental analyses[c] %C	elemental analyses[c] %H
A	72/3.4	41.65 (41.57)	4.68 (4.80)
B	87−90/2.0	38.85 (38.87)	4.66 (4.48)
C	83/1.8	47.09 (47.07)	4.47 (4.34)
D	110−113/1.0	44.37 (44.28)	4.22 (4.09)
1	65−66/1.8	56.57 (57.08)	8.41 (8.62)
2	90/1.1	52.90 (53.03)	7.98 (8.01)
3	60−64/0.9	61.03 (61.48)	7.72 (7.74)
4	97/0.5	57.32 (57.54)	7.41 (7.24)
5	210−226/0.1[a]	59.14 (59.70)	7.19 (7.10)
6	−[b]	53.96 (54.28)	6.62 (6.45)
7	105−110/0.1	58.75 (58.90)	7.60 (7.56)
8	184−202/0.025[a]	53.57 (53.91)	7.06 (6.92)

[a] Boiling point from Kugelrohr distillation. [b] Not distillable; after silica gel treatment. [c] Anal. calcd in parentheses.

Table 1, and all spectral data are tabulated in the Supporting Information.

Polymerization. Addition of Karstedt's catalyst (platinum−divinyltetramethyldisiloxane complex) to room-temperature THF solutions of monomers **1**−**8** resulted in rapid hydrosilylation polymerization to give the corresponding polymers **1P**−**8P**. Reaction times ranged from 10 min to several hours, and the progress of polymerization was monitored by noting the disappearance of the Si−H absorbance in the IR spectrum. Most of the polymers were isolated by precipitation into methanol or hexane at low temperatures. In the cases where the polymers did not precipitate, they were isolated by removal of volatiles under vacuum. Final yields ranged from 78% to 98%.

While monomers **3**−**8** yielded hyperbranched polymers, monomers **1** and **2** gave rise to linear polymers, which were synthesized for comparison purposes. Interestingly, when polymer **1P** was heated under vacuum to remove the last traces of solvent, a small amount of highly crystalline material sublimed onto the neck of the flask. X-ray crystallography revealed these crystals to be the dimeric compound, formed by intramolecular hydrosilylation of the initially formed adduct (Scheme 4).

Scheme 4. Formation of Dimer from Monomer 1

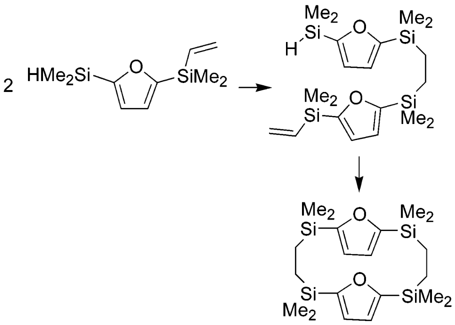


Table 2. Yields, T_g Data, and Molecular Weight Data for Polymers 1P-8P

polymer	% yield[a]	T_g[b] (°C)	VPO M_n	GPC M_n	GPC M_w	D[c]
1P	81	−34	3050	4900	20 500	4.18
2P	87	−12[d]	4120	4900	18 200	3.71
3P	95	−61	1360	1600	3800	2.38
4P	88	−24	3220	3100	7400	2.39
5P	98	−19	1980	2400	4200	1.75
6P	80	−32	2600	3800	7100	1.87
7P	83	−23	1790	2300	5700	2.48
8P	78	−7	2240	2900	6900	2.38

[a] Isolated yield. [b] DSC glass transition temperature measurement. [c] Polydispersity. [d] **2P** had a melting point of 78 °C.

Polymer Characterization. Polymers **1P**−**8P** were completely air- and moisture-stable, and ranged in appearance from viscous oils to clear tacky solids. Characterization included ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (Supporting Information), differential scanning calorimetry, and molecular weight determinations (Table 2). All of the polymers were highly soluble in common solvents including diethyl ether, THF, hexane, and chloroform.

