Synthesis of Hyperbranched Polysiloxanes by Base-Catalyzed Proton-Transfer Polymerization. Comparison of Hyperbranched Polymer Microstructure and Properties to Those of Linear Analogues Prepared by Cationic or Anionic Ring-Opening Polymerization

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ABSTRACT: Treatment of 1-(hydroxydimethylsiloxy)pentamethylcyclotrisiloxane (**II**), a latent $A_2A'B$ monomer, with a phosphazene P_4-*t*-Bu superbase followed by quenching with vinyldimethylchlorosilane/triethylamine leads to a hyperbranched polysiloxane (**III**). The microstructure and properties of **III** are compared to those of linear analogues obtained by cationic or living anionic polymerization of 1-(vinyldimethylsiloxydimethylsiloxy)pentamethylcyclotrisiloxane (**I**).

Introduction

There has been considerable interest in dendrimer[1−3] and hyperbranched materials.[4,5] These highly branched materials have similar properties which are distinct from analogous linear polymers. Dendrimers have a regular pattern of branching and are prepared by multistep sequential synthesis. Both convergent and divergent approaches to these macromolecules have been utilized. By comparison, hyperbranched materials do not have a well-defined architecture but rather an irregular pattern of branching. They are prepared by the direct polymerization of monomers that have two mutually reactive functional groups A and B, present in an unequal stoichiometric ratio such as AB_2, or by chain growth polymerization of monomers capable of undergoing active site exchange.[6] Both dendrimers and hyperbranched materials usually have a high degree of functionality that is found at the surface of dendrimers or at the termini of hyperbranched materials. The lower viscosity of both, compared to analogous linear polymers, is one of the potential benefits of these materials.[7]

Hyperbranched and dendritic silicon-based materials have been prepared.[8] Among these are highly branched poly(silanes),[9] poly(carbosilanes),[10−12] poly(carbosilane/siloxane)s,[13−16] and polysiloxanes. Pt-catalyzed hydrosilylation reactions have proved particularly valuable for the preparation of highly branched poly(carbosilane/siloxane)s. Tetraallylsilane or tetravinylsilane has often been used as the dendrimer core. These are derivatized by Pt-catalyzed hydrosilylation reactions.[17−20] A hyperbranched poly(carbosilane/siloxane) has been prepared from vinyltris(dimethylsiloxy)silane via Pt-catalyzed hydrosilylation polymerization.[21]

There are four previous examples of dendritic polysiloxanes whose backbones consist only of Si−O−Si linkages.[22−26] Palladium on carbon-catalyzed oxidation of ω-Si−H bonds of oligo dimethylsiloxanes with water to yield ω-Si−OH groups was a key step in the Masamune et al. synthesis of a third generation dendritic polysiloxane.[25] Alternatively, a fourth generation dendrimer was prepared by sequential repetition of the nucleophilic substitution of Si−Cl bonds by sodium diethoxylmethylsilanolate followed by conversion of the Si−OEt groups to Si−Cl bonds with $SOCl_2$.[26] Electrophilic cleavage of Si−phenyl bonds by bromine is essential to Kakimoto's synthesis of a third generation dendritic polysiloxane. The Si−Br groups are then converted to Si−NEt_2 groups by reaction with diethylamine. These, in turn, are reacted with a phenyl-substituted oligo siloxane/silanol.[22,23]

We have been interested in preparing hyperbranched poly(dimethylsiloxane)s (PDMS). While no hyperbranched polysiloxanes have been reported, a closely related polysilicate has been recently described.[27] Thus, Muzafarov et al. prepared an ethoxy-substituted hyperbranched polysilicate by an ammonia-catalyzed heteropolycondensation of triethoxysilanol.

Results

Lithium silanolates are well-known to catalyze anionic ring-opening polymerization (AROP) of cyclotrisiloxanes to yield narrow molecular weight distribution living lithium silanolate telechelic materials.[28,29] This reaction occurs much faster than base-catalyzed equilibration due to relief of ring strain in the cyclotrisiloxane. Monosubstituted pentamethylcyclotrisiloxanes undergo AROP with a high degree of chemoselectivity and regioselectivity.[30,31]

Isomeric regular linear polysiloxanes were prepared by AROP or by acid-catalyzed ring-opening polymerization (ACROP) of 1-(vinyldimethylsiloxydimethylsiloxy)-pentamethylcyclotrisiloxane (**I**). A related isomeric hyperbranched polysiloxane (**III**) was obtained via a phosphazene P_4-*t*-Bu superbase-catalyzed proton-transfer polymerization of 1-(hydroxydimethylsiloxy)pentamethylcyclotrisiloxane (**II**) followed by quenching with vinyldimethylchlorosilane. Recently, Fréchet described the base-catalyzed proton-transfer polymerizations of phenolic bisepoxides.[32] Independently, Frey reported the base-catalyzed proton-transfer polymerization of glycidol.[33] Several recent examples of preparation of hyperbranched materials by ring-opening polymerizations have been recorded.[34,35]

