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Modification of a Hyperbranched Hydridopolycarbosilane as a Route to New Polycarbosilanes

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ABSTRACT: A general method for introducing various side chains onto a highly branched polysilaethylene (HBPSE) backbone is described. This method starts with a commercial oligomer mixture which has a highly branched structure, consisting of [H_3SiCH_2], [SiH_2CH_2], [$SiH(CH_2)_2$], and [$Si(CH_2)_3$] subunits combined to give an overall "SiH_2CH_2" average formula. Several alkyl-, aryl-, and allyl-substituted HBPSEs were prepared by first converting the parent HBPSE into a highly reactive bromo-substituted derivative which was then treated with organolithium reagents (RLi, R = C_4H_9, C_6H_{13}, C_8H_{17}, C_6H_5, $C_6H_4N(Me)_2$) or Grignard reagents (RMgBr, R = Et, allyl). The parent HBPSE and its derivatives were characterized by means of NMR and IR spectroscopy, as well as elemental analysis, DSC, GPC, and VPO. It was shown that the allyl-substituted HBPSE can be used as a synthetic platform for attaching functional side chains via the hydrosilation reaction.

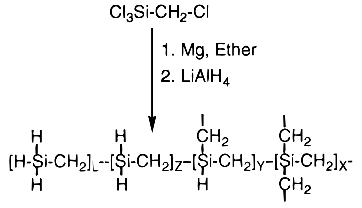
Introduction

Polysilylenemethylenes, PSMs, (polymers having the formula $[Si(R_1)(R_2)\text{-}CH_2]_n$), constitute a rather neglected class of organic−inorganic hybrid polymers which are currently undergoing a resurgence in interest. Among the potential advantages that this class of polymers may have as compared to the existing classes of inorganic and organic polymers are a combination of low T_g's and high synthetic versatility similar to that of such inorganic backbone polymers as the polyphosphazenes and polysiloxanes with good chemical backbone stability similar to that of the polyolefins.[1,2]

Two general routes have been developed for the preparation of linear PSMs having desired substituents attached to the silicon. One route involves the ring-opening polymerization (ROP) of the correspondingly substituted disilacyclobutane. This method works best for alkyl- and phenyl-substituted disilacyclobutanes.[3] An alternative route involves the preparation of polymers having reactive (Cl, OR, or H) functionalities attached to the silicon and then introduction of the desired substituents through substitution or addition (hydrosilation) reactions.[2] Both routes rely on the use of disilacyclobutane compounds as monomers. Unfortunately, the preparation of the required disilacyclobutanes can be problematic, involving a multistep procedure with low to moderate overall yields.[3d,4] This represents a serious obstacle to the full development of this new and interesting class of polymers and their prospective application as functional polymeric materials.

Several years ago a rather different approach to the preparation of methylene-bridged polycarbosilanes was reported.[5] This approach involves the condensation via a Grignard reaction and subsequent reduction of (chloromethyl)trichlorosilane so as to form a hyperbranched oligomeric/polymeric carbosilane having a nominal "$SiCH_4$" formula on pyrolysis (Scheme 1). This "hydridopolycarbosilane" was found to give nearly stoichiometric silicon carbide (SiC) in high yield. Recently, a new process for the kilogram-scale production of this hyperbranched hydridopolycarbosilane (HPCS) has been developed by Starfire Systems, Inc.[6]

Scheme 1



In addition to offering the prospect of a more convenient and readily available starting point for the preparation of new substituted polycarbosilanes, this highly branched version of polysilaethylene,[5] which we will refer to here as HBPSE (**1**), is also of independent interest from the perspective of its highly branched structure. Such hyperbranched polymers and their relatives, the dendritic polymers, have attracted a great deal of attention recently and are being widely studied for a variety of potential applications, ranging from solvent-free paints to agents for delivering drugs or genes into cells.[7] Examples of dendritic carbosilanes have been reported in the literature; however, the synthesis of these polymers is rather tedious, discouraging their consideration for most potential applications.[8]

All these considerations led us to realize the importance of developing convenient synthetic methods for the modification of HBPSE (**1**). This paper describes our first efforts in this direction.

Characterization Of The Parent HBPSE. HBPSE (**1**) was obtained as a viscous, yellowish liquid. The relative amounts of the units that comprise its hyperbranched, oligomeric structure were estimated from its quantitative ^{29}Si NMR spectrum (Figure 1a). The assignments of the peaks in these spectra to the $(CH_2)_4Si$, $(CH_2)_3SiH$, $(CH_2)_2SiH_2$, and $(CH_2)SiH_3$ units of the oligomers were carried out as previously described.[5] The integration data indicate that the relative values of $X/Y/Z/L$ (Scheme 1) are about 2/8/20/11, which is similar to results previously reported.[5] As can be seen from its ^1H NMR spectrum (Figure 1b), this sample of **1** does not have the extraneous ethyl groups on Si that resulted from cleavage of the diethyl ether solvent in the earlier preparation.[5] Elemental analysis also corresponds reasonably well to the CH_4Si composition expected for the "average" "$[SiH_2CH_2]_n$" repeat unit (Calc: C, 27.24; H, 9.08. Found: C, 25.74, H, 9.10.). For

