Syntheses of Hyperbranched Poly(carbosilarylenes)

Kunsang Yoon and David Y. Son*

Department of Chemistry, P.O. Box 750314, Southern Methodist University, Dallas, Texas 75275-0314

Received February 10, 1999; Revised Manuscript Received June 3, 1999

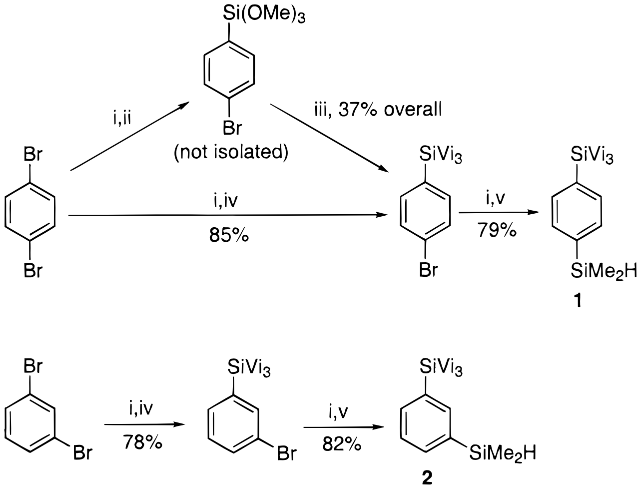
ABSTRACT: New hyperbranched poly(carbosilarylenes) are described that exhibit low glass transition temperatures and high thermal stabilities. The incorporation of Si−O−Si linkages into the branches leads to a polymer of increased flexibility but considerably lower thermal stability. The hyperbranched polymers are prepared via a one-pot hydrosilylation polymerization of aromatic AB_3 monomers. The monomers are prepared from commercially available reagents using lithium−halogen exchange reactions followed by treatment with chlorosilanes. The glass transition temperatures of the hyperbranched polymers range from −45 °C for the siloxane-containing polymer to 12 °C for the 1,4-substituted polymer. Number-average molecular weights (GPC) range from 2560 to 5600. The degree of branching in these polymers was determined by quantitative ^{29}Si NMR spectroscopy and found to be very close to the theoretical value of 0.44 for AB_3 systems.

Introduction

The syntheses and properties of new high-temperature elastomers continue to attract a great amount of interest. A great need for these elastomers exists in numerous fields including aerospace, electrical, and adhesives applications. For these and other applications, high-temperature elastomers should exhibit stability to air and moisture at temperatures approaching 350 °C and should also maintain flexibility to temperatures below ambient. Thus far, poly(siloxanes) have shown considerable promise as high-temperature elastomers.[1] Poly(siloxanes) generally possess excellent elasticity in addition to relatively good thermal stability. Poly(siloxanes) containing arylene groups in the backbone have received special attention due to the increased thermal stability and improved mechanical properties afforded by the arylene groups.[2] However, the elevated glass transition temperatures (T_g's) and increased crystallinity of these poly(silarylene−siloxanes) limit their application at lower temperatures. Furthermore, the presence of arylene groups does not prohibit thermal depolymerization of the polymers,[3] which occurs via the formation of volatile low molecular weight siloxane oligomers beginning at temperatures around 400 °C.[3,4] This thermal depolymerization process is common to poly(siloxanes) in general and places limitations on the maximum temperatures at which poly(siloxanes) may be used. Elimination of the siloxane linkages in the poly(silarylene−siloxane) backbones would seem to be an obvious method for avoiding this depolymerization; however, the resulting loss of flexibility in the polymer structures leads to powdery products.[5]

Recently, hyperbranched polymers have attracted much research interest.[6] These unique highly branched polymers possess lower melt viscosities and greater solubilities compared to analogous linear polymers. Furthermore, in contrast to dendrimers, hyperbranched polymers are prepared in a single-step process from starting monomer. In view of these desirable characteristics, the design of hyperbranched poly(*carbosilarylenes*) seemed a practical and realistic goal. Although hyperbranched poly(carbosilanes) are known,[7] no examples of aryl-containing hyperbranched poly(carbosilanes) have been reported. As mentioned previously, the presence of arylene groups would enhance the thermal stability in the polymer. Furthermore, the removal of siloxane linkages from the polymer might also increase the thermal stability by eliminating the thermal depolymerization process. The corresponding loss of flexibility might then be counterbalanced by the inherent flexible nature of hyperbranched polymers in the bulk, which could possibly lead to nonpowdery polymers of relatively low T_g's. Therefore, hyperbranched poly(carbosilarylenes) could conceivably be precursors to elastomeric networks. In this report we describe the syntheses of these polymers that, in addition to possessing potentially useful properties, represent a new structural type of hyperbranched polymer accessible by hydrosilylation polymerization.

Scheme 1. Vi = $CH{=}CH_2$. Reagents and Conditions (i): 1 equiv *n*-BuLi/THF; (ii) 1 equiv $ClSi(OMe)_3$; (iii) 3 equiv ViMgBr; (iv) 1 equiv $ClSiVi_3$; (v) 1 equiv $ClSiMe_2H$



Results and Discussion

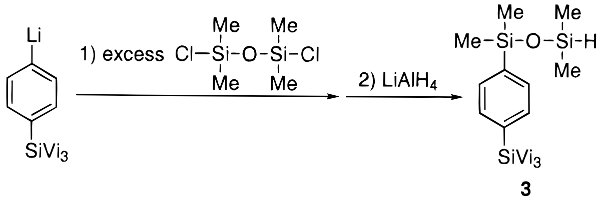
Monomer Synthesis. The silarylene monomers we chose to synthesize for this investigation are AB_3 monomers, shown in Scheme 1 as **1** and **2**. These

---

* Corresponding author. E-mail: dson@mail.smu.edu.