AROP of **I** proceeds with high regioselectivity. Single peaks are observed for each type of silicon atom in the

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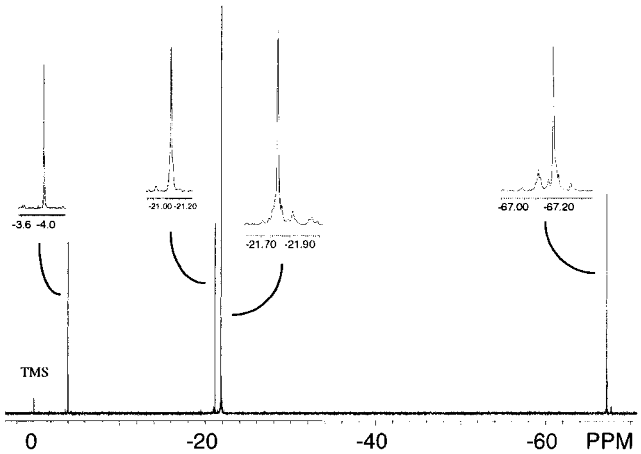

Figure 1. ^{29}Si NMR of **IV**.

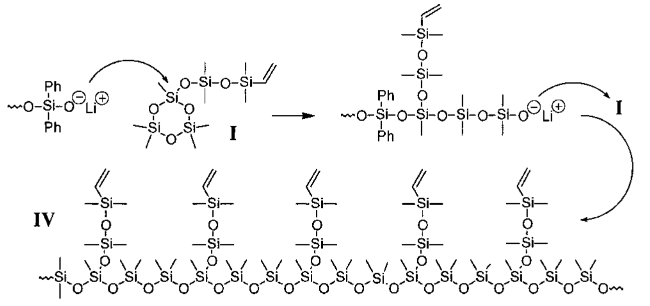

Figure 2. Proposed mechanism for AROP of **I**.

^{29}Si NMR (Figure 1) of the product poly[1-(vinyldimethylsiloxydimethylsiloxy)pentamethyltrisiloxane] (**IV**). Thus, the ^{29}Si NMR of **IV** shows only a DD*T*(DM)DD pentad for the T unit at −67.18, a DT*D*DT pentad for the D unit at −21.79, the side chain D at −21.09 and the vinyldimethylsiloxy (M) unit at −3.97 ppm (Figure 1).

Formation of **IV** may result from exclusive anionic attack at the T-silicon atoms of **I** which are substituted by three electron-withdrawing oxygen atoms. This makes the T-silicon atom more electrophilic and thus susceptible to nucleophilic attack. Ring opening results in a growing polysiloxane chain that contains a regular head-to-tail sequence of TDD units terminated by a dimethylsilanolate anion (Figure 2).

ACROP of **I** at low temperature gives a quite regular polysiloxane **V** whose microstructure is different from that of **IV**. Two equal peaks due to T units are observed in the ^{29}Si NMR at −67.17 and −67.11 ppm. D units in the polymer backbone give resonances at −21.93, −21.92, −21.84, −21.76, −21.75, and −21.68 ppm. The D unit adjacent to the M unit is found at −21.04 ppm. Two equal intensity peaks due to M units are detected at −3.95 and −3.94 ppm. These results can be explained if the TDD triad from **I** adds in a chemoselective random manner to another triad of **I** in either a head-to-tail, head-to-head, or tail-to-tail manner. This leads to two equally probable T-centered pentads DD*T(*DM)DD and DD*T(*DM)TD. In addition, this model predicts six heptads for the D units in the polymer chain in ratio of 1:1:3:1:1:1. See ^{29}Si NMR (Figure 3).

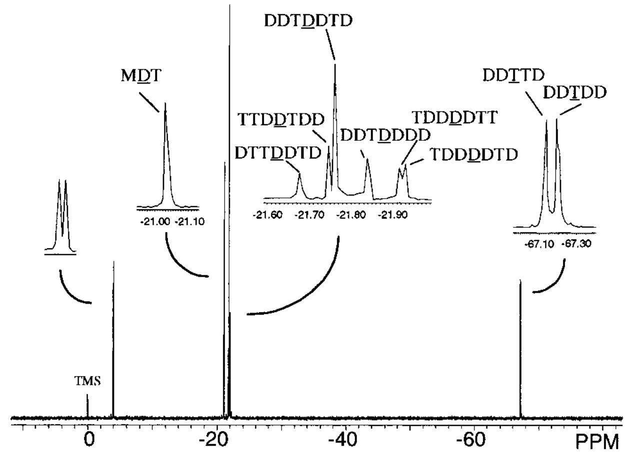

Figure 3. ^{29}Si NMR of **V**.