Molecular weights of the polymers were rather low with broad weight distributions. Vapor pressure osmometry (VPO) measurements gave values that were in good agreement with M_n values determined by GPC. This was somewhat unusual, as the GPC data were based on linear polystyrene calibration standards, which do not always lead to accurate molecular weight values for highly branched polymer systems. The high polydispersity values for linear polymers **1P** and **2P** could be explained by the presence of a significant shoulder in the low molecular weight region for both polymers that was not present in the GPC data for **3P**−**8P**. Polymers **3P**, **5P**, and **7P** could not be purified by precipitation due to their excellent solubilities even at low temperatures. As a result, their molecular weight values were lower compared to the others, reflecting the presence of oligomeric products still present in the product. All of the polymers possessed reproducible glass transition temperatures (T_g) below room temperature. Somewhat to our surprise, we observed that the T_g values for the linear polymers (**1P** and **2P**) were not significantly higher than the values for the hyperbranched polymers (**3P**−**8P**). This is in marked contrast to our previously reported comparison of linear and hyperbranched poly(carbosilarylenes).[13] Furthermore, the T_g's of the hyperbranched polymers containing more

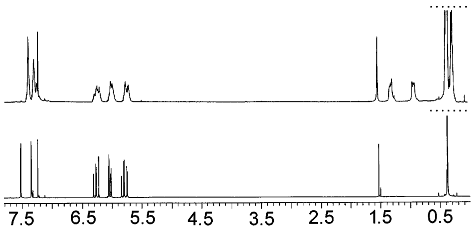


Figure 2. ^{1}H NMR spectra of **6** (bottom) and **6P** (top).

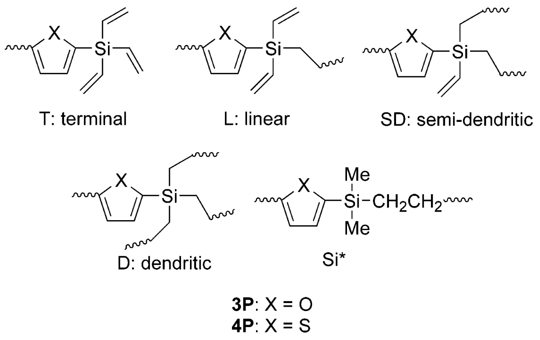


Figure 3. Five possible Si environments in polymers **3P** and **4P**.

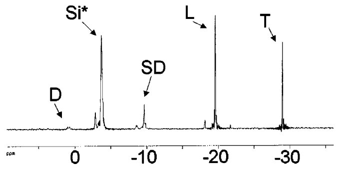


Figure 4. ^{29}Si NMR spectrum of **4P**.

aryl groups in each repeat unit (**5P**−**8P**) were not significantly higher than the polymers containing only one aryl group per repeat unit (**3P** and **4P**). However, this can possibly be explained by the lower average degrees of polymerization for **5P**−**8P**. Finally, for **5P**−**8P**, whether the starting monomers were AB_2 or AB_3 apparently had little effect on the physical properties of the resulting polymers.

The excellent solubilities of these polymers allowed us to easily obtain spectral data. Figure 2 shows the ^{1}H NMR spectra of **6** and **6P**. The obvious differences are the increased broadness of the peaks, and the appearance of new resonances corresponding to $-CH_2CH_2-$ in **6P**. These differences were apparent in the other monomer/polymer pairs. ^{13}C and ^{29}Si NMR data also confirmed the hydrosilylated products (see Supporting Information).

As in our earlier report on hyperbranched poly(carbosilarylenes),[13] we were able in this study to determine the degree of branching (DB)[27−29] in polymers **3P** and **4P** using quantitative ^{29}Si NMR spectroscopy. To calculate DB, one must know the relative amounts of the various branch units in the polymer. Unfortunately, ^{29}Si NMR spectroscopy cannot provide this information for polymers **5P**−**8P** because the branch point silicon atoms in each polymer all have virtually the same chemical shifts. However, quantitative ^{29}Si NMR spectroscopy is an excellent analytical tool for **3P** and **4P**. In theory, there should be five possible environments for the silicon atoms in **3P** and **4P** (Figure 3), which are readily apparent in the ^{29}Si NMR spectrum (**4P**, Figure 4). We attribute the minor signals in the spectrum to differences in microenvironment due to the random nature of the polymer molecular structure in addition to the large molecular size distribution. The D:SD:L:T ratios in **3P** and **4P** were found to be 1:3.4:6.9:7.9 and 1:5.1:14.6:9.6, respectively (1:6:12:8 theoretical). Using the equations derived by Frey and coworkers,[29] we obtained DB values of 0.49 for **3P** and 0.38 for **4P**, values reasonably close to the theoretical value of 0.44 for AB_3 systems.