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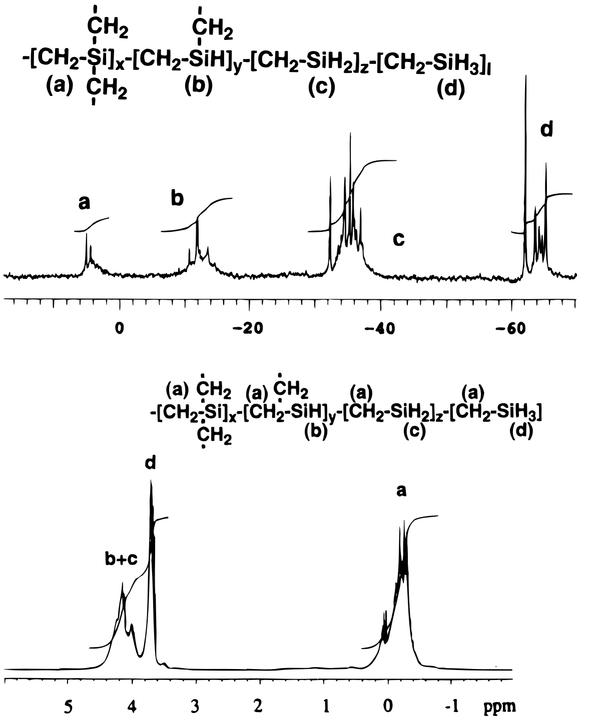


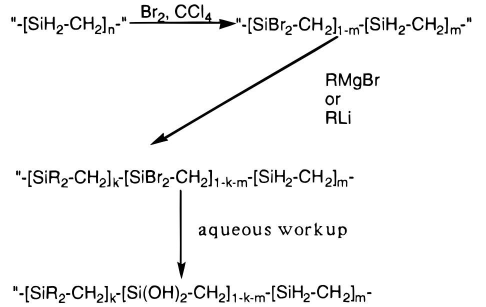
Figure 1. (a, top) Quantitative ^{29}Si NMR spectrum of HBPSE. (b, bottom) ^{1}H NMR spectrum of HBPSE.

Table 1. Reagents Used and Degree of Substitution of the “[Si(R)$_2$CH$_2$]” Polymers

oligomer	side chain	reagent used	degree of substitution (%)
2	ethyl	C_2H_5MgBr	80^{a}
3	allyl	C_3H_5MgBr	75^{a} (70^{b}−79^{c})
4	butyl	C_4H_9Li	90^{a} (74^{b}−82^{c})
5	hexyl	$C_6H_{13}Li$	90^{a} (70^{b}−80^{c})
6	octyl	$C_8H_{17}Li$	85^{a} (67^{b}−77^{c})
7	phenyl	C_6H_5Li	85^{a} (71^{b}−84^{c})
8	*N*,*N*-dimethylanaline	$Me_2NC_6H_4Li$	80^{a}

[a] Determined by integration of the ^{1}H NMR peaks. [b] Calculated from the elemental analysis assuming the average composition $[Si(H)_{2-x}(R)_xCH_2]_n$. [c] Calculated from the elemental analysis assuming the average composition $[Si(OH)_{2-x}(R)_xCH_2]$.

Scheme 2



the sake of simplicity, from this point on we will use this “average” repeat unit “$[SiH_2CH_2]_n$” to refer to the structure of HBPSE.

Typically, the molecular weight of HBPSE (M_p), as estimated by GPC relative to polystyrene standards, was around 600 (corresponding to a degree of polymerization of about 13) and varied slightly from batch to batch. The polydispersity (PD) of HBPSE was found to be around 1.5−1.8. Since the hydrodynamic volume of HBPSE can differ significantly from that of the polystyrene standards used for GPC calibration, a sample of HBPSE with a GPC-estimated molecular weight (M_n) of 720 was examined by vapor pressure osmometry (VPO). The VPO-determined molecular weight was 740, showing that, in this case at least, GPC gives a quite reasonable estimate of the molecular weight.

Derivatization of HBPSE. The convenience of the hydrosilation process lead us to first try this reaction as a means of modifying HBPSE.[1] However we found that the Si−H bonds in this case are essentially inactive toward addition to olefins by using the usual Pt complex catalysts. For example, after treatment of **1** with 1-hexene and Karstedt’s catalyst for 24 h under reflux in an inert atmosphere, hydrosilation proceeded only to the extent of 3−5%, on the basis of the NMR spectra of the product. Since the most accessible Si atoms in HBPSE have two or even three hydrogen atoms attached to them, this is in line with the reported sluggish Pt-catalyzed hydrosilation of olefins by di- and trihydridosilanes. Catalyst poisoning has been suggested as a possible cause of this problem.[9] It is also well-known that electropositive and bulky groups attached to the silicon retard the hydrosilation process.[10]

We therefore decided to convert HBPSE into a more reactive intermediate. We found that the Si−H bonds of **1** can be conveniently converted to Si−Br bonds by reaction with bromine in chlorinated solvents (Scheme 2).[11] The ^{1}H NMR spectrum[12] of the brominated HBPSE shows numerous peaks that we attribute to the various “$[SiBr_2CH_2]$” units in the area 0.5−2.7 ppm and a very small amount (<3%) of Si*H* protons. The possibility of backbone cleavage during this process was evaluated after reduction of the brominated material by comparing the molecular weight of the resulting HBPSE with that of the original one. It was found that while the bromination did not affect the M_p of HBPSE, the M_w of HBPSE had been reduced from the original value of 990 amu to 810 amu after the bromination/reduction procedure.

From these data it is obvious that while some loss of the higher molecular weight fraction occurs, HBPSE backbone cleavage is not a significant problem here. The brominated oligomer is a viscous brown liquid at room temperature which is quite soluble in most organic solvents except hydrocarbons. No detailed characterization of this material was conducted because of its hydrolytic sensitivity.