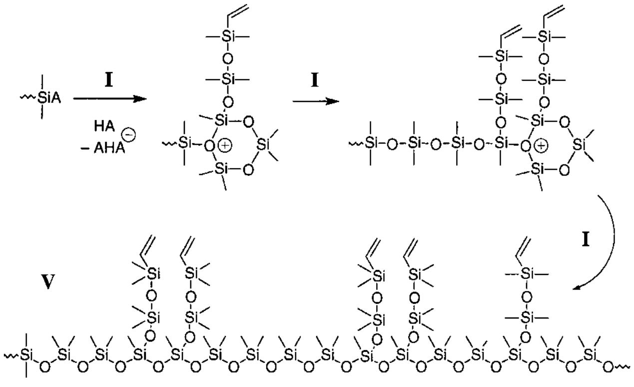

Figure 4. ACROP of **I**.

This chemo- and regioselectivity observed in the ACROP of **I** may result from regioselective protonation of the oxygen atoms of **I** which are located between D and T silicons. While protonation at oxygen is a key step in ACROP of cyclosiloxanes, an important industrial process, there are no experimental values for the relative or absolute basicity of siloxane oxygen atoms. Recently ^{13}C and ^{29}Si NMR of related trisilyloxonium ions as well as an ab initio calculation of protonated cyclic siloxanes have been reported.[36] On the other hand, it is well-known that strained cyclic ethers such as THF are more basic than open chain ethers.[37] On this basis, it is expected that the oxygen atoms of the cyclotrisiloxane ring of **I** will be protonated in preference to the oxygen of the side chain siloxane group or the oxygens of **V**. Consistent with this suggestion, acid-catalyzed equilibration of **V** does not occur. The ab initio calculation also predicts that protonation of the oxygen atoms of the cyclotrisiloxane will be favored.[38] However, the apparent greater basicity of the oxygen atoms between the T and D silicon atoms compared to the oxygen located between the two D silicon atoms is unexpected. A semiempirical calculation shows that protonation between T and D unit is favored by ∼2 kcal/mol.[39] A mechanism for ACROP of **I** which accounts for the chemo- and regiospecificity observed is outlined (Figure 4).

We have carried out AROP of **II** catalyzed by the superbase [1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylideneamino]-$2\lambda^5,4\lambda^5$-catenadi(phosphazene)] (phosphazene P_4-*t*-Bu superbase) to yield, after quenching with vinyldimethylchlorosilane and triethylamine, a soluble hyperbranched material (**III**). The ^{1}H NMR integration of signals due to the vinyl protons of the M units compared to those due to the methyl groups of M, D, and T units is predicted to be 3:27. In fact, a ratio of 2.92:27 is observed. Thus, the expected base-catalyzed silanol condensation to yield siloxane bonds is not significant.

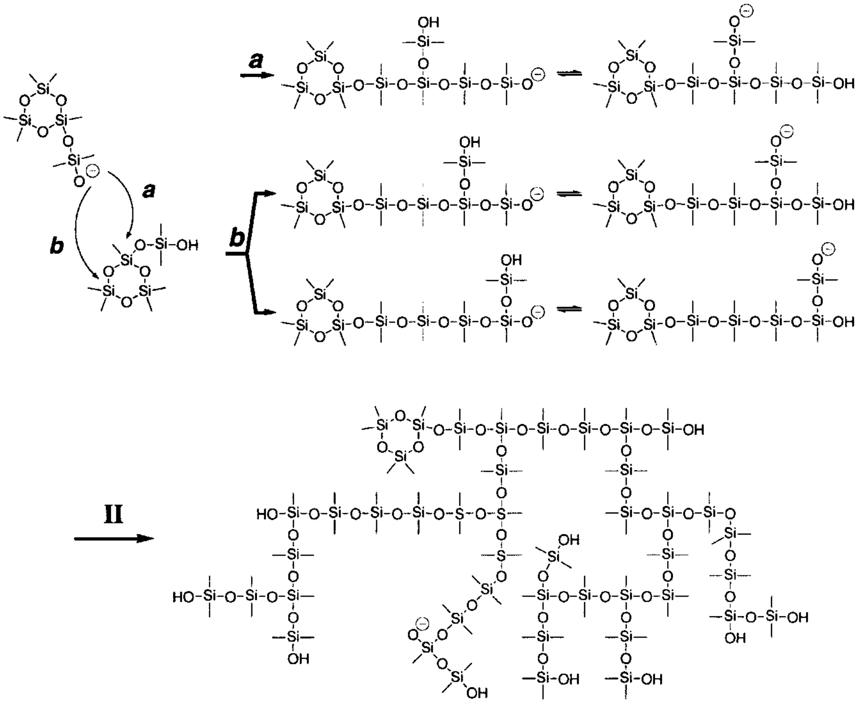

Figure 5. Proposed reaction mechanism and the resulting idealized hyperbranched polysiloxane with vinyldimethylchlorosilane/triethylamine before quenching.