Conclusion

We have prepared new hyperbranched polymers in high yields from silyl-substituted furan and thiophene monomers. The polymers are highly soluble and are air- and moisture-stable. This work demonstrates the relative ease with which different functional groups can be incorporated into an organosilicon hyperbranched structure. These polymers are attractive candidates for future studies. The unreacted vinyl groups in the polymers should allow facile chemical modification. Furthermore, the presence of furan and thiophene may impart ligand or metal stabilization properties to the polymers.

Experimental Section

Materials and General Comments. All reactions were performed under an atmosphere of dry nitrogen. The following reagents were obtained from commercial sources and used without further purification: *n*-BuLi (2.5 M in hexane), 2-bromothiophene, diisopropylamine, chlorodimethylvinylsilane, chlorodimethylsilane, chlorotrivinysilane, trichlorosilane, dichloromethylsilane, furan, bromine, dodecane, *N*,*N*-diethylaniline, diethyl ether, ammonium chloride, sodium chloride, and magnesium turnings. Tetrahydrofuran (THF) was distilled from Na/benzophenone under a N_2 atmosphere prior to use. Dimethylformamide (DMF) was dried over calcium hydride (CaH_2; 5% w/v) and distilled under a N_2 atmosphere prior to use. Karstedt's catalyst in xylene (platinum−divinyltetramethyldisiloxane complex, Pt−DVTMDSO) was used as a polymerization catalyst. 2-Bromofuran was synthesized according to a literature preparation.[30]

^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained using a 400 MHz Bruker AVANCE DRX multinuclear NMR spectrometer. $CDCl_3$ was used as the solvent. Quantitative ^{29}Si NMR spectroscopy was performed using an inverse gated ^{1}H decoupling sequence. Samples were prepared in $Cr(acac)_3/CDCl_3$ solution (0.1 M $Cr(acac)_3$). Elemental analyses were obtained from Galbraith Laboratory, Knoxville, TN. Glass transition temperatures (T_g) were measured using a TA Instruments DSC model 2010 instrument equipped with a TA operating software module and data analysis data station. Temperature was increased at a heating rate of 10 °C/min. Molecular weights were also obtained on a Wescan Instruments, Inc., vapor pressure osmometer (VPO) model 233 instrument, using chloroform as solvent. Average values of repeated measurements are reported. Gel permeation chromatography measurements were performed on a Waters Associates GPC II instrument using 500, 10^4, 10^5, and 10^6 Å μ-Styragel columns and UV or refractive index detectors. The operating conditions consisted of a flow rate of 1.5 mL/min of unstabilized HPLC-grade THF containing 0.1% tetra-*n*-butylammonium bromide [$(n\text{-Bu})_4NBr$], a column temperature of 30 °C, and sample injection volume of 0.05−0.1 mL of a 0.1% solution. The system was calibrated with a series of narrow molecular weight polystyrene standards in the molecular weight range of ca. 10^3−10^6.

Preparation of 2-Bromo-5-dimethylvinylsilylfuran (A). A 500 mL round-bottomed single-neck flask equipped with a septum, a N_2 gas inlet, and a magnetic stir bar was charged with 16.4 g of diisopropylamine (0.16 mol) and 150 mL of THF. The flask was cooled in an acetone/dry ice bath, and 56.0 mL of *n*-BuLi (0.14 mol) was added slowly via a cannula. After the addition was complete, the mixture was stirred for 1 h in a water/ice bath and then recooled in an acetone/dry ice bath. 2-Bromofuran (17.0 g, 0.12 mol) was added dropwise by cannula, and the mixture was stirred for 1 h at −78 °C. Chlorodimethylvinylsilane (19.3 mL, 0.14 mol) was added slowly via a syringe, and the mixture was allowed to warm to room temperature and left overnight. The mixture was poured into an ice-cold solution of saturated aqueous ammonium chloride. The layers were separated and the aqueous layer was extracted twice with ether. The combined organic layers were washed twice with distilled water and once with saturated aqueous sodium chloride solution. The clear yellow organic layer was dried over anhydrous magnesium sulfate and then filtered. All volatiles were removed using a rotary evaporator. Further purification of the crude product by distillation gave 2-bromo-5-dimethylvinylsilylfuran as a clear colorless liquid in 72% yield (20.4 g, bp 72 °C/3.4 mmHg).

