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Radical Reactivity of Hydrovinylsilanes: Homooligomers[1]

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ABSTRACT: Diphenylvinylsilane (**1**) undergoes oligomerization when initiated by azobis(isobutyronitrile) or peroxide initiators (benzoyl peroxide, di-*tert*-butyl peroxide, dicumyl peroxide). With the exception of the reaction with di-*tert*-butyl peroxide, the efficiency of the radical reactions is very low: 15% starting material was recovered even with 1 equiv of added initiator. The Si−vinyl groups are consumed preferentially to the Si−H groups. The magnitude of the relative rates of consumption depends upon the reaction conditions and the nature of the initiator. At lower temperatures (80 °C), $k_{\mathrm{Si-CH=CH2}}/k_{\mathrm{Si-H}} \approx 2$, which decreases to about 1.2 at elevated temperatures (160 °C). The relative radical reactivities of the two functional groups are discussed. The residual Si−H moieties can be subsequently coupled by hydrosilation with alkynes or vinylsilicones to form star silicones.

Introduction

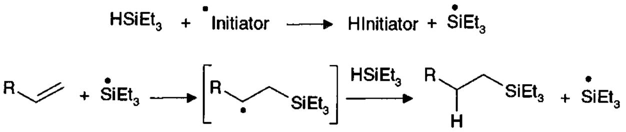
Hydrosilanes are remarkably versatile compounds which serve as convenient starting materials for the introduction of silicon-based groups into organic molecules. The relatively weak Si−H bond[2] is susceptible to cleavage under ionic, transition metal-catalyzed, or radical conditions.[3] In the last case, while the silyl radical generated may participate in a variety of radical chain reactions, with chlorinated hydrocarbons for instance,[4] the most synthetically interesting application is the hydrosilation reaction (Scheme 1). As hydrosilanes are "efficient chain-transfer agents",[5] polymerization only occurs if the olefin is extremely reactive, as in the case of styrene, methyl acrylate, etc.

Vinylsilanes are also important silafunctional materials. Radical additions to vinylsilanes, for instance, can be very efficient; the radical cross-linking of vinylsilicones with unfunctionalized silicones is an important commercial technology for forming silicone rubbers.[6]

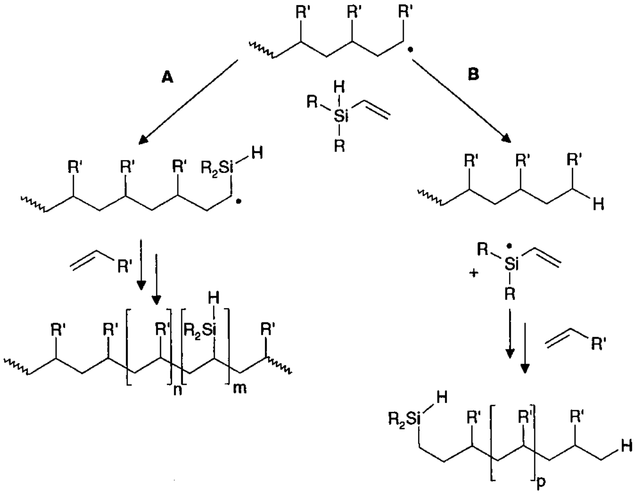
We were interested in examining the radical reactivity of silane moieties that bear both Si−H and Si−CH=CH$_2$ functional groups.[7] If the reactivities of the Si−H and Si−CH=CH$_2$ groups when on the same silicon nucleus are sufficiently different under radical conditions, it may be possible to use the groups independently in sequential radical reactions. For instance, in a copolymerization one could expect a backbone-functionalized polymer if $k_{\mathrm{Si-H}} \ll k_{\mathrm{Si-CH=CH_2}}$ (Scheme 2A), whereas end-functionalized polymers would result if the relative rates are reversed (Scheme 2B).[17] In either case, the surviving functional groups would be available for reaction under radical or other conditions.

The reactivity of hydrovinylsilanes has been explored primarily under transition metal catalysis. Thus, Asanuma and co-workers and Corriu and co-workers have examined the sequential reactivity of hydrovinylsilanes. The vinyl group was first reacted using Ziegler−Natta copolymerization[8,9] or hydrosilation.[10−12] Subsequent cross-linking through Si−H groups and residual vinyl groups was induced using hydrosilation,[13] γ-[14] or UV-irradiation,[15] or pyrolysis.[10−12] In these cases, it is difficult to gauge the relative reactivity of the two functional groups or the nature of the radicals produced, if any.