The Grignard reaction was employed first as a means of modifying this brominated HBPSE. Two Grignard reagents were tried, EtMgBr and allylMgBr (Table 1). The incomplete alkylation of the brominated HBPSE even with these rather small Grignard reagents indicated the need to use the more potent organolithium compounds to introduce larger substituents onto the HBPSE backbone.

In order to fully explore this method, several organolithium reagents containing organic groups of varying sizes and types (alkyl vs aryl) were employed in reactions with the brominated HBPSE (Table 1). The prospect of the preparation of a water-soluble HBPSE derivative and the ready availability of the (*N*,*N*-dimethylanilino)lithium reagent lead us to prepare the derivative **8**.

Derivatives **2**−**6** were obtained as viscous liquids while derivatives **7** and **8** occurred as solids. All of the products are quite soluble in ethers and chlorinated solvents. Derivatives **2**−**6** are also soluble in hexane. The dimethylaniline derivative **8** is soluble in alcohols and aqueous acids but insoluble in neutral water.

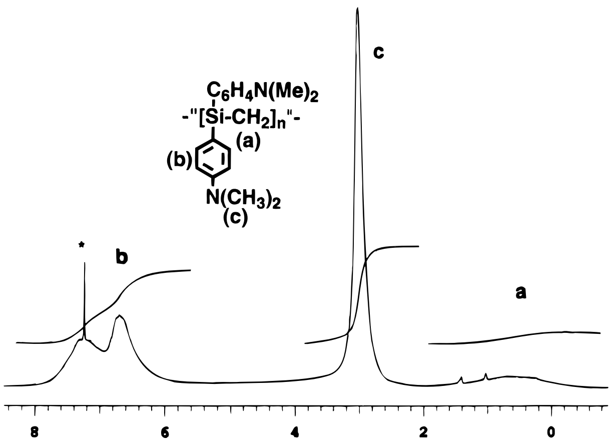


Figure 2. ^{1}H NMR spectrum of the dimethylaniline-substituted HBPSE.

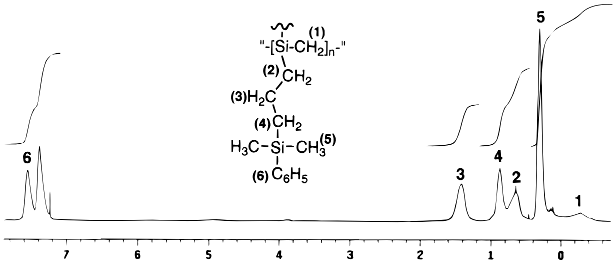


Figure 3. ^{1}H NMR spectrum of **11**.

As illustrated in Scheme 2, the composition of the products can be formally represented as $[SiR_2-CH_2]_k[SiH_2-CH_2]_m[Si(OH)_2-CH_2]_{1-m-k}$.[13] The degree of alkylation (the k value) was evaluated from the elemental analyses[14] of the products and from their ^{1}H NMR spectra (Figure 2) by integration of the peak due to the backbone methylene protons at about 0 ppm relative to the peaks of the substituent group (R) protons (the peaks at 0.5−1.5 ppm in the case of alkyl-substituted oligomers or the peak at 7−8 in the case of the aryl-substituted oligomers) (Table 1). As can be seen in Table 1, in most cases there are significant differences between the NMR-determined and the elemental analysis-determined degrees of substitution. These differences could be due to uncertainties either in the integration, due to the broad and overlapping peaks, or in the elemental analyses.[14]

The presence of residual Si−H groups can be detected from the IR spectra of all of the derivatives as a small peak at 2100 cm^{-1} as well as from the ^{29}Si spectra of most of the polymers as a very minor peak in the range −10 to (−12) ppm (Figure 3). However, as we determined earlier from the NMR spectrum of the brominated HBPSE, the amount of residual Si−H groups should not exceed 3%. The rest of the silicon sites [about 12−17%; calculated as $1 - m - k$ (Scheme 2)] apparently bear mainly OH groups (we assume the complete hydrolysis of the unreacted SiBr groups), as is evidenced by the OH peak at 3500 cm^{-1} and the relatively weak Si−H peak at ca. 2100 cm^{-1} in the IR spectra of the oligomers. Therefore the elemental analysis-determined degree of substitution calculated for the "$[Si(R)_x(OH)_{2-x}CH_2]$" composition should be closer to reality than the degree of substitution calculated for the "$[Si(R)_xH_{2-x}CH_2]$" formula.

Table 2. Properties of the "$[Si(R_2)-CH_2]_n$" Polymers

polymer	M_p (calc)	M_p (exp)	M_w (exp)	PD	T_g (°C)
2	1260^a	800^c	6950^c	5.21^c	-74
3	1516^b	1220^c	1900^c	1.70^c	-63
4	1850^b	1850^c	3200^c	1.61^c	-69
		(888^d)	(1680^d)	(1.44^d)	
5	2560^b	2180^c	3770^c	1.35^c	-81
		(1271^d)	(2110^d)	(1.33^d)	
6	2900^b	3800^c	6354^c	1.40^c	-74
		(1790^d)	(2950^d)	(1.34^d)	
7	2270^b	1010^c	1460^c	1.35^c	101
		(1060^d)	(1525^d)	(1.33^d)	
8	3200^a	1000^c	1470^c	1.35^c	164

[a] Calculated from the NMR-determined degree of substitution assuming the average formula $[SiR_n(OH)_{2-n}CH_2]$. [b] Calculated from the elemental analysis-determined degree of substitution assuming the average formula $[SiR_n(OH)_{2-n}CH_2]$. [c] GPC was performed using toluene as eluent. [d] GPC was performed using THF as eluent.