Preparation of 2-Bromo-5-dimethylvinylsilylthiophene (B). The procedure used in the preparation of **A** was employed here with the following exception: after 2-bromothiophene was added, the mixture was warmed to 0 °C and then recooled to −78 °C before chlorodimethylvinylsilane was added. 2-Bromothiophene (24.5 g 0.15 mol), diisopropylamine (21.3 g, 0.21 mol), *n*-BuLi (71.0 mL, 0.18 mol), and chlorodimethylvinylsilane (25.0 mL, 0.18 mol) were allowed to react in 200 mL of THF. Distillation of the crude mixture provided 2-bromo-5-dimethylvinylsilylthiophene as a clear colorless liquid in 84% yield (31.2 g, bp 87−90 °C/2 mmHg).

Preparation of 2-Bromo-5-trivinylsilylfuran (C). The procedure used in the preparation of **A** was employed here, but using chlorotrivinylsilane (1.7% ethyl impurities) instead of chlorodimethylvinylsilane. 2-Bromofuran (26.3 g, 0.18 mol), diisopropylamine (25.3 g, 0.25 mol), *n*-BuLi (86.0 mL, 0.21 mol), and chlorotrivinylsilane (31.0 g. 0.21 mol) were allowed to react in 200 mL of THF. Distillation of the crude mixture provided 2-bromo-5-trivinylsilylfuran as a clear colorless liquid in 64% yield (29.5 g, bp 83 °C/1.8 mmHg).

Preparation of 2-Bromo-5-trivinylsilylthiophene (D). The procedure used in the preparation of **B** was employed here, but using chlorotrivinylsilane (2.2% ethyl impurities) instead of chlorodimethylvinylsilane. 2-Bromothiophene (24.5 g, 0.15 mol), diisopropylamine (21.3 g, 0.21 mol), *n*-BuLi (72.0 mL, 0.18 mol), and chlorotrivinylsilane (26.0 g, 0.18 mol) were allowed to react in 200 mL of THF. Distillation of the crude mixture provided 2-bromo-5-trivinylsilylthiophene as a clear colorless liquid in 58% yield (23.7 g, bp 110−113 °C/1.0 mmHg).

Preparation of 2-Dimethylsilyl-5-dimethylvinylsilylfuran (1). A 100 mL round-bottomed single-neck flask equipped with a septum, a N_2 gas inlet, and a magnetic stir bar was charged with 0.73 g of magnesium turnings (30.0 mmol). THF was transferred using a cannula to just cover the stir bar. Five drops of compound **A** were added to the flask using a syringe. After the reaction mixture turned green and a precipitate formed, THF (40.0 mL) and compound **A** (6.9 g, 30.0 mmol) were added slowly. After complete disappearance of the magnesium turnings, chlorodimethylsilane (2.7 g, 60.0 mmol) was added slowly via a syringe to the Grignard solution chilled in a water/ice bath. The mixture was then stirred overnight. After a normal aqueous workup, distillation of the crude product provided 2-dimethylsilyl-5-dimethylvinylsilylfuran as a colorless clear liquid in 53% yield (3.36 g, bp 65−66 °C/1.8 mmHg). IR (neat) cm^{-1}: 2133 (Si−H).

Preparation of 2-dimethylsilyl-5-dimethylvinylsilylthiophene (2). The procedure used in the preparation of **1** was employed here. Compound **B** (12.0 g, 48.5 mmol), magnesium turnings (1.8 g, 48.5 mmol), and chlorodimethylsilane (9.2 g, 97.0 mmol) were allowed to react in 60 mL of THF. Distillation of the crude mixture provided 2-dimethylsilyl-5-dimethylvinylsilylthiophene as a clear colorless liquid in 52% yield (5.7 g, bp 90 °C/1.1 mmHg). IR (neat) cm^{-1}: 2129 (Si−H).