10.1021/ma9901902 CCC: $18.00

Scheme 2. Synthesis of Monomer 3



3
50% overall

monomers are designed to undergo polymerization via hydrosilylation, a method of choice for the preparation of hyperbranched poly(carbosilanes)[7b−d] and poly(carbosiloxanes).[8] In our initial synthesis of **1**, we prepared 1-bromo-4-trimethoxysilylbenzene from the reaction of 1-bromo-4-lithiobenzene[9] with chlorotrimethoxysilane. This product was then reacted in situ with vinylmagnesium bromide, and the intermediate 1-bromo-4-trivinylsilylbenzene was obtained in 37% distilled yield. While this yield was acceptable to us, we sought to improve the yield and perhaps shorten this part of the monomer synthesis. At this point, we discovered the commercial availability of chlorotrivinylsilane.[10] Treating 1-bromo-4-lithiobenzene with this compound gave 1-bromo-4-trivinylsilylbenzene in 85% yield after distillation. This represents our preferred synthesis of 1-bromo-4-trivinylsilylbenzene due to the shorter reaction sequence and the augmented yield. Subsequent treatment of this compound with *n*-BuLi followed by reaction with chlorodimethylsilane gave **1** in 79% yield after distillation (67% overall from 1,4-dibromobenzene). Monomer **2** was prepared in an analogous manner from 1,3-dibromobenzene (64% overall yield, Scheme 1). Both compounds **1** and **2** are clear, colorless liquids and are stable to air and moisture. An additional feature of this general synthetic sequence is that it may conceivably be used to prepare similar monomers from any starting compound that can be sequentially functionalized via anionic intermediates.

Monomer **3** was also prepared as shown in Scheme 2. The addition of 1-lithio-4-trivinylsilylbenzene to excess 1,3-dichlorotetramethyldisiloxane followed by $LiAlH_4$ reduction yielded **3** in 50% isolated yield. Unlike compounds **1** and **2**, monomer **3** contains a siloxane linkage which should result in a polymer of greater flexibility but decreased thermal stability. This would then provide a useful comparison to the polymers derived from **1** and **2**.

Polymerizations and Characterization. The hydrosilylation polymerizations of **1**−**3** proved to be straightforward and rapid. In a typical experiment, 3.04 g of **1** (12.4 mmol) and 10 mL of THF were added to a 25 mL two-necked round-bottomed flask equipped with a stir bar. Several drops of platinum catalyst solution[11] were added to the mixture at room temperature. Commencement of reaction was noted by the evolution of heat within 5 min. After the heat had dissipated, the flask was heated intermittently with a heat gun for 10 min and then stirred at room temperature for 1 h. The reaction was complete at this point, as observed by the total disappearance of the Si−H absorbance in the IR spectrum (2119−2124 cm^{-1}). The hyperbranched polymer (**1P**) was isolated by adding the reaction mixture dropwise to a large excess of methanol cooled in a dry ice/acetone bath followed by rapid vacuum filtration. The general stepwise formation of **1P** is shown in Scheme 3. The polymerizations of **2** and **3** to yield hyperbranched polymers **2P** and **3P** were performed in a similar fashion. Polymers **1P**, **2P**, and **3P** are soluble in common organic solvents and are completely stable to air and moisture. One feature of these polymerizations is that a large excess of vinyl groups will remain unreacted in the hyperbranched polymers. These groups can be used for vulcanization or for further functionalization reactions.

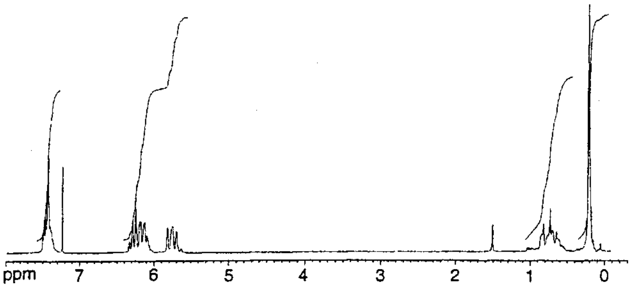
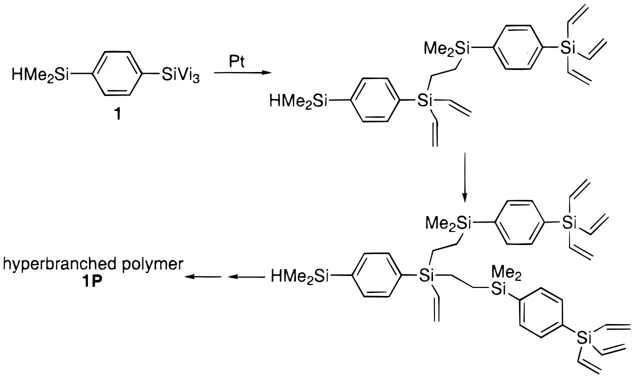
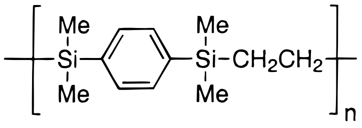


Figure 1. ^1H NMR spectrum of **1P** in $CDCl_3$ (peak at δ 1.5 is attributed to H_2O).

Scheme 3. Synthesis and General Structure of 1P



Polymer **1P** was isolated as a white, sticky solid in 93% yield after precipitation. The ^1H NMR spectrum of **1P** (Figure 1) indicates that the polymerization proceeded as expected. The peak corresponding to Si−H protons has disappeared (δ 4.41), and new peaks are evident in the region δ 0.5−1.0 corresponding to the newly formed $-CH_2CH_2-$ groups. GPC molecular weight data for **1P** ($M_n = 5600$, $M_w = 16\,000$, referenced to poly(styrene)) indicated a broad weight distribution, a common characteristic of hyperbranched polymers.[6] Vapor pressure osmometry (VPO) measurements indicated a molecular weight of 4060. The branched nature of the polymer was verified by ^{29}Si NMR spectroscopy, which indicated signals for the various types of silicon atom branch points (vide infra). Polymer **1P** exhibits both good flexibility and excellent thermal stability. Differential scanning calorimetry (DSC) indicated a relatively low T_g of 12 °C despite the presence of arylene groups along the backbone and the lack of flexible siloxane linkages in the polymer. No melting point was observed. An exothermic process also occurred with maximum heat evolution at 349 °C, as indicated by DSC. The explanation for this is unclear at this point but may possibly indicate a cross-linking reaction occurring between the vinyl groups in the polymer. Thermogravimetric analysis (TGA) indicated only a 31% weight loss when **1P** was heated to 975 °C in a nitrogen atmosphere. This is increased stability compared to the case of conventional linear poly(silarylene−siloxanes).[12] Preliminary isothermal heating studies were also carried out on **1P**. Heating **1P** at 277 °C in nitrogen for



4

Figure 2. Known linear polymer **4**.