Table 3. Properties of the Oligomers 9−13

polymer	degree of hydrosilation (%)	M_n	M_w	T_g (°C)
9	50	6310	84800	−57
10	90−95	2050	2220	−86
11	90−95	2930	5410	−52
12		2840	4600	
13	90−95	5360	6160	−84

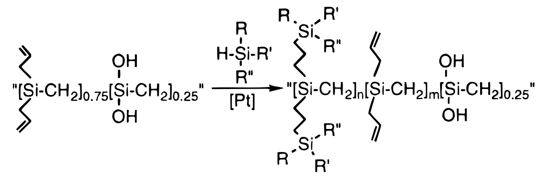
The molecular weight for the products was estimated by using GPC (Tables 2 and 3). It was found that, in the series of alkyl-substituted HBPSE's, the apparent molecular weight increase was approximately proportional to the size of the side chain. In most cases the polydispersity stayed low, again indicating the insignificance of any decomposition/cross-linking reactions. The ethyl-substituted product, however, shows a substantial increase in the M_w value and a broadening of the molecular weight distribution after several days of storage in air. Intermolecular condensation of the Si−OH groups to form siloxane bonds is the most probable cause of the molecular weight increase in this case. In the case of the other derivatives, the steric bulk of the side chains probably prevents intermolecular condensation of this type.

The apparent molecular weight of the aryl-substituted HBPSEs was surprisingly low. Since no decomposition reactions were noticed when any of the other RLi reagents were used, it seemed likely that this low apparent molecular weight was due to differences in the hydrodynamic volume between the aryl- and alkyl-substituted oligomers. In order to confirm this, VPO measurements of the phenyl-substituted HBPSE with a GPC-determined $M_n = 970$ (eluent, toluene) were carried out. The VPO-determined M_n was 2000, quite consistent with the calculated value of 2100). Of course, in general, the GPC-determined molecular weight should be taken with great discretion. As an illustration of this problem, the molecular weights determined by GPC using THF as an eluent differ significantly from the molecular weights determined using toluene (Table 3).

As an expected consequence of their irregular structure, all of the substituted HBPSE derivatives show only glass transitions. The value of T_g (Table 3) obviously varies with the size and nature of the side chain. As expected,[2a] the aryl-substituted HBPSE possesses a much higher T_g than the alkyl-substituted HBPSEs. However, among the alkyl-substituted products we did not observe any obvious correlation in T_g with the size of the side chain.

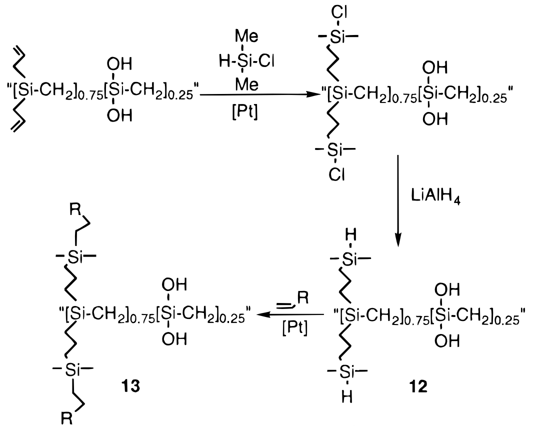
Modification of the Allyl-Substituted HBPSE through Hydrosilation. According to the literature sources[15] and our own experience[2c] the hydrosilation reaction is by far the most powerful and versatile

Scheme 3



Where R=R'=R"=Et (**9**)
or R=R'=Me and R"=Hexyl (**10**)
or R=R'=Me and R"=Ph (**11**)

Scheme 4



Where R=$CH_2OC_2H_4OC_2H_4OCH_3$

synthetic tool for the introduction of various functional groups onto the backbone of silicon containing polymers. These considerations led us to choose the allyl-substituted HBPSE (**3**)[16] as a starting material for the preparation of various highly branched polycarbosilanes through synthetic routes involving hydrosilation. The sample of the allyl-HBPSE (**3**) employed in all of the syntheses described below was prepared as described in Scheme 2 and had a GPC-determined $M_n = 1300$ and a VPO-determined $M_n = 1500$.

First, the direct hydrosilation of the allyl-substituted HBPSE by using simple monohydridosilanes was carried out (Scheme 3). These reactions were found to proceed in high yield to give the expected hydrosilated products. Next, attempts were made to prepare a bis(ethylene glycol)-substituted polycarbosilane, which may have potential application as a polymeric electrolyte,[17] by carrying out a reaction between **3** and $(H)(Me)_2Si(C_3H_6OC_2H_4OC_2H_4OCH_3)$.[12] In this case we were not able to separate the resulting product **13** from the excess of the silane, since both compounds have similar solubility properties and the silane has too high a boiling point to be removed in vacuum.

In order to avoid the aforementioned problems, **3** was first converted into the intermediate **12** (Scheme 4), which contains the tertiary Si−H bond. The silane-terminated oligomer **12** was then used to hydrosilate the olefins in the usual manner (Scheme 4).

