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New Hyperbranched Poly(siloxysilanes): Variation of the Branching Pattern and End-Functionalization

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ABSTRACT: The synthesis of new poly(siloxysilanes) by polyhydrosilation of AB_2, AB_4, and AB_6 monomers using a solid-supported catalyst is described. Analysis of the polymers by gel permeation chromatography shows weight-average molecular weight values near 5−10 000 amu with polydispersities of ∼2. Addition of fresh monomer to the polymerized material only leads to a slight increase in molecular weight. In all cases, polymerization is accompanied by significant intramolecular cyclization side reaction. These results can be explained by considering factors such as the unequal reactivity of the different oligomeric species and their tendency to form cyclic species, but no clear evidence for a growth-limiting effect arising from steric crowding could be seen. End capping of the terminal silicon hydride groups by hydrosilation with a variety of reagents has been demonstrated, affording a diversity of functionalized poly(siloxysilane) materials.

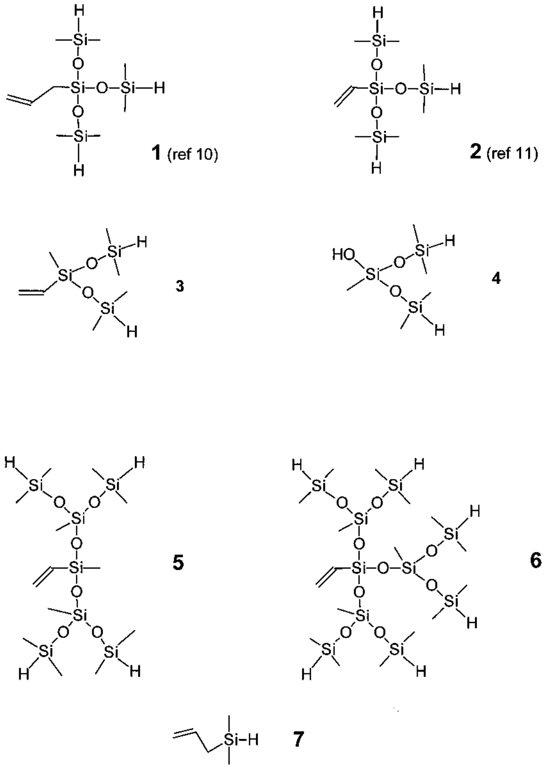
Introduction

Following early work in the development of hyperbranched polymers[1,2] and the study of their properties[3] that are somewhat reminiscent of those of dendrimers,[4] the study of hyperbranched siloxy-type polymers is an especially appealing target if one considers the widespread use of linear poly(siloxanes).[5] In particular, the synthesis of hyperbranched siloxy-type polymers with terminal silicon hydride groups is an attractive goal as a result of the feasibility of end-group chemical modification by means of the versatile hydrosilation reaction.[6] In this way, the remarkable properties of siloxy-based polymers and their derivatives, which are useful in areas[7] as varied as catalysis and adhesion, or as surface active materials, or even as conducting polymers, would be readily modified and modulated by the use of a hyperbranched structure containing a multiplicity of tunable end groups.

A few dendritic polysiloxanes or silicon-containing dendrimers, obtained either by convergent or divergent multistep syntheses, have been reported.[8] In addition, hyperbranched poly(siloxysilanes) and poly(alkoxysilanes) have been prepared by polyhydrosilation of AB_3 and AB_2 monomers containing SiH and alkene functionalities.[9−11]

Despite the fact that the molecular weight of hyperbranched polymers is largely uncontrollable, a self-regulating process has been suggested for the growth of these siloxy-type hyperbranched polymers. For example, Muzafarov, Möller, and co-workers[9] have reported the polymerization of an AB_2 monomer to afford a degradable hyperbranched poly(bis-alkoxymethylsilane) with a broad molecular weight distribution that does not vary significantly upon addition of more monomer. These authors suggest that this behavior is the result of the formation of a globular molecule for which further growth is limited by steric hindrance. In earlier work, Mathias and co-workers first reported[10a−d] the preparation of a hyperbranched poly(siloxysilane) by polymerization of allyltris(dimethylsiloxy)silane **1** (see Chart 1). Initial work[10a] suggested that the hyperbranched product had a narrow molecular weight distribution and was perhaps subject to steric inhibition to growth. Later reports on analogous systems by the same authors[10d,e] suggested that broader molecular distributions were obtained and that the intramolecular reaction of the monomer to give a six-membered cycle was prevalent in this system. Unfortunately, no yields were provided in the preliminary communications reporting this work.[10] Rubinsztajn[11] has also reported the synthesis of related poly(siloxysilane) polymers. For example, polyhydrosilation of the AB_3 type monomer **2** produced the corresponding hyperbranched polymer with a molecular weight of ∼10 000 and a polydispersity

Chart 1



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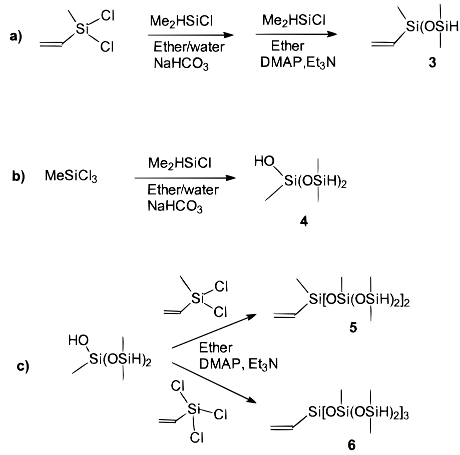
Scheme 1



of about ~2. The less favorable process of monomer cyclization to afford a five-membered ring was used to explain the reasonable yields (40−80%) of polymer isolated.

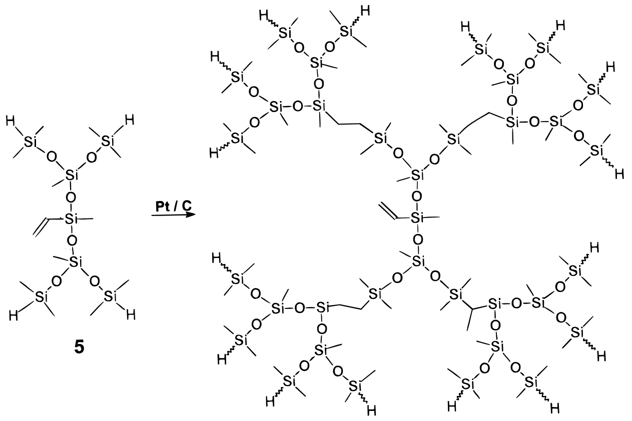
We now report the design and preparation of new hyperbranched poly(siloxysilanes) from monomers with different degrees of branching. One of our objectives was to investigate if growth inhibition due to increased steric congestion as the polymerization advances could be made easier to observe through the use of highly branched monomers. We also wished to explore the functionalization of the SiH chain-ends of the resulting hyperbranched polymers through the use of a variety of reagents.

Results and Discussion

Monomer Synthesis. The preparation of monomer **3**, methylvinylbis(dimethylsiloxy)silane, is shown in Scheme 1a. Monomer **3** is made according to a modification of the procedure described previously for the preparation of **2**,[11a] involving the condensation of vinylmethyldichlorosilane and dimethylchlorosilane in the presence of water. Sodium hydrogen carbonate is used to neutralize the hydrogen chloride that is formed, keeping the medium neutral to avoid the uncontrolled condensation of the intermediate silanol compounds that are formed. Addition of more dimethylchlorosilane in the second step of this synthesis is required to react with the considerable amount of methylvinyl(dimethylsiloxy)silanol that is present at the end of the first step. Compound **3** is isolated in 65% yield after distillation under reduced pressure.