Table 1. Comparison of Properties between 1P and 4

	polymer **1P**	polymer **4**
physical appearance	white, sticky solid	white powder
molecular weight[a]	$M_n = 5600$	$M_n = 7300$
T_g	12 °C	none
melting point	none	182−184 °C
solubility	very soluble in common solvents including hexane, $CHCl_3$, THF, and toluene	>200 mL of either $CHCl_3$, THF, or toluene required to dissolve 1 g[b]
TGA weight loss (in N_2)	31% (to 975 °C)	27.6% (to 500 °C); ~45% (to 580 °C)

[a] GPC, calibrated to poly(styrene). [b] Solubility for samples of molecular weight ~1000 was also low.

2.5 h resulted in only a 2.6% weight loss. On performing the same experiment in air, a 1% weight loss was observed. Heating **1P** at 365 °C for 2.5 h separately in air and nitrogen resulted in 5% and 21% weight losses, respectively.

On comparing these overall properties of **1P** to those of an analogous linear polymer, we observed several differences that would be expected on the basis of the contrasting backbone structures. The structure of the known linear polymer (**4**)[13] is shown in Figure 2. General properties of **4** are listed in Table 1 along with those of **1P** for comparative purposes. As might be expected, it appears that the hyperbranched structure has significant effects on properties such as crystallinity and solubility. We noted a lack of crystallinity in **1P** and also excellent solubility in common solvents including hexane. The thermal stability of **1P** is also significantly enhanced compared to the case of **4**. However, it should be noted that this may be due to the presence of vinyl groups in **1P** rather than the difference in backbone structure; pendant vinyl groups are known to improve thermal stability in poly(siloxanes) and poly(carbosilanes).[14]

The reason for preparing and polymerizing monomer **2** was to examine the effects of introducing meta-bending linkages into the hyperbranched polymer backbone. In linear polymers, such linkages are known to decrease polymer crystallinity and increase processability.[2c,15] The effects of these meta-bending linkages were immediately apparent in the physical appearance of polymer **2P**, which was isolated as a viscous white *oil* in 87% yield after precipitation. The IR and NMR spectral data were similar to the results obtained for **1P**. Molecular weight values were slightly lower (M_n = 3200, M_w = 7500, VPO: 2420) compared to the case of **1P**. As expected, the T_g of **2P** (−25 °C) was significantly lower than that of **1P**, an effect we attribute to the meta-bending linkages. However, the bending linkages appeared to have little or no effect on thermal stability, evidenced by polymer **2P** exhibiting only a 32% weight loss when heated to 975 °C in nitrogen.

Since the preparations of both **1P** and **2P** are identical, it should also be possible to synthesize random copolymers from mixtures of **1** and **2**. These copolymers could then possess properties intermediate to those of **1P** and **2P**. To test the feasibility of this approach, we polymerized a 50/50 mixture of **1** and **2** in the usual manner. The resulting polymer was isolated in 95% yield after precipitation as a very thick, white oil. The molecular weight values (M_n = 4400, M_w = 11 000, VPO: 3080) and T_g (−15 °C) were indeed intermediate to the values obtained separately for **1P** and **2P**. Thermal stability was also similar, with this copolymer losing only 29% of its mass on heating to 975 °C in nitrogen. Thus, it would seem possible to selectively prepare a copolymer of specific properties by simply varying the ratio of starting monomers.

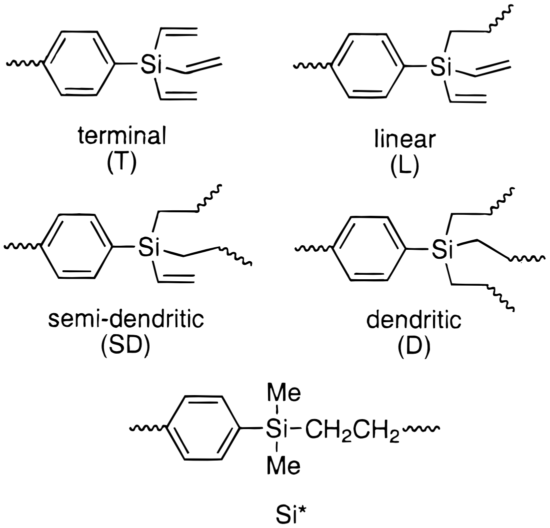


Figure 3. Five possible environments for silicon atoms in **1P**.

For the purpose of thermal stability comparisons, hyperbranched polymer **3P** was prepared from monomer **3**. The polymerization proceeded in the usual manner, and polymer **3P** was obtained as a yellow viscous oil in 89% yield after low-temperature precipitation from methanol. The IR and NMR spectra indicated that the expected polymerization had taken place. As expected, the T_g of **3P** was lower (−45 °C) than that of either **1P** or **2P**. Thermal stability was also poorer, indicated by a 45% weight loss on heating to 940 °C in a nitrogen atmosphere. This decreased thermal stability can be attributed to the thermal depolymerization mechanism common to poly(silarylene−siloxanes).[3,4]

Structure and Degree of Branching. Due to the nature of the polymerization process, the hyperbranched polymers possess random, highly branched structures. In theory, each of the silicon atoms in the polymers exists in one of five possible local environments, as illustrated in Figure 3 for polymer **1P**. The silicon atom labeled "Si*" represents the silicon atoms that were originally bonded to hydrogen in the starting monomer. It should be apparent that the sum of the terminal (T), linear (L), semidendritic (SD), and dendritic (D) silicon atoms should equal the total number of Si* silicon atoms. The degree of branching (DB)[16] can also be calculated if the relative amounts of each type of silicon atom can be determined.

^{29}Si NMR spectroscopy proved to be a useful tool to verify the branched nature of the polymers and for the determination of degree of branching. The quantitative ^{29}Si NMR spectrum of polymer **1P** is shown in Figure 4 (integrals are omitted for clarity). To obtain quantitative ^{29}Si NMR data, it was necessary to employ an inverse

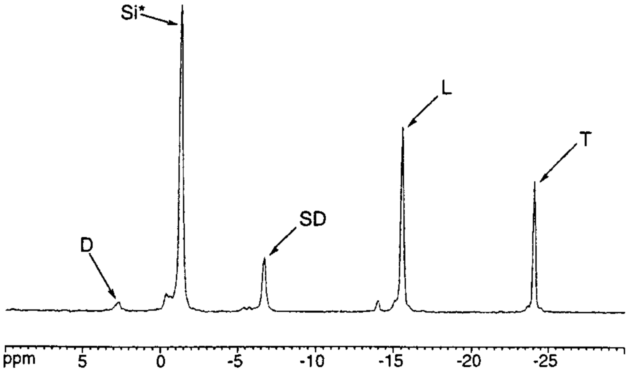


Figure 4. Quantitative ^{29}Si NMR spectrum of **1P** in Cr(acac)$_3$/CDCl$_3$ (0.1 M Cr(acac)$_3$).