In this method the final product is prepared by the reaction of the polycarbosilane with a relatively small compound which makes the separation and purification of the products easier. While this paper was undergoing revision, a similar approach was reported for the modification of vinyl-substituted siloxanes.[18]

Except for the bulky silane-terminated material **9**, both methods (Schemes 3 and 4) produce products without any olefinic signals in their ^1H and ^{13}C NMR spectra.[12] The derivative **13** has a very weak Si−H peak in its IR spectrum.[12] The integration of the side chain protons and the protons of the backbone of the products **9**−**12** gave the ^1H NMR-determined degree of hydrosilation[12] (Table 3, Figure 3). The elemental analysis of the phenylsilane product **11** confirms the ^1H NMR results. The GPC-determined molecular weights and the T_g's for the products **9**−**13** are also given in Table 3.

All of the derivatives **9**−**13** were obtained as dark (presumably due to colloidal Pt from the platinum hydrosilation catalyst employed) transparent melts. The platinum colloid precipitated over the prolonged storage, leaving yellowish products. Oligomers **9**−**12** are soluble in many common organic solvents but insoluble in alcohols. The bis(ethylene glycol)-terminated oligomer **13** is soluble in all common organic solvents tested (including alcohols and acetonitrile) but insoluble in water.

The GPC trace of the bulky triethylsilane-terminated derivative **9** shows a very broad, bimodal molecular weight distribution. Apparently the unreacted allyl groups of this oligomer (40%) undergo some kind of cross-linking reaction, the nature of which was not investigated. However, these cross-linking reactions did not result in the gelation of the polymer even after storage for about 6 months in the open air. It is clear that the latent reactivity in partially olefin-terminated derivatives of this type can be used to advantage in applications which require cross-linking of the polymer after, for example, film casting.[19]

Conclusions

Capitalizing on the unique combination, found in carbosilanes, of the high reactivity of the Si−X (X = H, Br) bond and the chemical stability of the backbone Si−C bonds, we have developed a novel synthetic route for the modification of HBPSE through bromination/alkylation reactions using Li or Mg organometallic compounds. A high degree of substitution was achieved, especially with organolithium reagents. The products were characterized by NMR, IR spectroscopy, GPC, and DSC methods. It was shown that the oligomer **3** can be a convenient synthetic platform for the preparation of novel carbosilane materials through hydrosilation reactions. We are currently exploring the use of this approach as a means of attaching a wide range of chromophoric, ion-solvating, and mesogenic groups to a chemically stable carbosilane backbone.

Experimental Section

All manipulations involving air- and/or moisture-sensitive materials were performed under N_2. All ether and hydrocarbon solvents were distilled before use from their purple sodium/benzophenone solutions. The allyl, hexyl, octyl, and phenyl bromides as well as butyl chloride and 4-bromo-*N*,*N*-dimethylaniline were purchased from Aldrich and dried over molecular sieves. Lithium[20] and magnesium[21] compounds were prepared according to the literature procedures. EtMgBr (3 M solution in ether) was purchased from Aldrich. NMR spectra were obtained on Unity-300 or Unity-500 instruments. ^1H and ^{13}C spectra were referenced to the solvent peaks. Quantitative ^{29}Si NMR studies of HBPSE were performed in benzene-d_6 (Aldrich) solution with 0.1% (wt) of $Cr(acac)_3$ as relaxation agent on a Unity-500 instrument (90° pulse, delay time, 16 s).[4c] Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.[14] Gel permeation chromatography (GPC) was performed in toluene or THF solution, using a Waters 600 Multisolvent Delivery System with a differential refractometer detector and two PLgel, 5μ mixed D columns in series (Polymer Laboratories); molecular weights are referenced to polystyrene standards. The GPC data were worked up using PL Caliber software (Polymer

Laboratories). All DSC measurements were performed by using a heating rate of 10 °C/min on a TA 2920 instrument. The T_g was determined as the inflection point in the heating portion of the DSC curve, after an initial heating/cooling cycle.

VPO measurments were performed on a Vapor Pressure Osmometer 070 (UIC Inc., Jolliet, IL) in toluene solution at 45 °C. The instrument was calibrated using dodecane (Aldrich, redistilled, 99.9% pure by GC) as a standard. Calibration was confirmed by measuring the molecular weights of polystyrene standards. Each sample was run at least twice.

Preparation of the Alkyl- and Aryl-Substituted HBPSEs 2−8. Excess bromine ($\mathrm{Br_2}$) (5 mL) was added slowly to a solution of HBPSE (1 g) in 10 mL of $\mathrm{CCl_4}$ at room temperature. The reaction mixture was continuously flushed with $\mathrm{N_2}$ to remove the HBr formed during the reaction. After the addition was completed, the reaction mixture was refluxed for 3 h and cooled down, and then all volatiles were removed under vacuum. The resulting brominated product was dissolved in 2 mL of toluene and added slowly to the twofold excess of the ether solution of the Grignard reagent or the hexane solution of the organolithium reagent. After the addition was completed and the exothermic reaction had subsided, the mixture was refluxed for 24 h, cooled to room temperature, and added slowly to 200 mL of saturated aqueous $\mathrm{NH_4Cl}$ solution. The organic layer was separated and dried, and all volatiles were removed under vacuum. The viscous residue was examined by GPC. For NMR analysis the derivatives **2**−**4** and **7** were reprecipitated from ether/methanol; **5** was reprecipitated from ether/acetone; **6** was reprecipitated from ether/methyl ethyl ketone, and **8** was reprecipitated from ether/hexane mixtures. The yield of each product was typically in the range 70−75%.