Preparation of 2-Dimethylsilyl-5-trivinylsilylfuran (3). The procedure used in the preparation of **1** was employed here. After completion of the addition, the mixture was stirred for 2 h at room temperature and refluxed overnight. Compound **C** (10.0 g, 39.2 mmol), magnesium turnings (0.95 g, 39.2 mmol), and chlorodimethylsilane (7.4 g, 78.4 mmol) were allowed to react in 50 mL of THF. Distillation of the crude mixture provided 2-dimethylsilyl-5-trivinylsilylfuran as a clear colorless liquid in 42% yield (3.9 g, bp 60−64 °C/0.9 mmHg). IR (neat) cm^{-1}: 2134 (Si−H).

Preparation of 2-Dimethylsilyl-5-trivinylsilylthiophene (4). The procedure used in the preparation of **3** was employed here. Compound **D** (8.1 g, 30.0 mmol), magnesium turnings (0.73 g, 30.0 mmol), and chlorodimethylsilane (5.7 g, 60.0 mmol) were allowed to react in 40 mL of THF. Distillation of the crude mixture provided 2-dimethylsilyl-5-trivinylsilylthiophene as a clear colorless liquid in 33% yield (2.5 g, bp 97 °C/0.5 mmHg). IR (neat) cm^{-1}: 2129 (Si−H).

Preparation of Tris(5-dimethylvinylsilyl-2-furyl)silane (5). The procedure used in the preparation of **3** was employed here. Compound **A** (10.0 g, 43.3 mmol), magnesium turnings (1.05 g, 43.3 mmol), and trichlorosilane (1.95 g, 14.4 mmol) were allowed to react in 50 mL of THF. Kugelrohr distillation of the crude mixture provided tris(5-dimethylvinylsilyl-2-furyl)silane as a clear yellow liquid in 50% yield (3.5 g, bp 210−226 °C/0.1 mmHg). IR (neat) cm^{-1}: 2163 (Si−H).

Preparation of Tris(5-dimethylvinylsilyl-2-thienyl)silane (6). The procedure used in the preparation of **3** was employed here. Compound **B** (12.0 g, 48.5 mmol), magnesium turnings (1.19 g, 48.5 mmol), and trichlorosilane (1.65 g, 12.13 mmol) were allowed to react in 50 mL of THF. After all the volatiles were removed under reduced pressure, the crude mixture was dissolved in hexane and filtered through SiO_2. Removal of solvent provided tris(5-dimethylvinylsilyl-2-thienyl)silane as a clear yellow liquid in 64% yield (4.2 g). IR (neat) cm^{-1}: 2144 (Si−H).

Preparation of Bis(5-dimethylvinylsilyl-2-furyl)methylsilane (7). The procedure used in the preparation of **3** was employed here. Compound **A** (10.0 g, 43.3 mmol), magnesium turnings (1.05 g, 43.3 mmol), and dichloromethylsilane (2.48 g, 21.6 mmol) were allowed to react in 50 mL of THF. Distillation of the crude mixture provided bis(5-dimethylvinylsilyl-2-furyl)methylsilane as a clear yellow liquid in 45% yield (3.4 g, bp 105−110 °C/0.1 mmHg). IR (neat) cm^{-1}: 2150 (Si−H).

Preparation of Bis(5-dimethylvinylsilyl-2-thienyl)methylsilane (8). The procedure used in the preparation of **3** was employed here. Compound **B** (12.0 g, 48.5 mmol), magnesium turnings (1.19 g, 48.5 mmol), and dichloromethylsilane (1.87 g, 16.2 mmol) were allowed to react in 50 mL of THF. Kugelrohr distillation of the crude mixture provided bis-(5-dimethylvinylsilyl-2-thienyl)methylsilane as a clear yellow liquid in 60% yield (3.7 g, bp 184−202 °C/0.025 mmHg). IR (neat) cm^{-1}: 2137 (Si−H).