The formation of intermediate silanol-type compounds observed during the preparation of **3** was exploited for the synthesis of methylbis(dimethylsiloxy)silanol, **4** (Scheme 1b). Reaction of dimethylchlorosilane with trichloromethylsilane in a mixture of ether and water in the presence of sodium hydrogen carbonate afforded **4** in 32% yield after distillation. Though low, the yield for this reaction is satisfactory given the large number of possible side reactions. Compound **4** is a very useful building block for the synthesis of more complex siloxy-type molecules. It is well-known that silanols can easily undergo self-condensation to give the corresponding siloxane, but this reaction is strongly dependent on steric effects.[12] In our case, silanol **4** was stable when stored for several days at 4 °C. Given the feasibility of silanol−silicon hydride coupling reaction,[13] **4** can be considered as an AB_2 monomer for the synthesis of hyperbranched polysiloxanes. However, using a variety of rhodium and platinum catalysts we were not able to carry out the desired polycondensation, probably because of the hindered nature of the silanol functionality in **4**.

Scheme 2



Monomers **5** and **6** were prepared by reaction of the appropriate chlorosilane compound with silanol **4** (Scheme 1c). The use of triethylamine as base and (dimethylamino)pyridine (DMAP) as catalyst is known to favor SiCl/SiOH condensation, minimizing silanol self-condensation in this type of reaction.[5] Using this procedure, monomers **5** and **6** are obtained in ~80% yield.

Polymerization. Polyhydrosilation of monomers **3**, **5**, and **6,** accomplished with platinum-on-active charcoal as the catalyst, afforded hyperbranched polymers with silicon hydride terminal groups. A heterogeneous catalyst is used because it can be easily removed by filtration during polymer workup. Although the use of a heterogeneous catalyst may initially appear to be strange because access to the core of the hyperbranched molecule may be restricted, it is necessary to avoid cross-linking of the SiH terminated product in the later stages of reaction or during storage. Indeed, the use of a soluble catalyst generally led to products with poor shelf life. A highly schematic representation of the final polymer obtained by polymerization of monomer **5** is shown in Scheme 2. In fact the hyperbranched polymer that is obtained does not have such a highly regular structure. As will be discussed later, intramolecular cyclization of a terminal SiH group with the focal vinyl group is a very common side reaction that affords both large and small cyclic species in this system.

The polymerization reaction was monitored by ^1H NMR and IR spectroscopy. Typically, when the reaction was performed at 50 °C, no remaining vinyl groups could be detected after a reaction time of 3 h (Figure 1). In an attempt to minimize undesired intramolecular reactions, the catalyst was added to the bulk monomer to keep the concentration of reactive functionalities as high as possible. The hyperbranched polymers were soluble in a variety of organic solvents, such as hexanes, halogenated alkanes, and ethers, but were insoluble in polar solvents, such as methanol or acetonitrile.

The relative molecular weights of the hyperbranched poly(siloxysilanes) were determined by gel permeation chromatography (GPC) analysis with polystyrene standards for calibration. As described in the section on end-functionalization, light scattering experiments carried out on derivatized poly(siloxysilanes) showed that the molecular weights obtained by the two techniques were roughly comparable.

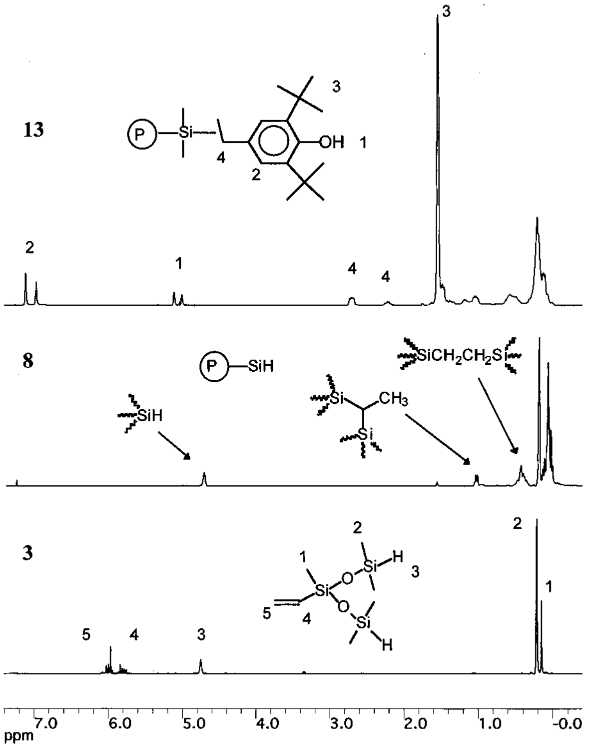


Figure 1. The ^{1}H NMR (CDCl$_3$) spectra of monomer **3** and polymers **8** and **13**.

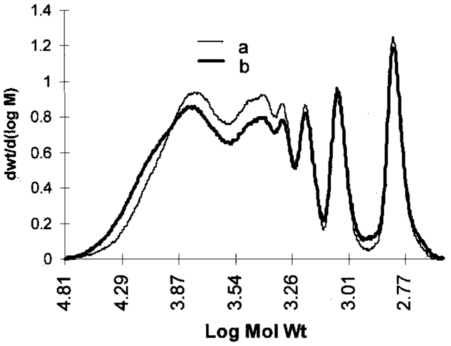


Figure 2. The GPC traces for the polymer obtained from monomer **6**; (a) GPC trace after the initial polymerization; (b) GPC trace after a second addition of monomer and catalyst.

Table 1. Yields and Molecular Weight Distribution Obtained for the Polymerization of Branched Monomers 3, 5, and 6

entry	starting material	M_w; M_w/M_n	M_w; M_w/M_n (after addition of extra monomer)[a]	yield, %[b]
1	**3**	5800; 1.7[c]	7800; 1.7[c]	68
2	**3** + **7**	5900; 1.8[c]	–	69
3	**5**	8900; 2.6	12 500; 3.8	69
4	**6**	6500; 2.2	8500; 2.7	55

[a] 1:1 polymer/monomer weight ratio. [b] After precipitation. [c] Values for the precipitated polymer.

In all cases, the GPC traces (see for example Figure 2) show the presence of multiple resolved peaks with elution volumes corresponding to low molecular weight compounds that may be assigned to oligomers. In particular, a large peak with a retention volume essentially identical to that of the monomer is seen. Because spectroscopic analysis of this material reveals no vinyl groups, this GPC peak likely corresponds to the product obtained by intramolecular cyclization of the monomer. Neighboring low molecular weight species also probably involve cyclized species. The flexibility of the monomer structure and the formation of medium size (five- to seven-membered) rings facilitate this process and similar ring formation has been described previously by Mathias[10] and by Fry and Neckers[14] in the preparation of linear polysilanes. The typical yields of hyperbranched polymers isolated after removal of these low molecular weight side-products are in the range 55–70%. It is nevertheless difficult to assess the exact extent to which this cyclization process is taking place in the different systems because the "hyperbranching" nature of the polymerization allows cyclic species to be partly incorporated into larger structures. Table 1 provides a summary of the typical molecular weight distributions obtained in the polymerization of the various monomers together with the yields of polymers after removal of the low oligomers by precipitation from ether into acetonitrile.

In a typical experiment, the polymerization of monomer **3** (entry 1, Table 1) afforded a material with a weight-average molecular weight (M_w) of 5800. Addition of more monomer **3** to the polymerized mixture led to a moderate increase in M_w to 7800, affording materials that, again, were contaminated with low molecular weight oligomers. Polymerization of the AB$_4$ monomer **5** (entry 3, Table 1) under analogous conditions resulted in a polymer with M_w of 8 900 and M_w/number-average molecular weight (M_n) = 2.6 (measured for a crude product without removal of oligomers). Addition of extra monomer afforded polymers with M_w up to 12 500 and $M_w/M_n = 3.8$. Removal of oligomers from the latter material gave a product with $M_w = 15\,700$ and $M_w/M_n = 2.2$.