For **2**. 300 MHz ^{1}H NMR (ppm) ($\mathrm{CDCl_3}$): δ 0.92 (4.8 H, br, $\mathrm{CH_2C}H_3$), 0.53 (3.2 H, br, $\mathrm{SiC}H_2\mathrm{CH_3}$), −0.20 (2H, very br, $\mathrm{SiC}H_2\mathrm{Si}$). 75 MHz ^{13}C NMR (ppm) ($\mathrm{CDCl_3}$): δ 7.9 ($\mathrm{CH_2}C\mathrm{H_3}$), 4.5 ($\mathrm{Si}C\mathrm{H_2CH_3}$), −1.0 (very br, $\mathrm{Si}C\mathrm{H_2Si}$). 99 MHz ^{29}Si NMR (ppm) ($\mathrm{CDCl_3}$): 5.6 δ ($\mathrm{CH_2}Si\mathrm{CH_2}$).

For **3**. 300 MHz ^{1}H NMR (ppm) ($\mathrm{CDCl_3}$): δ 5.77 (1.8 H, br, $\mathrm{CH_2{=}C}H$), 4.89 (3.6 H, br, $\mathrm{C}H_2\mathrm{{=}CH}$), 1.61 (3.6 H, br, $\mathrm{SiC}H_2\mathrm{CH{=}CH_2}$), −0.10 (2H, $\mathrm{SiC}H_2\mathrm{Si}$). 75 MHz ^{13}C NMR (ppm) ($\mathrm{CDCl_3}$): δ 134.2 ($\mathrm{CH_2{=}}C\mathrm{H}$), 114 ($\mathrm{CH_2{=}}C\mathrm{H}$), 24.7, 22.0 ($\mathrm{Si}C\mathrm{H_2CH{=}CH_2}$), −2.0 (very br, $\mathrm{Si}C\mathrm{H_2Si}$). 99 MHz ^{29}Si NMR (ppm) ($\mathrm{CDCl_3}$): δ 1.1 ($\mathrm{CH_2}Si\mathrm{CH_2}$). Elem anal. Found: C, 62.2; H, 9.2. Calc for $[\mathrm{Si(C_3H_5)_2{-}CH_2}]_n$, C=67.7; H, 9.4.

For **4**. 500 MHz ^{1}H NMR (ppm) ($\mathrm{CDCl_3}$): δ 1.31 (7.2 H, br, $\mathrm{SiCH_2C_2}H_4\mathrm{CH_3}$), 0.88 (5.5 H, br, $\mathrm{SiC_3H_6C}H_3$), 0.58, 0.51 (3.5 H, br, $\mathrm{SiC}H_2\mathrm{C_3H_7}$), −0.20 (2 H, very br, $\mathrm{SiC}H_2\mathrm{Si}$). 125 MHz ^{13}C NMR (ppm) ($\mathrm{CDCl_3}$): δ 27.0 (br, $\mathrm{SiCH_2}C_2\mathrm{H_4CH_3}$), 18.0 (very br, Si C $\mathrm{H_2C_3H_7}$), 16.1 ($\mathrm{SiC_3H_6CH_3}$), 0.0 (very br, $\mathrm{Si}C\mathrm{H_2Si}$). 99 MHz ^{29}Si NMR (ppm) ($\mathrm{CDCl_3}$): δ 3.5 ($\mathrm{CH_2}Si\mathrm{CH_2}$). Elem anal. Found: C, 65.4; H, 12.3. Calc for $[\mathrm{Si(C_4H_9)_2{-}CH_2}]_n$, C, 69.2; H, 12.8.

For **5**. 500 MHz ^{1}H NMR (ppm) ($\mathrm{CDCl_3}$): δ 1.27 (14.4 H, br, $\mathrm{SiCH_2C_4}H_8\mathrm{CH_3}$), 0.88 (5.5 H, br, $\mathrm{SiC_5H_{10}C}H_3$), 0.57, 050 (3.5 H, br, $\mathrm{SiC}H_2\mathrm{C_5H_{11}}$), −0.27 (2 H, very br, $\mathrm{SiC}H_2\mathrm{Si}$). 125 MHz ^{13}C NMR (ppm) ($\mathrm{CDCl_3}$): δ 33.8, 31.71, 24.7, 22.7 ($\mathrm{SiCH_2}C_4\mathrm{H_8CH_3}$), 17.5 (very br, $\mathrm{Si}C\mathrm{H_2C_5H_{11}}$), 14.2 ($\mathrm{SiC_5H_{10}}C\mathrm{H_3}$), 0.0 (very br, Si $C\mathrm{H_2Si}$). 99 MHz ^{29}Si NMR (ppm) ($\mathrm{CDCl_3}$): δ 3.5 ($\mathrm{CH_2}Si\mathrm{CH_2}$). Elem anal. Found: C, 70.0; H, 13.0. Calc for for $[\mathrm{Si(C_6H_{13})_2{-}CH_2}]_n$: C, 73.5; H, 13.2.