Phosphazene P$_4$-*t*-Bu superbase in combination with MeOH has previously been used to catalyze polymerization of D$_4$ and 1,3,5,7-tetraphenyl-1,3,5,7-tetramethylcyclotetrasiloxane.[40,41]

In our reaction, a catalytic amount of phosphazene P$_4$-*t*-Bu superbase generates an equal molar amount of reactive silanolate anion. The major difference between this catalytic system and a lithium silanolate systems is that the cation is much larger. Nucleophilic attack by the silanolate on one of the D centers of another molecule of **II** with ring opening leads to two isomeric silanolate/silanols. Each of these can equilibrate by rapid proton transfer. Alternatively, nucleophilic silanolate attack on the T center of another molecule of **II** with ring opening would lead to a silanolate/silanol which can also equilibrate by proton transfer to yield two isomeric silanolate/silanols (Figure 5). Since proton transfer is fast, further reaction can occur at any of the six silanolate/silanol centers. This results in branching. No evidence of isomerization of the silanolate of **II** to the silanolate of 1-hydroxyheptamethylcyclotetrasiloxane has been observed.

On the basis of this hypothesis, each hyperbranched polymer is initiated by the silanolate formed by deprotonation of **II**. In fact, two peaks in the ^{29}Si NMR at -8.49 and -58.07 ppm in a 2:1 ratio consistent with the presence of cyclotrisiloxane end groups are observed. Integration of the ring D peak at -8.49 ppm versus all D peaks gives a ratio of 1:45. Thus, for every cyclotrisiloxane focal group there are ~30 monomer units that have polymerized. On the basis of the ^{29}Si NMR integration, the number-average molecular weight is found to be $M_n = 11\,660$. GPC gives $M_w/M_n = 29\,650/11\,900$, and MALLS yields $M_w = 57\,400$. Differences between GPC and MALLS for hyperbranched materials have been reported.[32] The agreement of M_n by ^{29}Si NMR analysis of the focal group (cyclotrisiloxane) analysis with M_n determined by GPC is perhaps fortuitous since terminal silanolate groups can attack not only **II** but also the cyclotrisiloxane focal group. While the former process generates two potentially reactive sites, the latter only generates a single reactive silanolate. Thus, while it does not contribute to branching it is not a termination process.

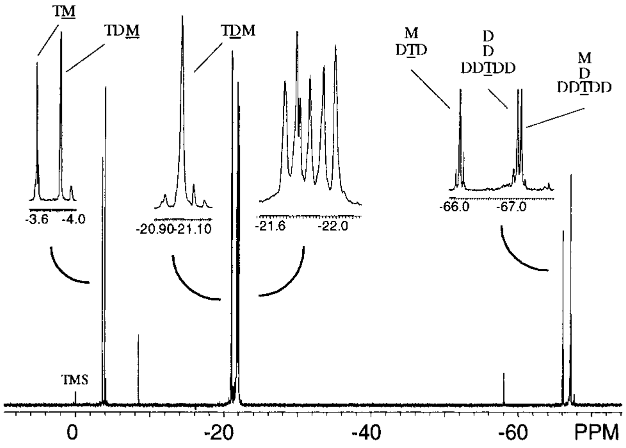

Figure 6. ^{29}Si NMR of **III**.

While the polymer backbone of the hyperbranched material is expected to be irregular, the ^{29}Si NMR is surprisingly simple (Figure 6). Specifically, three major peaks due to T units are observed at -67.20, -67.14, and -66.14 ppm in a ratio of ~13:11:10. Seven peaks due to D units are found at -22.05, -21.97, -21.89, -21.82, -21.80, -21.76, and -21.11 ppm in a ratio of 15:16:12:6:13:13:18. Finally, two major peaks due to M units are found at -4.00 and -3.66 ppm in a ratio of ~20:13.

The signal at -4.00 ppm is due to an M attached to a D unit, while the resonance at -21.11 ppm is due to D units bonded to M units. The resonance at -67.20 ppm is due to a T in a DD*T*(DM)DD unit, while the resonance at -67.14 ppm is due to a T in a DD*T*(DD)-DD unit. These assignments are based on the ^{29}Si NMR

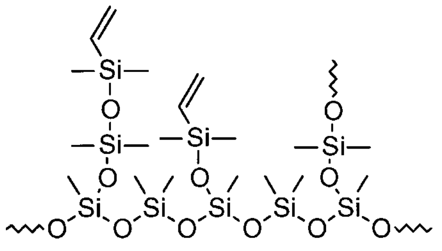

Figure 7. Structures of T units of **III**.

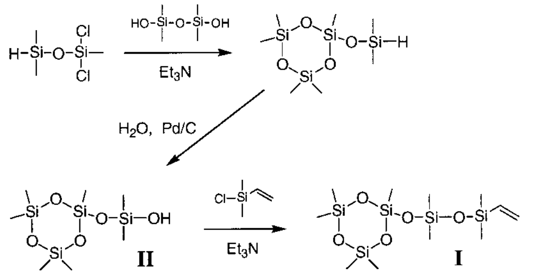

Figure 8. Preparation of **I** and **II**.

of **IV** and **V**. The signal −3.66 ppm is due to M units bonded to a T center (Figure 7), while the resonance at -66.20 ppm is due to a T unit bonded to an M unit. Consistent with this, two different vinyl groups are seen in the ^{1}H NMR.