gated ^1H-decoupling acquisition sequence in order to suppress NOE effects. In addition, Cr(acac)$_3$ was added to the CDCl$_3$ solvent as a relaxation agent. As indicated on the spectrum, the principal peaks in the spectrum correspond to the various types of silicon atoms in **1P**. The chemical shifts correspond closely with values for analogous small molecule model compounds.[17] Furthermore, the sum of the D, SD, L, and T peak integrations is within 3% of the Si* peak integration. From this spectral data, the relative amounts of each of the silicon atom types in **1P** can be calculated. The D:SD:L:T ratio in **1P** is 1:4.25:11:7, which is reasonably close to the statistically expected ratio of 1:6:12:8.[16c] Once this ratio had been determined, calculation of DB was a relatively simple process. Using the equations derived by Frey and co-workers,[16c] we obtained DB = 0.42 for polymer **1P**. This value is quite close to the theoretical value of 0.44 for AB$_3$ systems. These calculations can be repeated for polymer **2P**. For this polymer, we obtained a D:SD:L:T ratio of 1:3.9:9:5.9 and a DB = 0.44.

Conclusion

We have prepared novel hyperbranched poly(carbosilarylenes) that represent a new type of hyperbranched topology achievable via hydrosilylation polymerization. These highly branched polymers exhibit excellent thermal stability and relatively low glass transition temperatures in comparison to similar known linear polymers. As expected, incorporation of siloxane linkages into the hyperbranched polymer structure lowers the glass transition temperature and results in noticeably lower thermal stability. Glass transition temperatures can also be tailored by adjusting the ratio of 1,4- and 1,3-monomers in the initial polymerization mixture. The structures and degrees of branching in the polymers were investigated using ^{29}Si NMR spectroscopy and were found to correspond closely to theoretical predictions. These polymers can conceivably be converted to elastomeric networks by cross-linking reactions involving the excess unreacted vinyl groups in the polymers (e.g., hydrosilylation reactions with multifunctional SiH-containing compounds). Current investigations are focusing on devising more economical monomer preparations and also methods for controlling molecular weight in 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 (hexane solution, 2.5 M), 1,4-dibromobenzene, 1,3-dibromobenzene, chlorotrivinylsilane (Gelest), magnesium turnings, vinyl bromide, and chlorodimethylsilane. Tetrahydrofuran (THF) was distilled from Na/benzophenone under a N$_2$ atmosphere prior to use. Karstedt's catalyst in xylene (platinum−divinyltetramethyldisiloxane complex, Pt−DVTMDSO) was purchased from either Gelest, Inc., or United Chemical Technologies and used as received. Chlorotrimethoxysilane was synthesized according to a literature preparation.[18]

The ^1H, ^{13}C, and ^{29}Si NMR spectra were performed 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 ^1H decoupling sequence. Samples were prepared in Cr(acac)$_3$/CDCl$_3$ solution (0.1 M Cr(acac)$_3$). Elemental analyses were obtained from E+R Microanalytical Laboratory, Corona, NY. Glass transition temperatures (T_g) were measured using a Dupont DSC model 910 instrument equipped with a TA Operating Software Module and Data Analysis data station. Temperature was increased at a heating rate of 10 °C/min. 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-Bu)$_4$NBr], a column temperature of 30 °C, and a 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. 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.

Preparation of 1-Bromo-4-trivinylsilylbenzene Using Chlorotrimethoxysilane (First Approach). A 1 L round-bottomed flask equipped with a magnetic stir bar, septum, and a gas-inlet needle was charged with 47.2 g of 1,4-dibromobenzene (0.20 mol) and 400 mL of THF. The flask was cooled in an acetone/dry ice bath, and 84 mL of *n*-BuLi (0.21 mol, 2.5 M solution in hexanes) was then added slowly via syringe, which caused the formation of a yellowish-white precipitate. After stirring for an additional 1 h, the white suspension was cannulated into another 1 L round-bottomed flask charged with 0.21 mol of chlorotrimethoxysilane and 200 mL of THF. During the transfer, both flasks were placed in acetone/dry ice baths. The resulting mixture was a colorless clear solution. After stirring cold for an additional 15 min, the mixture was allowed to warm to room temperature and stirred overnight.

For the preparation of the vinyl Grignard reagent, a 2 L three-necked, round-bottomed flask equipped with a stir bar, septum, a pressure equalizing addition funnel with a rubber septum on top, and a dry ice condenser connected to a N$_2$ gas inlet tube was charged with 20.4 g of magnesium turnings (0.84 g atom). The magnesium turnings were stirred for several minutes while dry, and then a small piece of iodine was added to activate the magnesium. A 65.2 mL aliquot of vinyl bromide (0.924 mol) was measured in a graduated cylinder cooled in an acetone/dry ice bath, and then 60 mL of THF was added to the graduated cylinder. The vinyl bromide solution was cannulated to the addition funnel. Enough THF was added to barely cover the magnesium. Approximately 5 mL of the vinyl bromide solution was added to the reaction flask. After approximately 10 min of moderate heating with a heat gun, the flask became very warm, indicating that the reaction had started. Additional THF (160 mL) was added to the flask, and then the vinyl bromide solution was added slowly at a rate to maintain a gentle reflux. After all the magnesium had disappeared, the dry ice condenser was switched to a regular water condenser, and the mixture was refluxed for 30 min to remove unreacted vinyl bromide, leaving a clear brown solution.