Scheme 1



Scheme 2



Two groups have examined the relative reactivity of these two functional groups under radical conditions. The γ-ray-initiated polymerization of diethylvinylsilane has been examined by Hayakawa *et al.*[16] and the azobis(isobutyronitrile) (AIBN) catalyzed polymerization of phenylvinylsilane by the group of Iwakura.[17] In both cases, the Si−H group was found to be less reactive than the vinyl group although in neither case was this difference quantitated. Our exploration of the relative reactivity of these two functional groups under radical conditions and our synthetic modification of the resulting products are described below.

Results

Ph$_2$SiHCH=CH$_2$ (**1**)[18] was utilized in this study because of the convenience in following its reactions and the opportunity to modify the electronic demands of the phenyl groups: **1** was prepared from Ph$_2$SiClH in high yield using vinylmagnesium bromide in THF.

As a benchmark for the radical reactivity described below, **1** was polymerized by hydrosilation using Speier's

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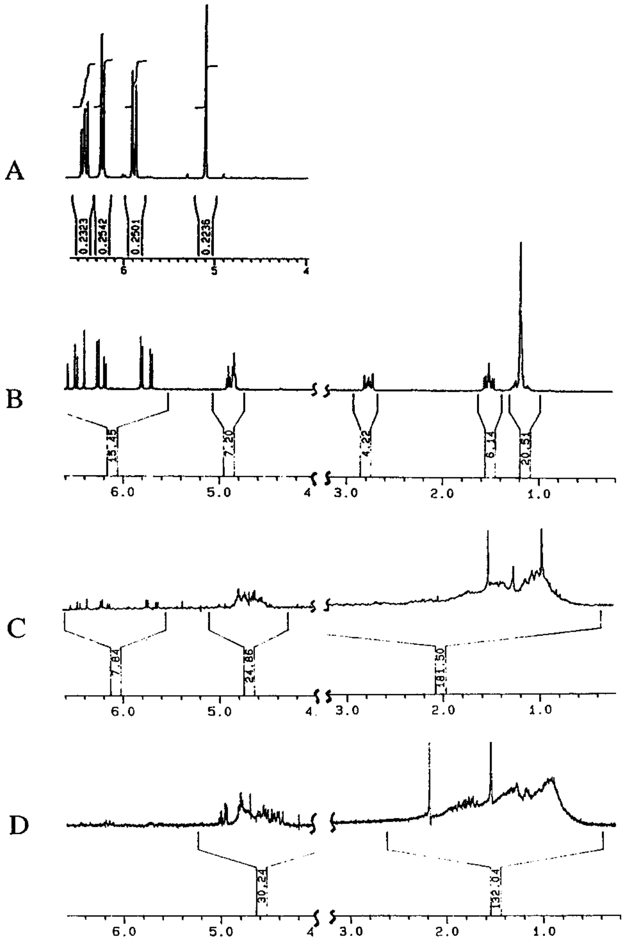


Figure 1. ^{1}H NMR plot (0−6 ppm) of the reaction of 1 with 10% BPO (A) before reaction, (B) after 3 h, (C) after 7 h, and (D) after 12 h.

catalyst (H_2PtCl_6)[19] in benzene. The resulting white polymer amorphous[20] **2** [$(Ph_2SiCH_2CH_2)_n$] had a low molecular weight of $\bar{M}_n = 2000$ with a polydispersity of 1.4, as determined by GPC. Residual Si—H and Si—CH=CH$_2$ (end) groups, in a 1:1 ratio as expected, could be seen in the ^{1}H NMR.

In a typical radical reaction, a benzene solution of **1** (0.6 M) was added to a benzene solution of an initiator such as benzoyl peroxide (BPO, 10 mol %) and heated to reflux. The oligomeric products were characterized by several spectroscopic techniques, primarily NMR. The ratio of Si—H to Si—CH=CH$_2$ groups was readily determined from ^{1}H NMR, as was the amount of residual starting material: homogeneous solutions in CDCl$_3$ were observed for all the products (Figure 1). The presence of Si—H groups in the product oligomer could be confirmed by IR spectrometry at 2110−2125 cm^{-1}, by observation of Si—H splittings in the coupled INEPT ^{29}Si NMR spectra at −11.6 and −14.9 ppm, by the peaks in the ^{1}H NMR between 4.5 and 5.4 ppm, and by the disappearance of those peaks following oxidative cleavage by *N*-bromosuccinimide.[21]

The molecular weights of the products were determined by two independent methods. GPC analysis gave relatively low molecular weights for the polymeric products. As the products from some of the reactions were amenable to chromatographic separation, silica gel chromatography was used to fractionate the polymers. In this manner, the molecular weight profile determined by GPC could be independently confirmed.