Branching occurs when chain growth in all three possible directions occurs at a T unit. T units are part of a linear segment when a T unit is bonded to either an M or a DM unit. Comparison of the integration of the resonances at −66.11 and −67.20 ppm which are assigned to linear DD*T*(DD)M and DD*T*(DD)DM units, respectively, to that the peak at −67.14 ppm which is assigned to branching DD*T*(DD)DD unit permits determination of the branching ratio ~0.3.

Mechanistic pathways consistent with these ^{29}Si NMR results are proposed. Since M units bonded to T centers can only arise from nucleophilic silanolate attack on D units of **II**, it appears that this pathway is favored. Our hypothesis can explain most of the peaks found in ^{29}Si NMR. However, it fails to account for one major D peak at −22.05 ppm, whose chemical shift is close to that of PDMS.

Monomer Synthesis

II was prepared by a Pd/C-catalyzed oxidation of 1-(dimethylsiloxy)pentamethylcyclotrisiloxane reaction with water.[42] 1-(Dimethylsiloxy)pentamethylcyclotrisiloxane was prepared by reaction of tetramethyldisiloxane-1,3-diol with 1,1-dichloro-1,3,3-trimethyldisiloxane and triethylamine.[43] Reaction of **II** with vinyldimethylchlorosilane and triethylamine gives **I** (Figure 8).

Conclusion and Discussion

Phosphazene P_4-*t*-Bu superbase is more effective for the preparation of high molecular weight hyperbranched polysiloxanes than conventional lithium silanolates which give large amounts of base-catalyzed silanol condensation products. Low ^{1}H NMR integration values for M groups are found on quenching dilithium diphenyldisilanolate-catalyzed polymerization of **II** with vinyldimethylchlorosilane/triethylamine. Both bases yield insoluble materials, if these reactions are carried out at ambient temperature. However, at −9 °C, we were able to run the polymerization of **II** for days without cross-linking using phosphazene P_4-*t*-Bu. Apparently, superbase does not catalyze the condensation of Si−OH groups under these conditions.

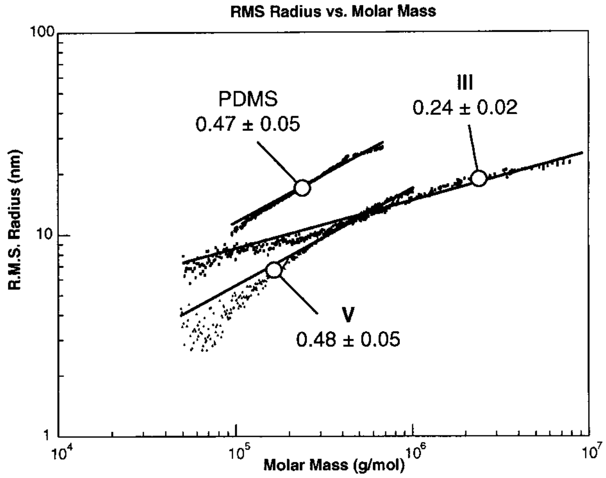

Figure 9. RMS radius (nm) vs molar mass of **III**, **V**, and PDMS.

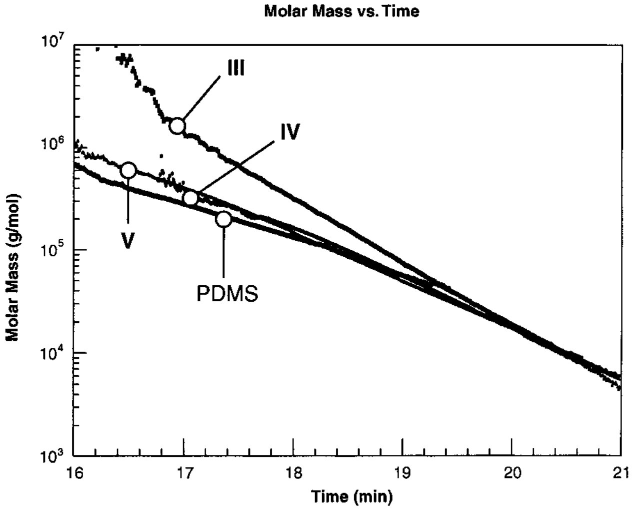

Figure 10. Molar mass vs elution time for **III**, **IV**, **V**, and PDMS.

Multiangle laser light scattering (MALLS) was used to determine the slope of a plot of root-mean-square (rms) radius vs molecular weight for **III**, **V**, and **PDMS** (Figure 9). The slope was approximately the same for both **V** and **PDMS** (0.48 and 0.47), whereas a lower value (0.24) was measured for **III**. This difference is consistent with a high degree of branching.[44] Despite this agreement, these results should be interpreted with caution because the molecular weights of **III** and **V** and thus their RMS radii are on the borderline of suitability (>10 nm) for this method.

Comparison of molar mass determined by light scattering versus elution time by GPC shows significant difference between **III**, **IV**, **V**, and PDMS (Figure 10). At comparable elution time, the molar mass of **III** is substantially higher. This is also consistent with the hyperbranched nature of **III**.