The flask containing the vinyl Grignard reagent was placed in a water/ice bath, and the prepared crude 1-bromo-4-trimethoxysilylbenzene solution was added slowly via cannula, which caused the clear brown solution to change to a greenishwhite color. The cold bath was removed, and the mixture was refluxed for 4 h. The mixture was quenched with an ice-cold aqueous solution of 10% HCl. The layers were separated, and the aqueous layer was extracted twice with ether. The organic layers were combined and 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. Most of the volatiles were removed using a rotary evaporator, leaving a clear brown liquid. Distillation of the crude product gave 1-bromo-4-trivinylsilylbenzene as a clear colorless liquid in 37% yield (19.7 g, bp 62−63 °C/0.005 mmHg). ^{1}H NMR: δ 5.79 (dd, 3 H, C═C*H*H, ^2J = 4.5 Hz, ^3J = 19.4 Hz), 6.19 (dd, 3 H, C═CH*H*, ^2J = 4.5 Hz, ^3J = 14.6 Hz), 6.27 (dd, 3 H, C*H*═CH$_2$, ^3J = 15 Hz, ^3J = 19.4 Hz), 7.38 (d, 2 H, aromatic, J = 7.9 Hz), 7.49 (d, 2 H, aromatic, J = 8.1 Hz). ^{13}C NMR: δ 124 (aromatic *C*Si), 131 (aromatic), 133.0 (aromatic), 133.1 (*C*Br), 136.1 (C═*C*H$_2$), 136.4 (*C*H═CH$_2$). IR (neat) cm^{-1}: 3051 (m), 3007 (w), 2969 (m), 2945 (m), 1590 (m), 1573 (s), 1552 (w), 1479 (m), 1402 (s), 1378 (m), 1108 (w), 1066 (s), 1009 (s), 959 (s), 808 (s), 729 (s), 640 (s). Anal. Calcd for $C_{12}H_{13}SiBr$: C, 54.34; H, 4.94. Found: C, 54.54; H, 4.93.

Preparation of 1-Bromo-4-trivinylsilylbenzene Using Chlorotrivinylsilane (Preferred Approach). A 1 L three-necked, round-bottomed flask equipped with a magnetic stir bar, septum, an addition funnel, and a gas inlet needle was charged with 70.8 g of 1,4-dibromobenzene (0.3 mol) and 600 mL of THF. The flask was cooled in an acetone/dry ice bath. To the addition funnel was cannulated 122 mL of *n*-BuLi (0.306 mol, 2.5 M solution in hexanes) from a graduated cylinder. The *n*-BuLi was added dropwise to the flask, resulting in the formation of a yellowish-white suspension. After the addition was complete, the mixture was stirred for an additional 50 min in the cold bath. Chlorotrivinylsilane (47.4 mL, 0.306 mol) was added slowly via syringe, and the mixture became a clear yellow solution. After an additional stirring for 10 min, the mixture was allowed to warm to room temperature for 1 h, resulting in a clear light yellow solution. The mixture was then poured into 400 mL of ice-cold 10% HCl solution. The layers were separated, and the aqueous layer was extracted twice with ether. The organic layers were combined and 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. Most of the volatiles were removed using a rotary evaporator leaving a clear yellow solution. Further purification of the crude product by distillation gave 1-bromo-4-trivinylsilylbenzene as a clear colorless liquid in 85% yield (67.5 g). See above for characterization details.

Preparation of 1-Dimethylsilyl-4-trivinylsilylbenzene, 1. A 1 L round-bottomed flask equipped with a magnetic stir bar, septum, and a gas inlet needle was charged with 54.1 g of 1-bromo-4-trivinylsilylbenzene (0.204 mol) and 300 mL of THF. The flask was cooled in an acetone/dry ice bath, and 81.6 mL of *n*-BuLi (0.204 mol, 2.5 M solution in hexanes) was added slowly via syringe, resulting in the formation of a yellow suspension. After an additional stirring for 1 h, chlorodimethylsilane (24.7 mL, 0.222 mol) was added quickly. After stirring cold for an additional 15 min, the mixture was allowed to warm up to room temperature for 1 h, after which it became a clear, colorless solution. The mixture was poured into an ice-cold solution of 10% hydrochloric acid. The layers were separated, and the aqueous layer was extracted twice with ether. The organic layers were combined and 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. Most of the volatiles were removed using a rotary evaporator. The crude product was further purified by distillation to give **1** as a clear, colorless liquid in 79% yield (39.4 g, bp 67−69 °C/0.03 mmHg). ^{1}H NMR: δ 0.33 (d, 6 H, SiC*H*$_3$, ^3J = 3.75), 4.41 (sept, 1 H, Si*H*, ^3J = 3.8 Hz), 5.82 (dd, 3 H, C═C*H*H, ^2J = 4.1 Hz, ^3J = 19.9 Hz), 6.19 (dd, 3 H, C═CH*H*, ^2J = 4.1 Hz, ^3J = 14.6 Hz), 6.31 (dd, 3 H, C*H*═CH$_2$, ^3J = 14.6 Hz, ^3J = 19.9 Hz), 7.53 (s, 4 H, aromatic). ^{13}C NMR: δ −3.88 (Si*C*H$_3$), 133.3 (aromatic), 133.7 (*C*H═CH$_2$), 134.4 (aromatic), 135.4 (aromatic *C*Si), 135.9 (CH═*C*H$_2$), 138.6 (aromatic *C*Si). ^{29}Si NMR: δ −23.9 (*Si*Vi$_3$), −16.98 (*Si*H, $J_{(\mathrm{SiH})}$ = 192.4 Hz). IR (neat) cm^{-1}: 3050 (s), 3004 (m), 2966 (s), 2945 (s), 2120 (s), 1591 (m), 1402 (s), 1379 (m), 1250 (s), 1134 (s), 1008 (s), 958 (s), 879 (s), 836 (s), 808 (m), 765 (s), 745 (s), 727 (s), 660 (s), 632 (s). Anal. Calcd for $C_{14}H_{20}Si_2$: C, 68.78; H, 8.25. Found: C, 68.98; H, 7.91.

Preparation of 1-Bromo-3-trivinylsilylbenzene. The second procedure used in the preparation of 1-bromo-4-trivinylsilylbenzene was employed for this preparation, using 1,3-dibromobenzene instead of 1,4-dibromobenzene. 1,3-Dibromobenzene (14.8 mL, 0.12 mol), 49.0 mL of *n*-BuLi (0.122 mol, 2.5 M solution in hexanes), and 19.0 mL of chlorotrivinylsilane (0.122 mol) were allowed to react in 200 mL of THF. The distillation of the crude mixture provided 1-bromo-3-trivinylsilylbenzene as a clear, colorless liquid in 78% yield (24.9 g, bp 65−66 °C/0.01 mmHg). ^{1}H NMR: δ 5.82 (dd, 3 H, C═C*H*H, ^2J = 4.9 Hz, ^3J = 19.6 Hz), 6.21 (dd, 3 H, C═CH*H*, ^2J = 4.8 Hz, ^3J = 14.6 Hz), 6.28 (dd, 3 H, C*H*═CH$_2$, ^3J = 14.6 Hz, ^3J = 19.0 Hz), 7.22 (t, 1 H, aromatic, J = 7.6 Hz), 7.44 (d, 1 H, aromatic, J = 8.0 Hz), 7.50 (d, 1H, aromatic, J = 8.0), 7.63 (s, 1H, aromatic). ^{13}C NMR: δ 122.8 (aromatic *C*Si), 129.4 (aromatic), 132.2 (aromatic), 133.2 (aromatic), 137.3 (aromatic), 132.8 (*C*H═CH$_2$), 136.3 (CH═*C*H$_2$). IR (neat) cm^{-1}: 3051 (m), 3007 (w), 2969 (m), 2945 (m), 1591 (m), 1552 (m), 1464 (m), 1402 (s), 1385 (s), 1125 (s), 1113 (m), 1085 (w), 1069 (m), 1007 (s), 960 (s), 780 (m), 758 (m), 730 (s), 689 (m), 659 (s), 621 (m), 550 (s). Anal. Calcd for $C_{12}H_{13}SiBr$: C, 54.34; H, 4.94. Found: C, 54.36; H, 4.96.