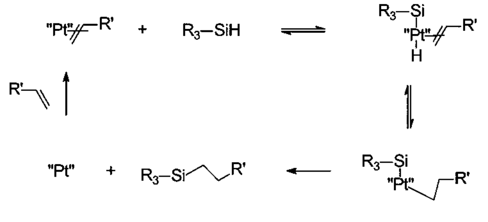
Finally, the polymerization of the most highly branched AB$_6$ monomer **6** (entry 4) afforded a material of lower molecular weight than that obtained from polymerization of **5** ($M_w = 6500$; $M_w/M_n = 2.2$ without removal of oligomers). As observed with the other monomers, addition of extra monomer resulted in a material that had a GPC trace (Figure 2, trace b) very similar to that of the starting polymer (Figure 2, trace a). Once the oligomers were removed, a polymer with $M_w = 9500$ and $M_w/M_n = 1.7$ was obtained.

In previous experiments[15] we reported that the polymerization of monomers **5** and **6** afforded higher molecular weight polymers. Although the molecular weight measurements themselves were accurate, this observation was actually caused by the presence of residual DMAP, used as catalyst for the monomer synthesis, which caused a slow coupling process to occur within the polymers after their isolation. We believe that despite careful precipitation, the DMAP remained trapped inside the globular polymers. The ability of dendritic polymers to retain solvents and small molecules within their globular structures has been reported previously.[4]

To explain the limited molecular weights that are achieved, several factors that can influence the growth of polymers in the preparation of hyperbranched materials may be considered. Therefore, the molecular weight distribution is likely to be affected by intramolecular cyclization of monomer and oligomers, by steric crowding within the structure, and also by the presumably lower reactivity of the functional groups in the hyperbranched polymers caused by steric crowding.

The similar tendencies observed for the different monomers, including the limited growth and oligomer formation upon addition of extra monomer, seem to

Scheme 3



suggest that no special behavior results from the very significant changes in the extent of branching of the various monomers. Moreover, a comparison between the results described for entries 1 (polymerization of an AB_2 monomer) and 2 (copolymerization of an AB_2 and an AB monomer) in Table 1 clearly suggests that crowding within the polymer structure is not the only factor that can explain the limitation in the molecular weights achieved. In these entries, similar results are obtained for the homopolymerization of **3** and for its copolymerization with the AB monomer **7**, despite the fact lesser crowding of functionalities is expected in the latter case. It should be noted that for this polymerization, catalyst lifetime and turnover are not significant issues and these factors have been studied extensively by others for analogous linear systems;[6,10,14] for example, addition of fresh catalyst at the end of a polymerization run did not have any noticeable effect. Because a widely accepted mechanism for the hydrosilation reaction[6a] requires the simultaneous coordination of both the vinyl and silane functionalities to the platinum catalyst (Scheme 3), the occurrence of intramolecular cyclization has a very significant effect on the process of polymer growth. For example, it is likely that few large molecules still possess a vinyl group at their focal point, and the number of vinyl-depleted molecules, large or small, grows very rapidly as the reaction proceeds. Therefore, upon batch addition of monomer and catalyst to the previously formed polymer, reactions involving the entire distribution of molecules occur, leading to a very low increase in overall molecular weight. Because of the mechanism of the reaction, steric and kinetic considerations may be especially important in determining the fate of the different species involved. Incorporation of fresh monomer molecules into large polymer molecules may be significantly slower than their intramolecular cyclization or their reaction with other monomer units or small oligomers. In this way, the fresh monomer would tend to be transformed preferentially into new oligomeric species rather than incorporated into larger preexisting polymer molecules. Overall, it is unlikely that substantial molecular weight buildup can be achieved by a simple batch addition of monomer and catalyst as long as large quantities of cyclized monomer and vinyl-depleted low oligomers are present or formed rapidly in the reaction mixture.

Structure of the Hyperbranched Polymers. In all cases, ^1H and ^{13}C NMR spectroscopy show that the hydrosilation reaction yields preferentially β addition products although a nonnegligible proportion of α addition products is also observed. For example, analysis of polymer **8** by ^1H NMR spectroscopy (Figure 1) reveals a signal at 1.1 ppm that can be assigned to the methyl group resulting from α addition, whereas β addition gives rise to a signal at 0.3–0.5 ppm. Relative integration of α and β signals indicates that α addition is present in ~30% of the linkages. The ^{13}C NMR spectra of the polymers clearly confirm that both types of addition are taking place. For example, the polymerization of **5** (Figure 3), affords a product, **9**, with ^{13}C NMR signals corresponding to CH_3^- and CH– units resulting from α addition at 7 and 12 ppm and signals of CH_2^- units due to β addition between 8 and 10 ppm.

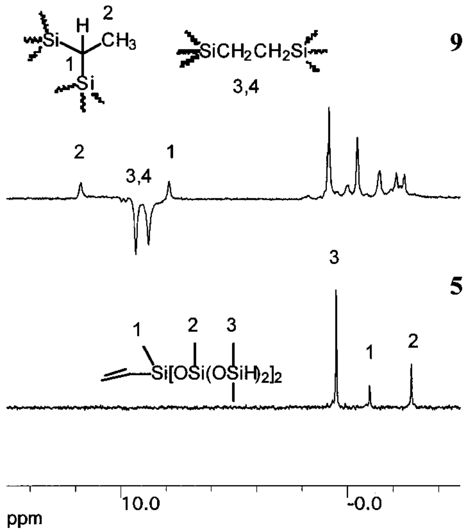


Figure 3. The ^{13}C (APT) NMR ($CDCl_3$) spectra of monomer **5** and polymer **9**.

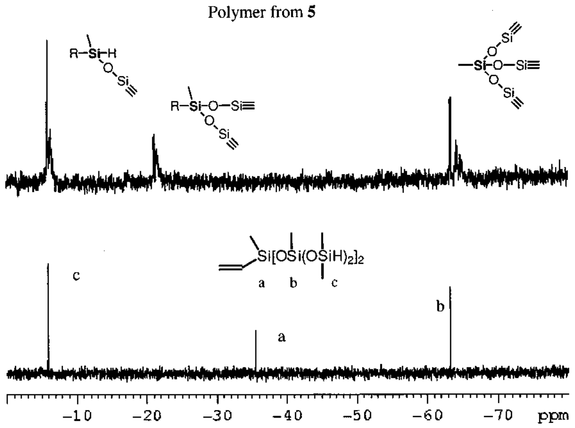


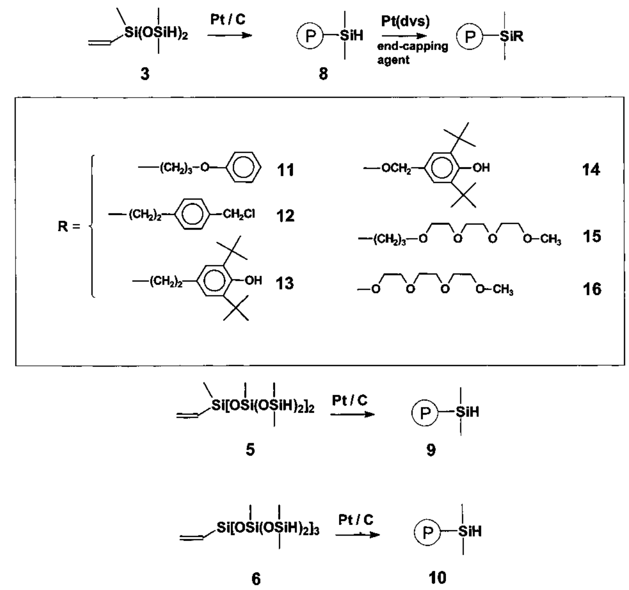
Figure 4. The ^{29}Si NMR ($CDCl_3$) spectra of monomer **5** and polymer **9**.