Preparation of Linear Polymer 1P. A 25 mL round-bottomed single-neck flask equipped with a septum, a N_2 gas inlet, and a magnetic stir bar was charged with **1** (1.0 g, 4.8 mmol) and 2 mL of THF. At room temperature, 2 drops of Pt−DVTMDSO were added to the flask. The reaction flask became warm within 10 min. The reaction was monitored using IR spectroscopy. After the reaction was completed, all the volatiles were removed under pressure. The crude product was purified by dissolving in chloroform and precipitating into a large excess of methanol chilled in an acetone/dry ice bath. All volatiles were removed under full vacuum with heating at 70 °C to give **1P** as a black colored sticky polymer in 81% yield (0.81 g). If desired, the black color (possibly colloidal platinum) could be removed by dissolving the crude polymer in hexane and filtering through a pad of silica gel. After precipitation, the polymer was obtained as a yellow sticky material, with properties nearly identical to those of the black-colored polymer.

Preparation of Linear Polymer 2P. The procedure used in the preparation of **1P** was employed here. Compound **2** (1.0 g, 4.4 mmol) was polymerized with 2 drops of Pt−DVTMDSO in 2 mL of THF. Polymer **2P** was obtained as a beige colored solid in 87% yield (0.87 g). As with **1P**, the color could be removed by dissolving the crude polymer in hexane and filtering through a pad of silica gel. After precipitation, the polymer was obtained as a light-yellow powder, with properties nearly identical to those of the beige-colored polymer.

Preparation of Hyperbranched Polymer 3P. A 25 mL round-bottomed single-neck flask equipped with a septum, a N_2 gas inlet, and a magnetic stir bar was charged with **3** (1.0 g, 4.3 mmol) and 2 mL of THF. At room temperature, 2 drops of Pt−DVTMDSO were added to the flask. The reaction flask became warm within 3 h. The reaction was monitored using IR spectroscopy. After the reaction was complete, all volatiles were removed under pressure. Polymer **3P** was obtained as a clear yellow viscous oil in 95% yield (0.95 g).

Preparation of Hyperbranched Polymer 4P. The procedure used in the preparation of **1P** was employed here. Monomer **4** (1.0 g, 4.0 mmol) was polymerized with 2 drops of Pt−DVTMDSO in 2 mL of THF. Polymer **4P** was obtained as a clear yellow tacky polymer in 88% yield (0.88 g).

Preparation of Hyperbranched Polymer 5P. The procedure used in the preparation of **3P** was employed here. Compound **5** (1.0 g, 2.1 mmol) was polymerized with 2 drops of Pt−DVTMDSO in 2 mL of THF. The reaction was complete within 10 min. Polymer **5P** was obtained as a clear yellow viscous oil in 98% yield (0.98 g).

Preparation of Hyperbranched Polymer 6P. The procedure used in the preparation of **1P** was employed here. Compound **6** (1.0 g, 1.9 mmol) was polymerized with 2 drops of Pt−DVTMDSO in 2 mL of THF. Polymer **6P** was obtained as a clear yellow tacky polymer in 80% yield (0.80 g).

Preparation of Hyperbranched Polymer 7P. The procedure used in the preparation of **3P** was employed here. Compound **7** (1.0 g, 2.9 mmol) was polymerized with 2 drops of Pt−DVTMDSO in 2 mL of THF. The reaction was complete within 10 min. Polymer **7P** was obtained as a clear yellow tacky polymer in 83% yield (0.83 g).

Preparation of Hyperbranched Polymer 8P. The procedure used in the preparation of **1P** was employed here. Compound **8** (1.0 g, 2.6 mmol) was polymerized with 2 drops of Pt−DVTMDSO in 2 mL of THF. Polymer **8P** was obtained as a clear yellow sticky polymer in 78% yield (0.78 g).

Acknowledgment. We thank the Welch Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this research. We also thank Dr. Hongming Zhang for determining the X-ray crystal structure of the dimer from compound **1**.

Supporting Information Available: Tables of ^{1}H, ^{13}C, and ^{29}Si NMR data for **A**−**D**, **1**−**8**, and **1P**−**8P**. This material is available free of charge via the Internet at http://pubs.acs.org.

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