Preparation of 1-Dimethylsilyl-3-trivinylsilylbenzene, 2. The procedure used in the preparation of **1** was employed here, but using 1-bromo-3-trivinylsilylbenzene instead of 1-bromo-4-trivinylsilylbenzene. 1-Bromo-3-trivinylsilylbenzene (21.4 g, 80.7 mmol) and 32.3 mL of *n*-BuLi (80.7 mmol, 2.5 M solution in hexanes) were allowed to react in 140 mL of THF, and then 9.4 mL of chlorodimethylsilane (84.7 mmol) was added quickly. After a normal aqueous workup, the distillation of the crude product provided **2** as a colorless, clear liquid in 82% yield (16.1 g, bp 61 °C/0.025 mmHg). ^{1}H NMR: δ 0.33 (d, 6 H, SiC*H*$_3$, ^3J = 3.75), 4.41 (sept, 1H, Si*H*, ^3J = 3.7 Hz), 5.82 (dd, 3 H, C═C*H*H, ^2J = 4.1 Hz, ^3J = 19.9 Hz), 6.19 (dd, 3 H, C═CH*H*, ^2J = 4.1 Hz, ^3J = 14.6 Hz), 6.32 (dd, 3 H, C*H*═CH$_2$, ^3J = 14.6 Hz, ^3J = 20.0 Hz), 7.35 (t, 1 H, aromatic, J = 7.3 Hz), 7.55 (mult, 2 H, aromatic), 7.70 (s, 1 H, aromatic). ^{13}C NMR: δ −3.9 (Si*C*H$_3$), 127.2 (aromatic), 133.6 (aromatic *C*Si), 133.7 (aromatic), 133.7 (*C*H═CH$_2$), 135.7 (CH═*C*H$_2$), 135.8 (aromatic), 136.5 (aromatic *C*Si), 140.5 (aromatic). ^{29}Si NMR: δ −23.68 (*Si*Vi$_3$), −16.81 (*Si*H, $J_{(\mathrm{SiH})}$ = 188.5 Hz). IR (neat) cm^{-1}: 3051 (s), 3007 (m), 2965 (s), 2946 (s), 2902 (m), 2119 (s), 1591 (m), 1575 (w), 1402 (s), 1365 (s), 1250 (s), 1178 (w), 1143 (w), 1106 (s), 1008 (s), 958 (s), 882 (s), 837 (s), 778 (s), 760 (s), 728 (s), 678 (m), 648 (m), 626 (s), 550 (s). Anal. Calcd for $C_{14}H_{20}Si_2$: C, 68.78; H, 8.25. Found: C, 68.87; H, 8.23.

Preparation of 1-Tetramethyldisiloxyl-4-trivinylsilylbenzene, 3. A 250 mL Schlenk flask equipped with a septum, a magnetic stir bar, and gas inlet tube was charged with 1-bromo-4-trivinylsilylbenzene (25.0 g, 94.2 mmol) and 100 mL of THF. The flask was placed into an acetone/dry ice bath, and 37.7 mL of *n*-BuLi (94.2 mmol, 2.5 M solution in hexanes) was added slowly via syringe. After stirring cold for an additional 1 h, the clear yellow solution was cannulated slowly to another 500 mL round-bottomed flask which contained 36.8 mL of 1,3-dichlorotetramethyldisiloxane (188 mmol) and 130 mL of THF, cooled in an acetone/dry ice bath. The mixture was stirred for an additional 15 min and then allowed to warm up to room temperature over 1 h. A 1 L round-bottomed flask equipped with a septum and a nitrogen inlet needle was charged with $LiAlH_4$ (5.36 g, 0.141 mol) and 210 mL of THF and cooled in a water/ice bath. The reaction mixture was slowly cannulated to the $LiAlH_4$ suspension. After stirring for 15 min, the mixture was warmed to room temperature over 1 h. The dark gray suspension was poured into an ice-cold aqueous solution of 15% hydrochloric acid and then filtered over Celite. The layers were separated and the aqueous layer was extracted twice with ether. The organic layers were combined and washed twice with distilled water and once with saturated aqueous sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and then filtered. Most of the volatiles were removed using a rotary evaporator. The crude product was further purified by distillation and **3** was obtained as a clear, colorless liquid in 50% yield (14.7 g, bp 80 °C/0.005 mmHg). ^{1}H NMR: δ 0.17 (d, 6 H, HSiCH_3, $^3J = 3.75$), 0.32 (s, 6 H, SiCH_3) 4.73 (sept, 1H, SiH, $^3J = 2.7$ Hz), 5.81 (dd, 3 H, C=CHH, $^2J = 4.1$ Hz, $^3J = 19.9$ Hz), 6.19 (dd, 3 H, C=CHH, $^2J = 4.1$ Hz, $^3J = 14.6$ Hz), 6.31 (dd, 3 H, CH=CH$_2$, $^3J = 14.6$ Hz, $^3J = 19.9$ Hz), 7.53 (s, 4 H, aromatic). ^{13}C NMR: δ 0.37 (SiCH$_3$), 0.61 (SiCH$_3$), 132.1 (aromatic), 133.6 (CH=CH$_2$), 134.1 (aromatic), 135.4 (aromatic), 135.7 (CH=CH$_2$), 140.6 (aromatic). ^{29}Si NMR: δ −23.89 (SiVi$_3$), −5.31 (SiH, $J_{(\mathrm{SiH})} = 204.1$ Hz), −0.28 (PhSiO). IR (neat) cm^{-1}: 3051 (m), 3005 (w), 2959 (m), 2124 (m), 1591 (w), 1402 (s), 1380 (w), 1255 (s), 1135 (s), 1062 (br, s), 1008 (s), 958 (s), 911 (s), 833 (s), 818 (s), 803 (s), 783 (s), 745 (s), 729 (s), 708 (s), 660 (s), 636 (m). Anal. Calcd for $C_{16}H_{26}Si_3O$: C, 60.31; H, 8.23. Found: C, 59.70; H, 8.37.