^{29}Si NMR spectra for the monomers **3**, **5**, and **6** and their polymers were in accordance with the proposed structures. For example, Figure 4 shows that the signal at −36 ppm corresponding to the Si atom attached to the vinyl group of the monomer is shifted downfield upon hydrosilation, but the signals at −6 and −64 ppm, corresponding to the terminal SiH groups and to the central Si atoms of the monomer, respectively, remain essentially unchanged upon polymerization.

Information regarding the degree of branching of the polymers could not be obtained from ^1H, ^{13}C, or ^{29}Si NMR because of the very similar chemical shifts of the partially and completely substituted building blocks.

Control of Chain-End Functionalities. Doubtless, one of the most appealing characteristics of this type of polymer is the possibility to functionalize their terminal SiH groups. Hydrosilation is a versatile reaction that can potentially introduce a broad diversity of end groups into these polymers.[6,10c] End-capping with different reagents using Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex) was accomplished as illustrated in Scheme 4. Reactions were monitored by

Scheme 4



^{1}H NMR and IR spectroscopy, and disappearance of the SiH groups and new signals due to the linkages to the end-capping agent (Figure 1) could be observed in all cases.

The modification reactions monitored by GPC led to the expected increase in relative molecular weights. To obtain a rough calibration of the relative molecular weights obtained by GPC, some light scattering experiments were carried out on a batch of polymer with structure **11,** itself obtained from a higher molecular weight sample of its precursor with structure **8**. A higher molecular weight sample was selected for this experiment to increase the signal-to-noise ratio in the light scattering measurements. Therefore, a batch of polymer with structure **8** that had been enlarged twice by addition of fresh monomer **3** (GPC $M_w = 10\,000$) was end-capped by reaction with allylphenyl ether, leading to a polymer with structure **11**. Comparative light scattering and GPC studies on this polymer afforded comparable results; that is, light scattering indicated 25 400 ± 300 with a root mean square (RMS) radius of 18.0 ± 1.4 nm, whereas GPC indicated $M_w = 21\,600$ with $M_w/M_n = 2.8$.

Reaction of polymer **8** with 4-chloromethylstyrene was accomplished in quantitative yield by heating to reflux overnight in dichloromethane. The new polymer, **12**, has terminal benzyl chloride groups that are amenable to further modification with a variety of nucleophilic reagents. In addition, polymer **12** might be used to initiate the atom-transfer radical polymerization (ATRP) pseudo-living polymerization of other vinyl monomers to afford hybrid dendritic-linear star or star-branched copolymers.

The incorporation of 2,6-di-*tert*-butylphenol type units into polymeric structures has been used to create stable polyradicals[16a] and 4-allyl-2,6-di-*tert*-butylphenol has been linked to organosilicon polymers to impart antioxidant properties.[16b] In our case, end-capping of polymer with 4-vinyl-2,6-di-*tert*-butylphenol[17] affords a polymer (**13**) with a high concentration of antioxidant terminal groups that is a good candidate for application as an oxygen scavenger. Monitoring the disappearance of the SiH groups present in polymer **8** indicates that the reaction proceeds quantitatively in a few hours. Although aldehydes are also susceptible to hydrosilation, their reactivity is low and end-capping with 3,5-di*tert*-butyl-4-hydroxybenzaldehyde to give **14** proceeds too slowly to be useful as a means of complete functionalization and ~25% of the SiH units remain unreacted after 3 days of reaction. It may be possible to use this difference in reactivity between aldehydes and vinyl groups to introduce different substituents at different locations of the hyperbranched polymer structure.

Functionalization of **8** with allyl methyl triethylene glycol could be driven to completion to obtain the end-capped polymer **15**. Alcohols can also couple easily with SiH functionalities in the presence of a catalyst in a reaction that produces hydrogen gas.[12] Using this approach, triethylene glycol monomethyl ether was introduced as the terminal group to produce polymer **16** that had properties similar to those of polymer **15** but contained a more labile linkage to the siloxysilane skeleton. Unlike the starting polymer, these new polymers were soluble in methanol and methanol/water (2:1). The increased solubility in polar solvents and the biocompatibility of siloxy-type polymers suggests that these hybrid materials might potentially be put to use in biological applications as part of implants or drug delivery systems. Another potential application of these polymers would be in the field of conducting polymers where noncrystalline poly(ethylene glycol)-type materials have shown interesting properties.[18] Because the hyperbranched poly(siloxysilane) skeleton possesses high flexibility and amorphous characteristics these polymers are ideally suited for the development of conducting polyelectrolytes. In preliminary experiments we have shown that the glass transition temperature (T_g) of the polymer changes drastically upon addition of lithium perchlorate.

The SiH groups present on the polymers derived from monomers **5** and **6** are also fully accessible to external reagents. For example, the polymers readily react with allylphenyl ether under the standard conditions to yield materials that reveal no remaining SiH groups upon spectroscopic analysis.

End-capping reactions with reagents that contain a vinylphenyl unit (synthesis of polymers **12** and **13**) results in both α and β hydrosilation. In the case of **12**, ^{1}H NMR indicates that ~30% of the linkages to the end-capping agent corresponds to α hydrosilation, whereas the percentage is higher (~50%) for polymer **13**. The ^{1}H NMR of polymer **13** (Figure 1) shows distinct resonances for both species as can be seen for the phenolic (4.93 and 5.03 ppm) and aromatic protons (6.88 and 7.02 ppm). In contrast, the allylic end-capping agents (polymers **11** and **15**) only add to the β position.

Physical Properties. It has been shown that, as a result of the large number of end groups, the T_g of hyperbranched and dendritic polymers is greatly influenced by the characteristics of the terminal functionality.[19] As can be seen in Table 2, the SiH terminated polymers **8**, **9**, and **10** exhibit a very low T_g that reflects the conformational freedom of the carbosiloxane skeleton. End-capping of SiH terminated **8** with di-*tert*-butylphenol units dramatically increases the T_g of the polymers **13** and **14** to −2 °C (104 °C higher than the starting material) and −32 °C, respectively. It must be pointed out that the T_g value of polymer **14** is affected by the presence of its unreacted SiH groups. Phenyl ether- and chloromethylbenzene-terminated polymers show intermediate T_g values that are also considerably

Table 2. Thermal Properties of the Polymers 8–16

polymer	T_g (°C)	TGA, transition onset (°C)
8	−106	230
9	−117	256
10	−126	208
11	−60	411
12	−57	302
13	−2	394
14	−32	242
15	−92	325
16	−85	262

higher than that for the starting polymer **8**. In contrast, polymers with triethylene glycol type end groups have T_g values only slightly higher than those of the SiH-terminated polymers and they exhibit no melting transition, confirming that this approach affords highly amorphous poly(ethylene glycol)-type materials.

In dendritic and hyperbranched molecules, the number of branches (a factor that tends to increase T_g) and the number of end groups (a factor that tends to diminish T_g) grow in parallel and therefore no significant dependence of T_g values on molecular weights is expected.[20] In our case, polymers **8**, **9**, and **10**, which have similar molecular weight but different branching patterns, show slightly different T_g values that might originate from the different proportion of siloxy bonds within each polymer.