Radical Reactivity. Effect of Initiator and Monomer Concentrations on Conversion. Radical Chain Length. No reaction occurred when **1** was heated without initiator at 160 °C for 12 h. With radical initiation, the product mix (*vide infra*) was found to be very dependent upon the initiator type, concentration, stoichiometry, and reaction temperature (Table 1). With 1 mol % AIBN as initiator, for instance, essentially no reaction with **1** occurred; >95% of the starting material was recovered.[22] In order to observe a significant degree of conversion of starting material to product, the use of much larger initiator loads was required. The reaction of **1** with 10 mol % AIBN led to 50% product and 50% recovered starting material. In an attempt to force the reaction to completion, a 1:1 molar ratio of monomer:catalyst was used. In spite of the potential presence of 200 mol % radicals (it is recognized that the efficiency of AIBN initiation is typically much less that 100%), recovered **1** still accounted for 15% of the product mixture.

Peroxide initiators behaved similarly. BPO (1 mol %) was ineffective as an initiator, while a reaction with initiation by 10 mol % BPO gave comparable results to the reaction with 10% AIBN. More vigorous conditions, including temperatures in excess of 100 °C (neat or in 1,2,4-trichlorobenzene), and more reactive peroxides, dicumyl peroxide (DCP, 150 °C) or di-*tert*-butyl peroxide (BOOB, 160 °C), gave low molecular weight oligomers and incomplete conversion (Table 1); only in the case of BOOB was almost complete conversion of both functional groups observed. The loss of the Si—CH=CH$_2$ groups occurred more rapidly than that of the Si—H groups, as shown by ^{1}H NMR in all cases.

Two different attempts were made to extend conversion to products by maximizing radical chain lengths. In the first, the reaction was run with the very slow addition of initiator which, it was hoped, would minimize termination reactions. A syringe pump was used to add a solution of AIBN (20 mol %) to **1** (0.6 M) over a period of 12 h. Aliquots were taken each hour (Figure 2). Recovered **1** still comprised 40% of the product mixture.

In the second approach, the reaction was performed **neat** with 10 mol % AIBN in the hope of increasing the molecular weight of the product. However, under these conditions, 20% unreacted starting materials remained (Table 1). Irrespective of the reaction conditions used, once residual **1** had been removed from the product mix, the molecular weights of the products were very low and did not depend to a significant degree on the nature of the initiator (Table 1).

Relative Reactivities of Si—H and Si—CH=CH$_2$ Groups. The control of the composition of the oligomeric/polymeric products rests on the relative reactivity of the Si—H and Si—CH=CH$_2$ groups. Literature reports indicate the absolute rates of radical abstraction of Si—H and addition to Si—CH=CH$_2$ should both be accelerated when oxygen- rather than carbon-based radicals are used.[23] To determine if the relative reactivity of Si—H versus Si—CH=CH$_2$ was also affected by the initiator in the reaction with **1**, a comparison between carbon-based (AIBN) and peroxide initiators (BPO, DCP, BOOB) was made (Table 1). Irrespective of the reaction conditions or initiator, the relative reactivity of the Si—CH=CH$_2$ groups was larger than that of Si—H (Figure 1). This could be most clearly seen from the reaction in which the initiator AIBN was added over 12 h. The relative conversions of Si—H and

Table 1. Effect of Reaction Conditions on the Relative Consumption of Si—H and Si—CH=CH$_2$ Groups

initiator	mol %	[**1**]	Si—CH=CH reacted (mol %)	Si—H reacted (mol %)	ratio reacted Si—CH=CH$_2$/Si—H	recovered **1** (mol %)	product $\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
H_2PtCl_6	cat.	0.7 M	90	90	1	50	1800	1.4
AIBN	10	0.6 M	43	23	1.9	50	770	1.4
AIBN	10	neat	64	31	2.1	23	940	1.4
AIBN[a]	20	0.6 M	95	54	1.8	40	770	1.4
AIBN	100	0.6 M	65	35	1.8	15	690	1.5
BPO	1	0.6 M				95		
BPO	10	0.6 M	41	23	1.9	50	770	1.4
DCP	10	0.6			2.7[b]		590	1.4
DCP	10	neat	86	71	1.2	5.5	540	2.1
BOOB	10	neat	100	84	1.2		970	2.2

[a] Added over 12 h via a syringe pump. [b] Solution in 1,2,4-trichlorobenzene.