Preparation of Hyperbranched Polymer 1P. A 25 mL two-necked, round-bottomed, flask equipped with a septum, a magnetic stir bar, and a gas-inlet needle was charged with **1** (3.04 g, 12.4 mmol) and 10 mL of THF. At room temperature, several drops of Pt−DVTMDSO were added to the flask. The reaction flask became warm within 5 min. When the flask had cooled, the mixture was heated moderately with a heat gun for 10 min and was then stirred for 1 h at room temperature. The reaction was monitored using IR spectroscopy. After the reaction was complete, the mixture was cooled in an acetone/dry ice bath and then added dropwise to 100 mL of methanol cooled in an acetone/dry ice bath. A white powder was precipitated and then filtered quickly using a Buchner funnel. The powder was transferred to a 100 mL Schlenk flask before complete drying because the powder became sticky on warming to room temperature. Volatiles were removed under full vacuum for 24 h to give a white, slightly sticky solid in 93% yield ($T_g = 12$ °C). $M_n = 5620$, $M_w = 16\,000$, polydispersity = 2.84. VPO molecular weight: 4060. ^{1}H NMR: δ 0.20−0.23 (6 H, SiCH_3), 0.65−0.83 (4 H, CH_2CH_2), 5.64−6.31 (6 H, vinyl), 7.39−7.49 (4 H, aromatic). ^{13}C NMR: δ −3.89, 0.78, 3.68, 4.61, 7.33, 7.51, 132.7−140.3 (many peaks). ^{29}Si NMR: δ −24.2 (SiVi$_3$), −15.6 (SiVi$_2$), −6.68 (SiVi), −1.32 (SiCH$_3$), 2.69 (Si(CH$_2$CH$_2$)$_3$). IR (neat) cm^{-1}: 3048 (s), 2999 (m), 2950 (s), 2908 (s), 2878 (m), 2790 (w), 1591 (w), 1403 (s), 1379 (m), 1248 (s), 1133 (s), 1053 (m), 1008 (s), 957 (s), 838 (s), 816 (s), 801 (s), 758 (s), 729 (s), 650 (s), 499 (s). Anal. Calcd for $C_{14}H_{20}Si_2$: C, 68.78; H, 8.25. Found: C, 68.83; H, 8.27.

Preparation of Hyperbranched Polymer 2P. This hyperbranched polymer was prepared using essentially the same procedure used in the preparation of hyperbranched polymer **1P**. At room temperature, compound **2** (3.26 g, 13.3 mmol) and several drops of Pt−DVTMDSO were stirred in 10 mL of THF for 1 h. Low-temperature (−78 °C) precipitation provided a white, viscous oil in 87% yield ($T_g = -25$ °C). $M_n = 3180$, $M_w = 7540$, polydispersity = 2.37. VPO molecular weight: 2420. ^{1}H NMR: δ 0.22 (6 H, SiCH_3), 0.64−0.82 (4 H, CH_2CH_2), 5.70−6.30 (6 H, vinyl), 7.29−7.62 (4 H, aromatic). ^{13}C NMR: δ −3.64, 4.02, 4.90, 7.80, 126.9−140.2 (many peaks). ^{29}Si NMR: δ −24.0 (SiVi$_3$), −15.4 (SiVi$_2$), −6.54 (SiVi), −1.29 (SiCH$_3$), 2.66 (Si(CH$_2$CH$_2$)$_3$). IR (neat) cm^{-1}: 3048 (m), 3008 (m), 2951 (s), 2908 (m), 1591 (w), 1574 (w), 1402 (s), 1362 (s), 1248 (s), 1132 (s), 1106 (s), 1053 (m), 1008 (s), 956 (s), 838 (s), 774 (s), 754 (s), 709 (s), 626 (m).

Preparation of 50/50 Hyperbranched Copolymer from 1 and 2. This hyperbranched polymer was prepared using essentially the same procedure used in the preparation of hyperbranched polymers **1P** and **2P**. At room temperature, compound **1** (1.51 g, 6.19 mmol), compound **2** (1.51 g, 6.18 mmol), and several drops of Pt−DVTMDSO were stirred in 10 mL of THF for 1 h. Low-temperature (−78 °C) precipitation provided a white, very viscous oil in 95% yield ($T_g = -15$ °C). $M_n = 4370$, $M_w = 11\,150$, polydispersity = 2.55. VPO molecular weight: 3080. ^{1}H NMR: δ 0.24 (6 H, SiCH_3), 0.66−0.85 (4 H, CH_2CH_2), 5.72−6.36 (6 H, vinyl), 7.24−7.67 (4 H, aromatic). ^{13}C NMR: δ −3.54, −3.44, 4.15, 4.70, 4.98, 5.04, 7.86, 127.1−140.3 (many peaks). ^{29}Si NMR: δ −24.1 (SiVi$_3$), −15.6 (SiVi$_2$), −6.63 (SiVi), −1.32 (SiCH$_3$), 2.66 (Si(CH$_2$CH$_2$)$_3$). IR (neat)$^{-1}$: 3048 (s), 3003 (m), 2951 (s), 2906 (m), 1590 (w), 1403 (s), 1250 (s), 1133 (s), 1053 (m), 1007 (s), 956 (s), 836 (s), 757 (s), 713 (s), 643 (s).