As expected, thermal stability also depends to a significant extent on the type of terminal groups. The data displayed in Table 2 show that although SiH terminated polymer **8** has a decomposition onset temperature of 230 °C, the modified polymers are more stable. The derivatives with 2,6-di-*tert*-butylphenol units show markedly different decomposition onset temperatures. Although **14** still contains some unreacted SiH groups leading to a behavior similar to the original polymer, **13** shows a decomposition onset >150 °C higher than that of the starting material. End-capping with allylphenyl ether produces a polymer stable up to ~400 °C. Differences between polymers **15** and **16** are in agreement with the characteristics of their terminal groups because **16** has a labile alkoxysilane linkage whereas **15** contains a more stable carbosilane group.

Conclusions

New monomers for the synthesis of hyperbranched polysiloxanes have been prepared and polymerized. The M_w values of the SiH-terminated polymers are near 10 000 and increase only moderately upon addition of more monomer. In all cases, intramolecular cyclization reactions have been detected. We believe that these intramolecular side reactions that lead to vinyl-depleted structures, including low oligomers, are primarily responsible for the limited growth of the hyperbranched polymers. Our experiments, carried out with a variety of monomers with a different extent of branching, do not support earlier claims of steric limitations to growth as a result of crowding within the polymer structure. All of the hyperbranched polymers possess fully accessible terminal SiH groups that may be modified with a variety of external reagents. End-capping reactions have been performed to lead to polymers with antioxidant groups, hybrid siloxysilane poly(ethylene glycol)-type materials, and polymers with terminal benzyl chloride functionality that may possess interesting applications. The thermal properties of the polymers are strongly affected by the type of terminal groups.

Experimental Section

General Directions. All reactions were carried out under an inert atmosphere of dry argon. The T_g values were measured by differential scanning calorimetry (DSC) using a Mettler DSC 30 low-temperature cell coupled to a TC10A TA processor. Heating rates were 10 K min^{-1}. The T_g was taken as the midpoint of the inflection tangent. Data analysis was done with Mettler TA72 software. Thermogravimetric analyses (TGA) were measured on a Seiko, SSC/5200 device at 10 K min^{-1} heating rate. Infrared spectra were recorded on a Nicolet IR/44 spectrophotometer as thin films on NaCl disks. The ^{1}H and ^{13}C NMR (300 and 75 MHz respectively) spectra were recorded on solutions in $CDCl_3$ on a Bruker WM300 spectrometer with the solvent signals as standard. The ^{29}Si NMR spectra were recorded on a Bruker Avance DRX500 using tetramethylsilane (TMS) as reference. Size-exclusion chromatography (SEC) was performed at 45 °C on a line consisting of an M510 pump, a U6K universal injector, a UV 486 detector (all Waters), a differential refractive index detector (DRI, Milton Roy), and a model 110 differential viscometer (Viscotek). The separation was achieved across a set of four 5-μm PL Gel columns (Polymer Laboratories) with porosities of 100, 500, and 1000 Å and Mixed C (packed with beads of all three mixed porosities). The mobile phase was tetrahydrofuran (THF) eluting at a nominal flow rate of 1 mL min^{-1}. The molecular weight characteristics of the polymers were calculated by a polystyrene calibration curve constructed with 23 monodisperse polystyrene standards. Light scattering measurements were performed with a Wyatt Technology Corporation DAWN F Laser Photometer, data analysis was done with DAWN software and d*n*/d*c* measurements were done on a Wyatt Optilab 903.

Methylvinylbis(dimethylsiloxy)silane (3). Ether (100 mL), water (2.5 mL, 0.139 mol), and anhydrous sodium hydrogen carbonate (23.2 g, 0.276 mol) were charged into a two-necked round-bottomed flask equipped with an addition funnel and condenser and cooled into an ice bath. A solution of dimethylchlorosilane (16.5 mL, 0.148 mol) and dichloromethylvinylsilane (8.0 mL, 0.061 mol) was added in a dropwise manner with stirring for 45 min. The system was then allowed to warm to room temperature and stirred for another 45 min. Remaining sodium hydrogen carbonate was filtered off, and the ether solution was dried with magnesium sulfate. The solution was combined with Et_3N (5.0 mL, 0.036 mol) and 4-DMAP (70 mg, 5.7 10^{-4} mol) in a two-necked flask with an addition funnel and condenser. Additional dimethylchlorosilane (4.0 mL, 0.036 mol) was added in a dropwise manner for 15 min with stirring at 25 °C. The mixture was stirred for another 30 min. Precipitated triethylamine hydrochloride was filtered off, and the solvent removed under reduced pressure to give a colorless liquid that was distilled under reduced pressure to afford **3** (8.8 g; 66%; bp, 55 °C/20 mmHg). ^{1}H NMR: δ 0.13 (s, 3H, CH_3Si), 0.20 (d, 2.7 Hz, 12H, $(CH_3)_2Si$), 4.72 (hep, 2.7 Hz, 2H, SiH), 5.79 (m, 1H, HC=C), and 5.98 (m, 2H, H_2C=C). ^{13}C NMR: δ −1.04 (CH_3Si), 0.7 ($(CH_3)_2Si$), 133.15 (H_2*C*=C), and 136.64 (H*C*=C). ^{29}Si NMR: δ −6 (≡SiH), −32 (=SiO_2). MS (EI): 219 (M^+- H). IR: 1598 (C=C), 2128 (SiH) cm^{-1}.

Methylbis(dimethylsiloxy)silanol (4). Ether (250 mL), anhydrous sodium hydrogen carbonate (18.3 g, 0.218 mol) and dimethylchlorosilane (11.3 mL, 0.100 mol) were charged into a two-necked round-bottomed flask equipped with an addition funnel and condenser and cooled in an ice bath. Carefully, 25 mL of water was poured in the flask (first milliliter was poured very slowly). Then, with stirring, methyltrichlorosilane (4.0 mL, 0.033 mol) dissolved in 5 mL of anhydrous ether was added in a dropwise manner over a period of 5 min. The mixture was stirred overnight and then the ether phase was separated and dried over magnesium sulfate. Ether was removed under reduced pressure to yield a colorless liquid. Compound **4** was obtained after fractional distillation under reduced pressure. (2.2 g, 32%; bp, 32 °C/3 mmHg). ^{1}H NMR:

δ 0.13 (s, 3H, $\mathrm{CH_3Si}$), 0.23 (d, 2.7 Hz, 12H, $\mathrm{(CH_3)_2Si}$), 2.16 (broad, 1H, SiOH) and 4.72 (hep, 2.7 Hz, 2H, SiH). ^{13}C NMR: δ -3.57 ($\mathrm{CH_3Si}$) and 0.49 ($\mathrm{((CH_3)_2Si}$). IR: 2131 (SiH), 3404 (SiOH) $\mathrm{cm^{-1}}$.

Methylvinylbis[methylbis(dimethylsiloxy)siloxy]silane. (5) Anhydrous ether (50 mL), **4** (2.0 g, 9.5 10^{-3} mol), 4-(dimethylamino)pyridine (10 mg, 8.1 10^{-5} mol), and triethylamine (1.32 mL, 9.5 10^{-3} mol) were charged into a round-bottomed flask. Methylvinyldichlorosilane (0.63 mL, 4.75 10^{-3} mol) was added slowly with vigorous stirring over a period of 10 min. The mixture was stirred for an additional 30 min, and the precipitate of triethylamine hydrochloride was filtered off. The residue was dissolved in $\mathrm{CH_2Cl_2}$ (25 mL) and extracted with 2 × 20 mL of 3 N HCl to remove residual DMAP. The organic phase was then dried over $\mathrm{MgSO_4}$, and the solvent was removed to give a colorless liquid. Distillation under reduced pressure afforded **5** as a colorless liquid (2.0 g; 85%; bp, 80 °C/0.5 mmHg). ^{1}H NMR: δ 0.07 (s, 6H, $\mathrm{CH_3Si}$), 0.17 (s, 3H, $\mathrm{CH_3Si}$), 0.20 (d, 2.7 Hz, 24H, $\mathrm{(CH_3)_2Si}$), 4.72 (hep, 2.7 Hz, 4H, SiH), 5.83 (m, 1H, $\mathrm{HC{=}C}$), and 5.98 (m, 2H, $\mathrm{H_2C{=}C}$). ^{13}C NMR: δ -2.82 ($\mathrm{CH_3Si}$), -1.00 ($\mathrm{CH_3Si}$), 0.48 ($\mathrm{(CH_3)_2Si}$), 133.14 ($\mathrm{H_2\mathit{C}{=}C}$), and 136.41 ($\mathrm{H\mathit{C}{=}C}$). ^{29}Si NMR: δ -7 ($\equiv$SiH), -35 ($=\mathrm{SiO_2}$), -63 ($-\mathrm{SiO_3}$). MS (EI): 487 ($\mathrm{M^+ - H}$). IR 1599 ($\mathrm{C{=}C}$), 2131 (SiH) $\mathrm{cm^{-1}}$.