At +23 °C, linear **IV** (M_w = 43 500 g/mol) has a viscosity of 277 cP, while hyperbranched **III** (M_w = 57 400 g/mol) has viscosity of only 92 cP. These results are consistent with the well-known lower viscosity of branched polymers compared to linear analogues.

Thermogravimetric analysis (TGA) of **IV** and **V** shows similar thermal decomposition properties (Figure 11).

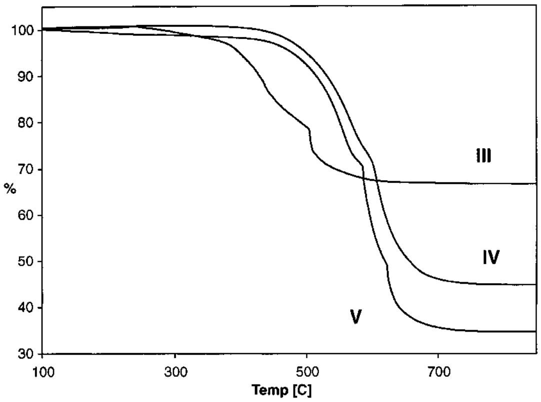

Figure 11. TGA of polymers **III**, **IV**, and **V**.

On the other hand, **III** starts to degrade at ~70 °C lower temperature but gives a higher final residue. Branching may suppress the formation of volatile cyclics, a common degradation process of linear polysiloxanes, while alternative decomposition mechanisms may be accelerated.[45]

The glass transition temperature (T_g) of hyperbranched materials has been shown in certain cases to be independent of the degree of branching.[46] Consistent with this, polymers **III**, **IV**, and **V** all have T_g at −124 °C.

Experimental Section

Spectroscopic Analysis. ^1H, ^{13}C, and ^{29}Si NMR spectra were obtained on a Bruker AMX-500 MHz spectrometer. ^1H NMR spectra were run on 5% w/v chloroform-*d* solutions. Forty percent w/v solutions in acetone-d_6 were used to obtain ^{29}Si and ^{13}C NMR spectra. ^{13}C NMR spectra were obtained with broad-band proton decoupling. An inverse gate decoupling pulse sequence with a 60 s delay was used to acquire ^{29}Si NMR spectra. TMS was used as an internal standard for ^1H, ^{13}C, and ^{29}Si NMR spectra. IR spectra of neat films on NaCl plates were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer.

Molecular Weight. GPC analysis of the molecular weight distribution of the polymers was performed on a Waters system equipped with a R401 refractive index detector (RI). HT 6E and HMW 6E columns in series were used for the analysis. The eluting solvent was toluene at a flow rate of 1.0 mL/min. The retention times were calibrated against known monodisperse polystyrene standards. MALLS analysis was performed on a Wyatt DAWN DSP connected to the GPC system. The M_w's were determined using the RI detector's calibration constant and assuming 100% mass recovery of a known amount of the injected polymer. Astra Chromatography Software, PC ver. 4.70.07, was used for data analysis.

Thermal Properties. TGA of the polymers was measured on a Shimadzu TGA-50 instrument. The temperature program was 4 °C/min from 25 to 850 °C. T_g of the polymers was determined by DSC on a Perkin-Elmer DSC-7 which was calibrated from T_g of PDMS (−125 °C) and crystal transition of cyclohexane (−87.06 °C) .[47] The temperature program for the analysis was begun at −150 °C. The temperature was increased at a rate of 10 °C/min.

Viscosity was measured on a Wells-Brookfield LVTDV-II viscometer equipped with a CP52 spindle.

Mass Spectroscopy−Elemental Analysis. Low-resolution mass spectra were obtained by GC/MS on a Hewlett-Packard 5890 series II GC with a Hewlett-Packard 5971 series mass selective detector. The gas chromatograph was equipped with a 30 m capillary column J&W 1225032. Satisfactory high-resolution mass spectra of I and II were acquired on a VG ZAB2SE high-resolution mass spectrometer at University of California High Resolution Mass Spectrometry Facility, Riverside, CA. They were calibrated against mass peaks of perfluorokerosene.

Reagents. 1,3-Dihydridotetramethyldisiloxane was purchased from Gelest and distilled before use. Diphenylsilanediol, methyltrichlorosilane, dimethyldichlorosilane, vinyldimethylchlorosilane, hexamethyldisilazane, and PDMS (M_w = 204 000) were also obtained from Gelest. They were used without further purification. Ferric chloride and ammonium chloride were purchased from Mallinckrodt. Triflic acid was obtained from the 3M Co. Phosphazene base P_4-*t*-Bu (1 M in *n*-hexane) was purchased from Fluka Chemie AG.

Reactions. All reactions were conducted in flame-dried glassware under an atmosphere of argon. Reactions were stirred with Teflon-covered magnetic stir bars.