For **6**. 500 MHz ^{1}H NMR (ppm) ($\mathrm{CDCl_3}$): δ 1.26 (19.5 H, br, $\mathrm{SiCH_2C_6}H_{12}\mathrm{CH_3}$), 0.870 (5.5 H, t, $J = 7$ Hz, $\mathrm{SiC_7H_{14}C}H_3$), 0.57 (3.5 H, br, $\mathrm{SiC}H_2\mathrm{C_7H_{15}}$), −0.27 (2H, very br, $\mathrm{SiC}H_2\mathrm{Si}$). 125 MHz ^{13}C (ppm) ($\mathrm{CDCl_3}$): δ 34.6, 32.5, 30.0, 25.0, 23.2 ($\mathrm{SiCH_2}C_6\mathrm{H_{12}CH_3}$), 18.4 (br, $\mathrm{Si}C\mathrm{H_2C_7H_{15}}$), 14.5 ($\mathrm{SiC_7H_{14}}C\mathrm{H_3}$), 0.0 (very br, $\mathrm{Si}C$ $\mathrm{H_2Si}$). 99 MHz ^{29}Si NMR (ppm) ($\mathrm{CDCl_3}$): δ 3.6 ($\mathrm{CH_2}Si\mathrm{CH_2}$). Elem anal. Found: C, 72.6; H, 12.7. Calc $[\mathrm{Si(C_8H_{17})_2{-}CH_2}]_n$, C, 76.1; H, 13.4.

For **7**. 500 MHz ^{1}H NMR (ppm) ($\mathrm{CDCl_3}$): δ 7.50 (8.5 H, br, $\mathrm{C_6}H_5$), 0.4 (2 H, very br, $\mathrm{SiC}H_2\mathrm{Si}$). 125 MHz ^{13}C NMR (ppm) ($\mathrm{CDCl_3}$): δ 137.0 (very br), 135.6, 134.1, 128.9, 127.5 ($C_6\mathrm{H_5}$), 0.0 (very br, $\mathrm{Si}C\mathrm{H_2Si}$). 99 MHz ^{29}Si (ppm) ($\mathrm{CDCl_3}$): δ 0.0 (very br), −8.0, −11.3. Elem anal. Found: C, 75.2; H, 5.9. Calc for $[\mathrm{Si(C_6H_5)_2{-}CH_2}]_n$: C, 79.6; H, 7.7.

For **8**. 500 MHz ^{1}H NMR (ppm) ($\mathrm{CDCl_3}$): δ 7.50, 6.60 (6.5 H, br, Ar), 2.90 {4.8 H, br, $\mathrm{N(C}H_3\mathrm{)_2}$}, 0.5 (2 H, very br, $\mathrm{SiC}H_2\mathrm{Si}$). 125 MHz ^{13}C NMR (ppm) ($\mathrm{CDCl_3}$): δ 150.5, 136.6 (br), 128.1 (br), 124.0 (br), 111.6 (Ar), 40.7 {$\mathrm{N(}C\mathrm{H_3)_2}$}, 0.0 (very br, $\mathrm{Si}C\mathrm{H_2Si}$). 99 MHz ^{29}Si NMR (ppm) ($\mathrm{CDCl_3}$): δ −2.0 (very br), −8.8, −12.4.

Preparation of the Silane-Terminated Product 13. The allyl-substituted HBPSE **3** (0.7 g) was dissolved in 5 mL of chlorodimethylsilane followed by the addition of 2−5 mg of chloroplatinic acid (Karstedt's catalyst was found to be inactive in this system). The reaction mixture was refluxed overnight, and then all volatiles were stripped off in vacuum. The viscous residue was dissolved in 10 mL of ether followed by addition of 0.23 g of $\mathrm{LiAlH_4}$. The reaction mixture was refluxed overnight, cooled down, and carefully worked up with an ice cold mixture of 3 M HCl (200 mL) with hexanes (50 mL). The organic layer was separated and dried, and all volatiles were removed in vacuo, yielding 0.96 g (70%) of the polymer **13**.

300 MHz ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.88 (1 H, $\mathrm{Si}H$), 1.41 (2 H, $\mathrm{SiCH_2C}H_2\mathrm{CH_2Si}$), 0.68 (4 H, $\mathrm{SiC}H_2\mathrm{CH_2C}H_2\mathrm{Si}$), 0.07, −0.24 (7 H, $\mathrm{SiC}H_3$ + $\mathrm{SiC}H_2\mathrm{Si}$). 75 MHz ^{13}C ($\mathrm{CDCl_3}$): δ 19.1 ($\mathrm{Si}C_3\mathrm{H_6Si}$), −4.9 ($\mathrm{Si}C\mathrm{H_3}$). 99 MHz ^{29}Si NMR ($\mathrm{CDCl_3}$): δ 1.8 (main chain silicon), −14.2 (side chain silicon).

Hydrosilation procedure. The olefinic-terminated carbosilane **3** (1 g, 8 mmol) or the silane-terminated carbosilane **13** (1 g, 7 mmol) was dissolved in a two-fold molar excess of the silane (in the case of **3**) or the olefin (in the case of **13**) followed by addition of 20 μL of Karstedt's catalyst (5% (wt [Pt]) solution in xylenes). The reaction mixture was stirred at 100 °C overnight. All volatiles were removed in vacuo. The residues were examined by GPC. Finally, the products **9**−**11** were purified by reprecipitation from an ether/methanol mixture; the product **12** was reprecipitated from an acetone/water mixture and examined by NMR spectroscopy.