Vinyltris[methylbis(dimethylsiloxy)siloxy]silane (6). Anhydrous ether (50 mL), **4** (2.0 g, 9.5 10^{-3} mol), 4-(dimethylamino)pyridine (10 mg, 8.1 10^{-5} mol), and triethylamine (1.32 mL 9.5 10^{-3} mol) were charged in a round-bottomed flask. Vinyltrichlorosilane (0.40 mL, 3.17 10^{-3} mol) was added slowly over 10 min under vigorous stirring. The mixture was stirred for an additional 30 min, and the precipitated triethylamine hydrochloride was filtered off. The residue was dissolved into $\mathrm{CH_2Cl_2}$ (25 mL) and extracted with 2 × 20 mL of 3 N HCl to remove residual DMAP. The organic phase was then dried over $\mathrm{MgSO_4}$, and the solvent was removed to give a colorless liquid. Removal of volatile materials under high vacuum at 60 °C for 30 min afforded the monomer **6** as a colorless liquid (1.9 g, 88%). ^{1}H NMR: δ 0.11 (s, 9H, $\mathrm{CH_3Si}$), 0.21 (d, 2.7 Hz, 36H, $\mathrm{(CH_3)_2Si}$), 4.73 (hep, 2.7 Hz, 6H, SiH), and 5.9 (m, 3H, $\mathrm{HC{=}CH_2}$). ^{13}C NMR: δ -2.84 $\mathrm{CH_3Si}$, 0.53 $\mathrm{(CH_3)_2Si}$, 132.29 ($\mathrm{H\mathit{C}{=}C}$), and 134.53 ($\mathrm{H_2\mathit{C}{=}C}$). ^{29}Si NMR: δ -6 ($\equiv$SiH), -64 ($-\mathrm{SiO_3}$). MS (EI): 681 ($\mathrm{M^+ - H}$). IR: 1602 ($\mathrm{C{=}C}$), 2134 (SiH) $\mathrm{cm^{-1}}$.

Polymer 8. Monomer **3** (2.0 g) and 7 mg of 5% Pt on C were charged into a round-bottomed flask under a stream of argon. The reaction was kept at 50 °C with vigorous stirring until no vinyl groups were detected by IR or NMR spectroscopy (typically 2 or 3 h) and then the reaction was allowed to cool to room temperature. The polymer was dissolved in diethyl ether, and carbon was filtered off through Celite. Solvent was evaporated, and the resulting colorless liquid was dissolved in 1 mL of diethyl ether and precipitated into acetonitrile (100 mL) several times. Polymer **8** was obtained as a colorless viscous liquid, with $T_g = -106$ °C, and TGA onset = 230 °C. ^{1}H NMR: δ $-0.03-0.25$ ($\mathrm{CH_3Si}$), 0.3 ($\mathrm{SiCH_2CH_2Si}$), 1.05 ($\mathrm{C\mathit{H}_3CHSi}$), and 4.72 (SiH). ^{13}C NMR: δ $-2-1$ ($\mathrm{CH_3Si}$), 7.6 ($\mathrm{CH_3C\mathit{H}}$), 8.5 ($\mathrm{CH_2Si}$), 9.1 ($\mathrm{CH_2Si}$), and 11.8 ($\mathrm{C\mathit{H}_3CH}$). IR: 2126 (SiH) $\mathrm{cm^{-1}}$. ^{29}Si NMR: δ $-5-7$ ($\equiv$SiH), $-18-22$ ($=\mathrm{SiO_2}$).

Polymer 9. Identical reaction conditions as for the synthesis of **8** were used. Polymer **9** was isolated as a colorless viscous liquid ($T_g = -117$ °C, TGA onset = 256 °C). ^{1}H NMR: δ $-2.7-0.6$ ($\mathrm{CH_3Si}$), 0.5 ($\mathrm{SiCH_2CH_2Si}$), 1.05 ($\mathrm{C\mathit{H}_3CHSi}$), and 4.72 (SiH). ^{13}C NMR: δ $-2-1$ ($\mathrm{CH_3Si}$), 7.6 ($\mathrm{CH_3C\mathit{H}}$), 8.5 ($\mathrm{CH_2Si}$), 9.1 ($\mathrm{CH_2Si}$), and 11.8 ($\mathrm{C\mathit{H}_3CH}$). ^{29}Si NMR: δ $-6-7$ ($\equiv$SiH), $-21-22$ ($=\mathrm{SiO_2}$), $-64-66$ ($-\mathrm{SiO_3}$). IR: 2126 (SiH) $\mathrm{cm^{-1}}$.

Polymer 10. Identical reaction conditions as for the synthesis of **8** were used. Polymer **10** was isolated as a colorless viscous liquid ($T_g = -126$ °C, TGA onset = 208 °C). ^{1}H NMR: δ 0.1 ($\mathrm{CH_3Si}$), 0.2 ($\mathrm{CH_3Si}$), 0.3–0.8 ($\mathrm{SiCH_2CH_2Si}$), 1.1 ($\mathrm{C\mathit{H}_3CHSi}$), and 4.72 (SiH). ^{13}C NMR: δ $-2.45-0.57$ ($\mathrm{CH_3Si}$), 5.4 ($\mathrm{CH_2Si}$), 6.2 ($\mathrm{CH_2Si}$), 7.9, 8.3 ($\mathrm{CH_3CH}$), 9.3 ($\mathrm{CH_2Si}$), and 9.7 ($\mathrm{CH_2Si}$). ^{29}Si NMR: δ $-6-7$ ($\equiv$SiH), $-64-70$ ($-\mathrm{SiO_3}$). IR: 2133 (SiH) $\mathrm{cm^{-1}}$.