Initiator. Dilithium diphenylsilanolate was prepared by treatment of diphenylsilanediol with *n*-butyllithium in THF. Styrene was used as an indicator.[48]

1,1-Dichloro-1,3,3-trimethyldisiloxane was prepared by an acid-catalyzed equilibration reaction between 1,3-dihydridotetramethyldisiloxane and methyltrichlorosilane as previously described in the literature.[41]

Tetramethyldisiloxane-1,3-diol was prepared by the controlled hydrolysis of dimethyldichlorosilane[49] or by Pd/C-catalyzed oxidation of 1,3-dihydridotetramethyldisiloxane by water.[50]

1-(Dimethylsiloxy)pentamethylcyclotrisiloxane. A 250 mL three-neck round-bottom flask was equipped with two pressure-equalizing addition funnels. A solution of 1,1-dichloro-1,3,3-trimethyldisiloxane (25.0 g, 0.13 mol) and 30 mL of Et_2O was placed in one of the funnels, while a solution of tetramethyldisiloxane-1,3-diol (22.0 g, 0.13 mol) and 30 mL of Et_2O was placed in the other. These were added simultaneously dropwise to a solution of Et_3N (28.0 g, 0.28 mol) and 170 mL of Et_2O in the flask over 1 h at room temperature. After stirring for 2 h, the reaction mixture was filtered and washed with water, dilute H_3PO_4 solution, and saturated $NaHCO_3$. It was dried over anhydrous $MgSO_4$ and filtered, and the volatiles were removed by evaporation under reduced pressure. Fractional distillation through a 10 cm vacuum jacketed column gave a fraction, 26.9 g (72% yield), bp 81 °C/ 40 mm. ^1H NMR δ: 0.09 (s, 3H), 0.12 (s, 6H), 0.14 (s, 6H), 0.20 (d, 6H, J = 3 Hz), 4.75 (sept, 1H, J = 3 Hz). ^{13}C NMR δ: −3.11, 0.52, 0.72, 0.82. ^{29}Si NMR δ: −56.20 (1Si), −8.50 (2Si), −5.72 (1Si). IR ν: 2966, 2907, 2133, 1406, 1260, 1089, 1020, 907, 862, 810, 770 cm^{-1}. Low-resolution MS *m*/*z* (relative intensity): 73 (100), 267 ($M^{\bullet+} - CH_3$, 83), 59 (83), 281 ($M^{\bullet+} - 1$, 42), 253 (31), 133 (27), 193 (24).

1-(Hydroxydimethylsiloxy)pentamethylcyclotrisiloxane (II). Pd/C (10%, 0.5 g) was added to a solution of 1-(dimethylsiloxy)pentamethylcyclotrisiloxane (20.0 g, 70 mmol), 250 mL of dioxane, and 30 mL of distilled water in three aliquots at room temperature, and the system was stirred for 12 h. After filtration and removal of volatiles by evaporation, fractional distillation gave a fraction, 19.6 g (66 mmol), 93% yield, bp 52 °C/ 0.1 mm. ^1H NMR δ: 0.10 (6H), 0.11 (3H), 0.12 (6H), 0.15 (6H), 5.15 (1H). ^{13}C NMR δ: −2.81, 0.34, 0.78, 0.85. ^{29}Si NMR δ: −57.63 (1Si), −12.45 (1Si), −8.32 (2Si). IR ν: 3339 (br), 2966, 2907, 1411, 1262, 1092, 1023, 880, 867, 809, 764 cm^{-1}.

1-(Vinyldimethylsiloxy-dimethylsiloxy)pentamethylcyclotrisiloxane (I). Vinyldimethylchlorosilane (4.0 g, 33 mmol) in 10 mL of Et_2O was added dropwise to a solution of **II** (4.85 g, 16 mmol), 60 mL of Et_2O, and Et_3N (4.0 g, 40 mmol) at room temperature over 20 min. After 5 h, the reaction was filtered. The filtrate was washed with water, dilute aqueous H_3PO_4, and saturated $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered. The final product was obtained in 79% yield (4.91 g, 0.13 mol) by fractional distillation at 50 °C/ 0.15 mm. ^1H NMR δ: 0.09 (s, 6H), 0.11 (s, 3H), 0.13 (s, 6H), 0.15 (d, 6H, J = 0.5 Hz), 0.17 (s, 6H), 5.76 (dd, 1H, J = 21 and 4 Hz), 5.93 (dd, 1H, J = 15 and 4 Hz), 6.14 (dd, 1H, J = 21 and 15 Hz). ^{13}C NMR δ: −2.73, 0.36, 0.77, 0.93, 1.07, 132.08, 139.69. ^{29}Si NMR δ: −58.11 (1Si), −20.30 (1Si), −8.40 (2Si), −3.53 (1Si). IR ν: 3052, 2965, 2906, 1596, 1408, 1261, 1068, 1021, 862, 839, 808, 763, 710 cm^{-1}. Elemental Anal. Calcd for $C_{11}H_{30}O_5Si_5$: C, 34.52; H, 7.90. Found: C, 34.26; H, 7.88.