For **9**. 300 MHz ^{1}H NMR ($\mathrm{CDCl_3}$): δ 6.00, 5.70, 1.80 (residual allyl groups), 1.30 ($\mathrm{SiCH_2C}H_2\mathrm{CH_2Si}$), 0.90 ($\mathrm{SiCH_2C}H_3$), 0.5 ($\mathrm{SiC}H_2\mathrm{CH_3}$ + $\mathrm{SiC}H_2\mathrm{CH_2C}H_2\mathrm{Si}$), −0.3 ($\mathrm{SiC}H_2\mathrm{Si}$). 75 MHz ^{13}C NMR ($\mathrm{CDCl_3}$): δ 144−130 (very br, residual olefinic carbons), 22.8, 20.1, 18.5, 17.0, 16.4 ($C\mathrm{H_2CH{=}CH_2}$ + $\mathrm{Si}C\mathrm{H_2}C\mathrm{H_2}C\mathrm{H_2Si}$), 7.5 ($\mathrm{SiCH_2}C\mathrm{H_3}$), 3.5 ($\mathrm{Si}C\mathrm{H_2CH_3}$).

For **10**. 300 MHz ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.30 ($\mathrm{SiCH_2C_4}H_8\mathrm{CH_3}$ + $\mathrm{SiCH_2C}H_2\mathrm{CH_2Si}$), 0.89 (t, $J = 7$ Hz, $\mathrm{C}H_3$), 0.58, 0.46 (br, $\mathrm{SiC}H_2\mathrm{C_5H_{11}}$ + $\mathrm{SiC}H_2\mathrm{CH_2C}H_2\mathrm{Si}$), −0.06 ($\mathrm{SiC}H_3$). 75 MHz ^{13}C NMR ($\mathrm{CDCl_3}$): δ 33.5, 31.7, 23.9, 22.7 ($\mathrm{SiCH_2}C_4\mathrm{H_8CH_3}$), 20.2 (br, $\mathrm{SiCH_2}C\mathrm{H_2CH_2Si}$), 18.5 (br, $\mathrm{Si}C\mathrm{H_2CH_2}C\mathrm{H_2Si}$), 15.5 ($C\mathrm{H_3}$), 14.1 (br, $\mathrm{Si}C\mathrm{H_2C_5H_{11}}$), −3.4 (br, $\mathrm{Si}C\mathrm{H_3}$).

For **11**. 300 MHz ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.56, 7.40 ($\mathrm{C_6}H_5$), 1.42 ($\mathrm{SiCH_2C}H_2\mathrm{CH_2Si}$), 0.88, 0.65 ($\mathrm{SiC}H_2\mathrm{CH_2C}H_2\mathrm{Si}$), 0.32 ($\mathrm{SiC}H_3$), −0.3 (br, $\mathrm{SiC}H_2\mathrm{Si}$). 75 MHz ^{13}C NMR ($\mathrm{CDCl_3}$): δ 139.6, 133.5, 128.7, 127.7 ($C_6\mathrm{H_5}$), 20.7, 18.4 ($\mathrm{Si}C_3\mathrm{H_6Si}$), −2.8 ($\mathrm{Si}C\mathrm{H_3}$). Elem anal. Found: C, 66.7; H, 9.7. Calc for $[\mathrm{Si\{C_3H_6Si(CH_3)_2C_6H_5\}_2{-}CH_2}]_{0.75}[\mathrm{Si(OH)_2{-}CH_2}]_{0.25}$: C, 66.3; H, 8.8.

For **12**. 300 MHz ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.88 (1 H, $\mathrm{Si}H$), 1.41 (2 H, $\mathrm{SiCH_2C}H_2\mathrm{CH_2Si}$), 0.68 (4 H, $\mathrm{SiC}H_2\mathrm{CH_2C}H_2\mathrm{Si}$), 0.07, −0.24 (7 H, $\mathrm{SiC}H_3$ + $\mathrm{SiC}H_2\mathrm{Si}$). 75 MHz ^{13}C ($\mathrm{CDCl_3}$): δ 19.1 ($\mathrm{Si}C_3\mathrm{H_6Si}$), −4.9 ($\mathrm{Si}C\mathrm{H_3}$). 99 MHz ^{29}Si NMR ($\mathrm{CDCl_3}$): δ 1.8 (main chain silicon), −14.2 (side chain silicon).

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Supporting Information Available: ^{1}H NMR spectrum of the brominated HBPSE; ^{1}H and ^{13}C spectra of **3**, **5**, **7**, and **9**−**13**; ^{29}Si NMR spectra of **4**, **8**, **11**, and **12**; IR spectra of **3**, **5**, **7**, **12**, and **13**; preparation and NMR profiles of hexyldimethylsilane, dimethylphenylsilane, and $\mathrm{HSi(Me)_2C_3H_6O{-}C_2H_4OC_2H_4OCH_3}$ (new compound) (21 pages). Ordering information is given on any current masthead page.

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(12) See Supporting Information for the experimental details and/or actual spectra or NMR profiles.

(13) It is clear that the actual structure of this product is more complex, involving both a distribution of $X_nSi(CH_2)_{n-3}$ sites and the various possible X groups (H, OH, and R) at each site.

(14) Our experience indicates that the elemental analyses for this type of polymer are not very reproducible. This problem could arise from the tendency of carbosilanes to form silicon carbide (or oxycarbide) on pyrolysis, rendering the complete combustion of the carbon difficult. For example, all of the analyses given above were done at Galbraith Laboratories, Inc., Knoxville, TN. Several of the same samples were also sent to Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada. The results are as follows. for allyl-substituted HBPSE: C, 61.72; H, 9.54. for butyl-substituted HBPSE: C, 66.11; H, 13.05. for phenyl-substituted HBPSE: C, 79.12; H, 6.17. Obviously, the analyses from Galbraith Laboratories give the most conservative estimate of the degree of substitution.

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