Polymer 11. One gram of **8** ($M_w = 7100$, $M_w/M_n = 1.9$) dissolved in 5 mL of hexanes, 0.90 mL of allylphenyl ether (6.6 10^{-3} mol), and 5 μL of 3% platinum divinyltetramethylsiloxane complex in xylene (United Chemical Technologies) were charged into a round-bottomed flask under a stream of argon. After heating to reflux for 3 h, no SiH groups could be detected by ^{1}H NMR or IR spectroscopy. The mixture was cooled to room temperature, and the solvent was removed under reduced pressure. After removal of the excess of allylphenyl ether under reduced pressure at 60 °C overnight,1.42 g of **11** were obtained ($M_w = 15\,600$, $M_w/M_n = 2.3$, $T_g = -60$ °C, TGA onset = 411 °C). ^{1}H NMR: δ $-0.1-0.2$ ($\mathrm{CH_3Si}$), 0.4 ($\mathrm{SiCH_2CH_2Si}$), 0.63 ($\mathrm{PhOCH_2CH_2C\mathit{H}_2Si}$), 1.10 ($\mathrm{C\mathit{H}_3CHSi}$), 1.82 ($\mathrm{PhOCH_2C\mathit{H}_2CH_2Si}$), 3.94 ($\mathrm{PhOC\mathit{H}_2CH_2CH_2Si}$), 6.89 (ArH), and 7.25 (ArH). ^{13}C NMR: δ $-1-0.3$ ($\mathrm{CH_3Si}$), 8.0 ($\mathrm{CH_3\mathit{C}HSi}$), 9.0 ($\mathrm{CH_2Si}$) 9.5 ($\mathrm{CH_2Si}$) 12.0 ($\mathrm{\mathit{C}H_3CHSi}$), 14.3 ($\mathrm{PhOCH_2CH_2C\mathit{H}_2Si}$), 23.2 ($\mathrm{PhOCH_2\mathit{C}H_2CH_2Si}$), 70.3 ($\mathrm{PhO\mathit{C}H_2CH_2CH_2Si}$), 114.4 ($\mathrm{C_{Ar}H}$), 120.4 ($\mathrm{C_{Ar}H}$), 129.3 ($\mathrm{C_{Ar}H}$), and 159.1 ($\mathrm{C_{Ar}}$). IR 1602 ($\mathrm{C_{Ar}{=}C_{Ar}}$), 1586 ($\mathrm{C_{Ar}{=}C_{Ar}}$) $\mathrm{cm^{-1}}$.

In a different experiment, a batch of polymer with structure **8** that had been enlarged twice by addition of fresh monomer **3** (GPC $M_w = 10\,000$) was end-capped by reaction with allylphenyl ether, as already described. Light scattering: $M_w = 25\,400 \pm 300$ (RMS radius = 18.0 ± 1.4 nm); GPC: $M_w = 21\,600$ ($M_w/M_n = 2.8$).

Polymer 12. One gram of **8** ($M_w = 7100$, $M_w/M_n = 1.9$) dissolved in 5 mL of dichloromethane, 1.00 mL of 4-(chloromethyl)styrene (7.0 10^{-3} mol), and 5 μL of 3% platinum divinyltetramethylsiloxane complex in xylene were charged into a round-bottomed flask under a stream of argon. After heating to reflux overnight, no SiH groups could be detected by NMR or IR spectroscopy. The mixture was cooled to room temperature, and the solvent was removed. The polymer was dissolved in 1 mL of ether and precipitated into acetonitrile to afford polymer **12**. (0.71 g, $M_w = 16\,500$, $M_w/M_n = 2.3$, $T_g = -57$ °C, TGA onset = 302 °C). ^{1}H NMR: δ $-0.1-0.3$ ($\mathrm{CH_3Si}$), 0.4 ($\mathrm{SiCH_2CH_2Si}$), 0.9 ($\mathrm{ArCH_2C\mathit{H}_2Si}$), 1.1 ($\mathrm{C\mathit{H}_3CHSi}$), 1.4 ($\mathrm{ArCHC\mathit{H}_3}$), 2.2 ($\mathrm{ArC\mathit{H}CH_3}$), 2.7 ($\mathrm{ArC\mathit{H}_2CH_2Si}$), 4.58 ($\mathrm{ArCH_2Cl}$), and 7.0–7.4 (ArH). ^{13}C NMR: δ 0.1–0.3 ($\mathrm{CH_3Si}$), 8.0 ($\mathrm{CH_3\mathit{C}HSi}$), 9.0 ($\mathrm{CH_2Si}$), 9.5 ($\mathrm{CH_2Si}$), 11.9 ($\mathrm{\mathit{C}H_3CHSi}$), 14.4 ($\mathrm{\mathit{C}H_3CHAr}$), 20.2 ($\mathrm{ArCH_2\mathit{C}H_2Si}$), 29.1 ($\mathrm{Ar\mathit{C}HSi}$), 31.2 ($\mathrm{Ar\mathit{C}H_2CH_2Si}$), 46.2 ($\mathrm{ArCH_2Cl}$), 46.4 ($\mathrm{ArCH_2Cl}$), 127.6 ($\mathrm{C_{Ar}H}$), 128.1 ($\mathrm{C_{Ar}H}$), 128.3 ($\mathrm{C_{Ar}H}$), 128.6 ($\mathrm{C_{Ar}H}$), 135.5 ($\mathrm{C_{Ar}}$), 134.7 ($\mathrm{C_{Ar}}$), and 145.5 ($\mathrm{C_{Ar}}$). IR 1513 ($\mathrm{C_{Ar}{=}C_{Ar}}$) $\mathrm{cm^{-1}}$.

Polymer 13. One gram of **8** ($M_w = 8100$, $M_w/M_n = 1.9$) dissolved in 5 mL of hexanes, 1.70 g (7.3 10^{-3} mol) of 2,6-di-*tert*-butyl-4-vinylphenol, and 5 μL of 3% platinum divinyltetramethylsiloxane complex in xylene were charged into a round-bottomed flask under a stream of argon with stirring. After heating to reflux for 2 h, no SiH groups could be detected by NMR or IR spectroscopy. The mixture was cooled to room temperature, and solvent was removed under reduced pressure. To remove the excess of end-capper, the polymer was dissolved in 1 mL of ether and precipitated into acetonitrile to give **13** (1.13 g, $M_w = 13\,500$, $M_w/M_n = 1.5$, T_g -2 °C, TGA onset = 394 °C). ^{1}H NMR: δ $-0.04-0.3$ ($\mathrm{CH_3Si}$), 0.31–0.56 ($\mathrm{SiCH_2CH_2Si}$), 0.87–1.13 ($\mathrm{ArCH_2C\mathit{H}_2Si}$, $\mathrm{C\mathit{H}_3CHSi}$), 1.38 ($\mathrm{ArCHC\mathit{H}_3}$), 1.45 (*tert*-butyl), 2.13 ($\mathrm{ArC\mathit{H}_2CH_3}$), 2.61 ($\mathrm{ArCH_2C\mathit{H}_2Si}$), 4.93 ($-$OH), 5.03 ($-$OH), 6.88 (ArH), and 7.02 (ArH). ^{13}C NMR: δ $-2.2-0.6$ ($\mathrm{CH_3Si}$), 8.0 ($\mathrm{CH_3\mathit{C}HSi}$), 9.0 ($\mathrm{SiCH_2CH_2Si}$), 9.6 ($\mathrm{SiCH_2CH_2Si}$), 12.0 ($\mathrm{\mathit{C}H_3CHSi}$), 14.7 ($\mathrm{\mathit{C}H_3CHAr}$), 20.4–20.7 ($\mathrm{ArCH_2\mathit{C}H_2Si}$), 29.2 ($\mathrm{Ar\mathit{C}HSi}$), 30.3 ($\mathrm{-C(\mathit{C}H_3)_3}$), 30.4 ($\mathrm{-C(\mathit{C}H_3)_3}$), 31.2 ($\mathrm{Ar\mathit{C}H_2CH_2Si}$), 34.3 ($\mathrm{\text{-}\mathit{C}(CH_3)_3}$), 123.7 ($\mathrm{C_{Ar}H}$), 124.1 ($\mathrm{C_{Ar}H}$), 135.0 ($\mathrm{C_{Ar}}$), 135.5 ($\mathrm{C_{Ar}}$), 135.7 ($\mathrm{C_{Ar}}$), 150.8 ($\mathrm{C_{Ar-}OH}$), and 151.6 ($\mathrm{C_{Ar}\text{-}OH}$). IR: 3650 ($-$OH) $\mathrm{cm^{-1}}$.