ACROP of I. 1,1,2-Trichlorotrifluoroethane (250 μL) and **I** (1.0 g, 2.6 mmol) were cooled to −78 °C, and 5 μL of trifluoromethanesulfonic acid (triflic acid) was injected into solution. Additional 1,1,2-trichlorotrifluoroethane (3 × 250 μL) was added when the system became too viscous to permit stirring. The reaction was quenched after 0.5 h by addition of hexamethyldisilazane (20 mg, 0.12 mmol). Polymer was precipitated three times from a mixture of Et_2O/MeOH and dried under vacuum for 12 h. In this way, **V** (0.48 g, 48% yield, $M_w/M_n = 83\,900/28\,300$ by GPC, $M_w = 78\,700$ by MALLS, $T_g = -124$ °C) was obtained. ^{1}H NMR δ: 0.08−0.18 (m, 27H), 5.75 (dd, 1H, $J = 20.5$ and 4 Hz), 5.92 (dd, 1H, $J = 15$ and 4 Hz), 6.13 (dd, 1H, $J = 20.5$ and 15 Hz). ^{13}C NMR δ: −2.04, −2.02, 0.39, 1.11, 1.15, 1.18, 1.20, 1.23, 1.28, 131.96, 139.57. ^{29}Si NMR δ: −67.17, −67.11, −21.93, −21.92, −21.84, −21.76, −21.75, −21.68, −21.04, −3.95, −3.94. IR ν: 3053, 2964, 2906, 1596, 1408, 1261, 1094, 1030, 956, 839, 799, 756, 707 cm^{-1}. Elemental Anal. Calcd for $C_{11}H_{30}O_5Si_5$: C, 34.52; H, 7.90. Found: C, 34.64; H, 7.76.

AROP of I. Initiator (70 μL, 15 μmol) was injected to a solution of **I** (1.5 g, 3.9 mmol), HMPA (10 μL), and 400 μL of THF at −7 °C. Polymerization was carried out for 3 h. It was quenched by addition of vinyldimethylchlorosilane (10 μL, 78 μmol) and Et_3N (5 μL, 36 μmol). **IV** was precipitated three times with Et_2O/MeOH and dried in a vacuum for 10 h, to yield 1.34 g (90%), $M_w/M_n = 43\,000/29\,050$ by GPC, $M_w = 43\,500$ by MALLS, $T_g = -124$ °C.^{1}H NMR δ: 0.09 (6H), 0.10 (3H), 0.13 (12H), 0.16 (6H), 5.75 (dd, 1H, $J = 20.5$ and 4 Hz), 5.92 (dd, 1H, $J = 15$ and 4 Hz), 6.13 (dd, 1H, $J = 20.5$ and 15 Hz). ^{13}C NMR δ: −2.09, 0.37, 1.14, 1.17, 131.86, 139.49. ^{29}Si NMR δ: −67.18 (1Si), −21.79 (2Si), −21.09 (1Si), −3.97 (1Si). IR ν: 3053, 2964, 2906, 1596, 1408, 1261, 1092, 1029, 956, 856, 839, 798, 756, 706 cm^{-1}. Elemental Anal. Calcd for $C_{11}H_{30}O_5Si_5$: C, 34.52; H, 7.90. Found: C, 34.70; H, 7.74.

Hyperbranched, III. THF (1.0 mL) and **II** (2.0 g, 6.7 mmol) were cooled to −9 °C, and phosphazene P_4-*t*-Bu (8 μL, 8 μmol) was injected. After 4 h, 1 mL of THF, Et_3N (2 mL, 7.3 mmol), and 1 mL of vinyldimethylchlorosilane were added. After 12 h, **III** was extracted into hexamethyldisiloxane, washed with aqueous NaCl, and precipitated five times from THF/MeOH. Yield 2.29 g (89%), $M_w/M_n = 29\,650/11\,900$ by GPC, $M_w = 57\,400$ by MALLS, $T_g = -124$ °C. ^{1}H NMR δ: 0.05−0.20 (m, 27H), 5.74 (dd, 0.65H, $J = 20.5$ and 4.5 Hz), 5.76 (dd, 0.35H, $J = 20.5$ and 4.5 Hz), 5.91 (dd, 0.65H, $J = 14$ and 4.5 Hz), 5.92 (dd, 0.35H, $J = 14$ and 4.5 Hz), 6.13 (dd, 0.65H, $J = 20.5$ and 14.5 Hz), 6.13 (dd, 0.35H, $J = 20.5$ and 14.5 Hz). ^{13}C NMR δ: −2.79, −2.11, 0.25, 0.36, 0.75−1.23 (m), 131.84, 131.97, 139.27, 139.49. ^{29}Si NMR δ: −67.27, −67.20, −67.14, −67.06, −66.20, −66.14, −66.06, −22.05, −21.97, −21.89, −21.82, −21.80, −21.76, −21.74, −21.11, −8.55, −4.00, −3.66, −3.64. IR ν: 3053, 2964, 2906, 1596, 1408, 1261, 1094, 1027, 956, 855, 839, 798, 756, 706 cm^{-1}. Elemental Anal. Calcd for $C_{11}H_{30}O_5Si_5$: C, 34.52; H, 7.90. Found: C, 34.58; H, 7.95.

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