Preparation of Hyperbranched Polymer 3P. A 25 mL two-necked, round-bottomed, flask equipped a with septum, a magnetic stir bar, and a gas-inlet needle was charged with **3** (2.79 g, 8.74 mmol) and 7 mL of THF. At room temperature, several drops of Pt−DVTMDSO were added to the flask, and the reaction mixture was stirred for 1 h and then stirred for 18 h at 46 °C. The reaction was monitored using IR spectroscopy. Low-temperature (−78 °C) precipitation provided a yellow, viscous oil in 89% yield ($T_g = -45$ °C). $M_n = 2560$, $M_w = 5550$, polydispersity = 2.16. VPO molecular weight: 1820. ^{1}H NMR: δ 0.03−0.08 (6 H, SiCH_3), 0.27−0.30 (6 H, PhSiCH_3), 0.39−0.52 (2 H, CH_2CH$_2$), 0.82−0.86 (2 H, CH$_2$CH_2), 5.71−6.31 (6 H, vinyl), 7.49−7.51 (4 H, aromatic). ^{13}C NMR: δ −0.84 (SiCH$_3$), 0.57 (SiCH$_3$), 0.73 (SiCH$_3$), 3.04 (SiCH$_3$), 4.00 (SiCH$_3$), 10.00 (SiCH$_3$), 10.10 (CH$_2$CH$_2$), 127.8−136.3 (many peaks, aromatic and vinyl). ^{29}Si NMR: δ −24.2 (SiVi$_3$), −15.6 (SiVi$_2$), −6.49 (SiVi), −2.57 (OSiCH$_2$), 9.56 (PhSiO); the dendritic Si atoms could not be identified due to excessive baseline noise. IR (neat) cm^{-1}: 3049 (s), 3004 (m), 2956 (s), 2910 (m), 1591 (m), 1403 (s), 1379 (m), 1253 (s), 1135 (s), 1051 (br, s), 1008 (s), 957 (s), 836 (br, s), 780 (br, s), 729 (br, s), 648 (br, s).

Acknowledgment. The authors are grateful to Research Corporation and the Welch Foundation for financial support of this research. The authors also thank Professor Patty Wisian-Neilson for assistance in obtaining GPC molecular weight data.

References and Notes

(1) Dvornic, P. R.; Lenz, R. W. *High-Temperature Siloxane Elastomers*; Huthig & Wepf: Basel, 1990.

(2) For example, see: (a) Dvornic, P. R.; Perpall, H. J.; Uden, P. C.; Lenz, R. W. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3503. (b) Dvornic, P. R.; Lenz, R. W. *Macromolecules* **1994**, *27*, 5833. (c) Zhang, R.; Pinhas, A. R.; Mark, J. E. *Macromolecules* **1997**, *30*, 2513.

(3) Corriu, R.; Leclercq, D.; Mutin, P. H.; Samson, H.; Vioux, A. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 187.

(4) Dvornic, P. R.; Lenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 951. (b) Dvornic, P. R.; Lenz, R. W. *Polymer* **1983**, *24*, 763. (c) Grassie, N.; Beattie, S. R. *Polym. Degrad. Stab.* **1984**, *7*, 109.

(5) Ohshita, J.; Ishii, M.; Ueno, Y.; Yamashita, A.; Ishikawa, M. *Macromolecules* **1994**, *27*, 5583. (b) Ohshita, J.; Watanabe, T.; Kanaya, D.; Ohsaki, H.; Ishikawa, M.; Ago, H.; Tanaka, K.; Yamabe, T. *Organometallics* **1994**, *13*, 5002. (c) Sakakura, T.; Kumberger, O.; Tan, R. P.; Arthur, M.-P.; Tanaka, M. *Chem. Commun.* **1995**, 193. (d) Fang, M.-C.; Watanabe, A.; Matsuda, M. *J. Organomet. Chem.* **1995**, *489*, 15.

(6) For reviews, see: (a) Malmstrom, E.; Hult, A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1997**, *C37*, 555. (b) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685.

(7) Whitmarsh, C. K.; Interrante, L. V. *Organometallics* **1991**, *10*, 1336. (b) Muzafarov, A. M.; Gorbatsevich, O. B.; Rebrov, E. A.; Ignat'eva, G. M.; Chenskaya, T. B.; Myakushev, V. D.; Bulkin, A. F.; Papkov, V. S. *Vysokomol. Soed.* **1993**, *35*, 1867. (c) Lach, C.; Muller, P.; Frey, H.; Mulhaupt, R. *Macromol. Rapid Commun.* **1997**, *18*, 253. (d) Lach, C.; Frey, H. *Macromolecules* **1998**, *31*, 2381.

(8) Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 4043. (b) Rubinsztajn, S. *J. Inorg. Organomet. Polym.* **1994**, *4*, 61. (c) Rubinsztajn, S.; Stein, J. *J. Inorg. Organomet. Polym.* **1995**, *5*, 43. (d) Muzafarov, A. M.; Golly, M.; Moller, M. *Macromolecules* **1995**, *28*, 8444. (e) Miravet, J. F.; Frechet, J. M. J. *Macromolecules* **1998**, *31*, 3461.

(9) Gilman, H.; Jones, R. G. *J. Am. Chem. Soc.* **1941**, *63*, 1443.

(10) Available from Gelest, Inc.

(11) Platinum−divinyltetramethyldisiloxane catalyst (Karstedt's catalyst) in xylene. Obtained from Gelest Inc. or United Chemical Technologies.

(12) See ref 1, p 170.

(13) Tsumura, M.; Iwahara, T.; Hirose, T. *Polym. J.* **1995**, *27*, 1048.

(14) For example, see: (a) Liao, C. X.; Weber, W. P. *Macromolecules* **1992**, *25*, 1639. (b) Zhu, H. D.; Kantor, S. W.; MacKnight, W. J. *Macromolecules* **1998**, *31*, 850.

(15) Eareckson, W. M. *J. Polym. Sci.* **1959**, *40*, 399. (b) St. Clair, A. K. *Adhes. Age* **1979**, *22* (1), 35. (c) Takekoshi, T.; Wirth, J. G.; Heath, D. R.; Kochanowski, J. E.; Manello, J. S.; Webber, M. J. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3069. (d) Trumbo, D. L.; Marvel, C. S. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 2311. (e) Kondo, K.; Okuda, M.; Fujitani, T. *Macromolecules* **1993**, *26*, 376. (f) Tsumura, M.; Iwahara, T.; Hirose, T. *J. Polym Sci., Part A: Polym. Chem.* **1996**, *34*, 3155. (g) Pang, Y.; Li, J.; Hu, B.; Karasz, F. E. *Macromolecules* **1998**, *31*, 6730.

(16) Hawker, C. J.; Lee, R.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583. (b) Kim, Y. H. *Macromol. Symp.* **1994**, *77*, 21. (c) Holter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30.

(17) Williams, E. A.; Cargioli, J. D. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: New York, 1979; Vol. 9, p 221.

(18) Corriu, R. J. P.; Moreau, J. J. E.; Thepot, P.; Man, M. W. C. *Chem. Mater.* **1992**, *4*, 1217.

MA9901902