Polymer 14. One gram of **8** ($M_w = 5600$, $M_w/M_n = 1.6$) dissolved in 5 mL of benzene, 1.50 g (6.4 10^{-3} mol) of anhydrous 2,6-di-*tert*-butyl-4-hydroxybenzaldehyde (7.3 10^{-3} mol), and 5 μL of 3% platinum divinyltetramethylsiloxane complex in xylene were charged into a round-bottomed flask under a stream of argon with stirring. After heating to reflux for 3 days, only ~75% (determined by ^{1}H NMR) of the SiH groups were functionalized. The mixture was cooled to room temperature, and the solvent was removed under reduced pressure. To remove the excess of end-capper, the polymer was dissolved in 1 mL of ether and precipitated into acetonitrile to give **14** (0.90 g, $M_w = 46\,700$, $M_w/M_n = 2.5$, $T_g = -32$

°C, TGA onset = 242 °C). ^{1}H NMR: δ −0.11−0.22 ($\mathrm{CH_3Si}$), 0.4 ($\mathrm{SiCH_2CH_2Si}$), 1.06 ($\mathrm{C}\mathit{H}_3\mathrm{CHSi}$), 1.4 (*tert*-butyl), 4.65 ($\mathrm{ArCH_2O}$−), 5.12 (−OH), and 7.12 (ArH). ^{13}C NMR: δ −0.5−1.3 ($\mathrm{CH_3Si}$), 7.9 ($\mathrm{CH_3}\mathit{C}\mathrm{H}$), 8.9 ($\mathrm{CH_2Si}$), 9.4 ($\mathrm{CH_2Si}$), 11.8 ($\mathit{C}\mathrm{H_3}$-CH), 30.2 ($-\mathrm{C}(\mathit{C}\mathrm{H_3})_3$), 34.3 ($-\mathit{C}(\mathrm{CH_3})_3$), 64.7 ($\mathrm{ArCH_2O}$-), 123.9 ($\mathrm{C_{Ar}H}$), 131.1 ($\mathrm{C_{Ar}}$), 135.6 ($\mathrm{C_{Ar}}$), and 153.0 ($\mathrm{C_{Ar}}$-OH). IR: 3647 (−OH), 2129 (SiH) cm^{-1}.

Polymer 15. One gram of **8** (M_w = 5700, $M_\mathrm{w}/M_\mathrm{n}$ = 1.7), 2.3 mL of triethylene glycol monomethyl ether (1.5 10^{-2} mol), and 5 μL of 3% platinum divinyltetramethylsiloxane complex in xylene were charged into a round-bottomed flask under a stream of argon with stirring. The mixture was stirred overnight at room temperature, and SiH groups could no longer be detected by ^{1}H NMR spectroscopy. The excess end-capper was removed by heating under reduced pressure at 60 °C overnight to give **15** (1.58 g, M_w = 11 400, $M_\mathrm{w}/M_\mathrm{n}$ = 2.4, T_g = −92 °C, TGA onset = 325 °C). ^{1}H NMR: δ −0.03−0.25 ($\mathrm{CH_3}$-Si), 0.42 ($\mathrm{SiCH_2CH_2Si}$), 1.04 ($\mathrm{C}\mathit{H}_3\mathrm{CHSi}$), 3.37 ($\mathrm{CH_3O}$−), 3.55 ($-\mathrm{OCH_2CH_2O}$-), 3.64 ($-\mathrm{OCH_2CH_2O}-$), and 3.79 ($-\mathrm{OCH_2}$-$\mathrm{CH_2O}-$). ^{13}C NMR: δ −1−0 ($\mathrm{CH_3Si}$), 7.6 ($\mathrm{CH_3}\mathit{C}\mathrm{H}$), 8.8 ($\mathrm{CH_2}$-Si), 9.5 ($\mathrm{CH_2Si}$), 12.0 ($\mathrm{CH_3CH}$), 59.0 ($\mathrm{CH_3O}$−), 61.5 ($-\mathrm{CH_2}$-OSi−), 70.5, 70.6 (double intensity), and 71.9, 72.4, and 76.5 ($-\mathrm{OCH_2CH_2O}-$). IR 1352 (C−O-), 1458 (C−O-) cm^{-1}.

Allyl methyl triethylene glycol.[19a] Two grams (0.012 mol) of triethylene glycol monomethyl ether, 400 mg of sodium hydride (0.017 mol), 2.3 mL of allyl bromide (0.027 mol), and 25 mL of dry THF were charged in a round-bottomed flask with stirring under an inert atmosphere. After 30 min, thin-layer chromatograph (TLC) showed that no starting monomethyl ether was remaining. After filtration, evaporation of the solvent, and removal of excess of allyl bromide under reduced pressure,1.54 g (82%) of target compound were obtained. ^{1}H NMR: δ 3.34 (s, 3H, $\mathrm{CH_3}$), 3.64 (m, 12H, $-\mathrm{OCH_2CH_2O}-$), 3.98 (d, 5.4 Hz, 2H, $\mathrm{CH_2{=}CH{-}C}\mathit{H}_2-$), 5.1−5.3 (m, 2H, $\mathit{CH}_2\mathrm{{=}CH-}$CH2−), and 5.75−5.95 (m, 1H, $\mathrm{CH_2{=}C}\mathit{H}\text{-}\mathrm{CH_2}-$). ^{13}C NMR: δ 58.92 ($-\mathrm{CH_3}-$)g, 61.5, 69.30, 70.32, 70.51 (double intensity), 71.84, 72.12, 118.38 (−CH=), and 134.68 ($\mathrm{CH_2}$=). Calcd for $\mathrm{C_{10}H_{20}O_4}$: C, 58.80; H, 9.87. Found: C, 59.04; H, 9.80.

Polymer 16. One gram of polymer **8** (M_w = 4500, $M_\mathrm{w}/M_\mathrm{n}$ = 1.6), 1.0 g of triethylene glycol allylmethyldiether (4.9 10^{-3} mol), and 5 μL of 3% platinum divinyltetramethydisiloxane complex in xylene were charged in a round-bottomed flask under a stream of argon with stirring. The mixture was stirred for 5 h at room temperature, and no remaining SiH groups could be detected by ^{1}H NMR spectroscopy. The excess end-capper was removed by heating under reduced pressure at 80 °C for 3 h to afford polymer **16** (1.97 g, M_w = 7800, $M_\mathrm{w}/M_\mathrm{n}$ 1.6, T_g = −85 °C, TGA onset = 262 °C). ^{1}H NMR: δ −0.04 0.13 ($\mathrm{CH_3Si}$), 0.25−0.42 ($\mathrm{SiCH_2CH_2Si}$), 0.44−0.52 ($\mathrm{SiC}\mathit{H}_2\mathrm{CH_2}$-$\mathrm{CH_2O}-$), 0.98 ($\mathrm{C}\mathit{H}_3\mathrm{CHSi}$), 1.57 ($\mathrm{SiCH_2C}\mathit{H}_2\mathrm{CH_2O}-$), 3.35 ($\mathrm{CH_3O}-$), 3.38 (t, 7.0 Hz, ($\mathrm{SiCH_2CH_2C}\mathit{H}_2\mathrm{O}-$)), and 3.5−3.7 ($-\mathrm{OCH_2CH_2O}-$). ^{13}C NMR: δ −1.2−0.2 ($\mathrm{CH_3Si}$), 7.9 ($\mathrm{CH_3}\mathit{C}\mathrm{H}$), 8.9 ($\mathrm{CH_2Si}$), 9.4 ($\mathrm{CH_2Si}$), 11.8 ($\mathrm{C}\mathit{H}_3\mathrm{CH}$), 14. 11 ($-\mathrm{CH_2}-$), 23.33 ($-\mathrm{CH_2}-$), 58.96 ($-\mathrm{CH_3}$), 69.95, 70.47, 70.55, 71.89, and 74.19, ($-\mathrm{OCH_2CH_2O}$-). IR: 1351 (C−O−), 1455 (C−O−) cm^{-1}.

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