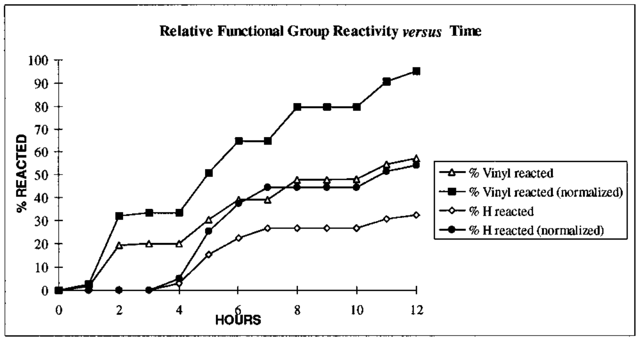
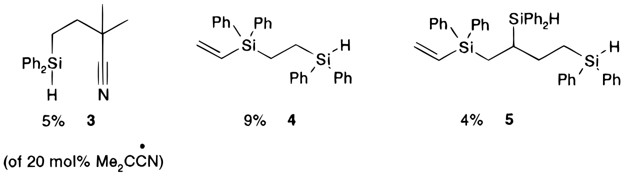


Figure 2. Plot of the relative reactivity (consumption) of Si—H and Si—CH=CH$_2$ groups (raw data, ◇ and △, respectively, and normalized to account for recovered starting material, ● and ■, respectively) in the reaction of **1** initiated by the slow addition of AIBN with time.

Chart 1

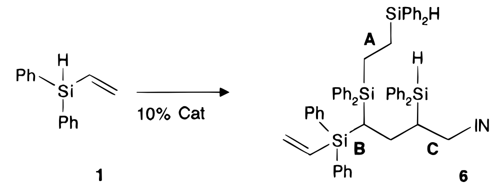


Si—CH=CH$_2$ are given in Figure 2. The magnitude of this difference was highest at lower temperatures and with less reactive initiators under which conditions the reactions occurred with enhanced selectivity for the vinyl groups. The overall ratio of rate constants at 80 °C, as judged by product composition, $k_{Si-CH=CH_2}/k_{Si-H} \approx 2$ but decreased to about 1.2 at elevated temperatures (160 °C, Table 1).

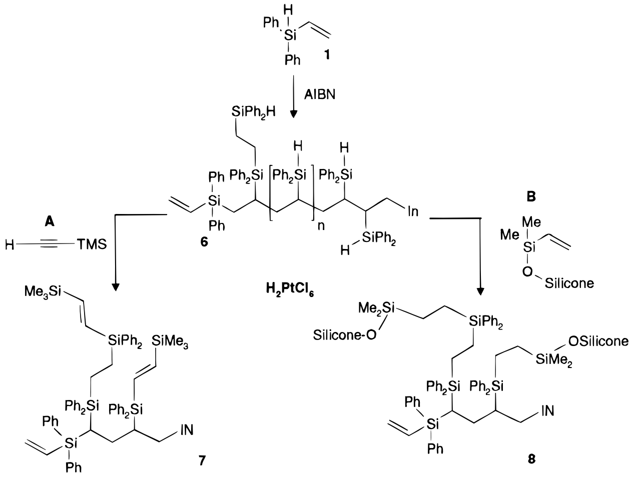
Product Composition. Some interesting low molecular weight products could be isolated (Chart 1) with AIBN (10 mol %) as initiator including the AIBN adduct **3**,[24] other incompletely characterized AIBN adducts, hydrosilated dimers **4**, trimers **5**, and higher oligomers. Compound **3** is of particular interest. Based on the amount of initiator added, it accounts for 25% of the AIBN added. This points out not only the efficacy of the addition of Me$_2$C•CCN to the vinylsilane but also the very short radical chain lengths of these radical reactions. The trimer **5** could also be isolated from the reactions initiated by BPO and DCP (Chart 1).

For all the radical reactions, irrespective of the initiator, it is clear that the product is not predominantly $(Ph_2SiCH_2CH_2)_n$; the ratio of Si—H to Si—CH=CH$_2$ end groups is not 1:1, as they must be for the hydrosilation oligomer/polymer. GPC results suggest that oligomers of $\overline{DP} = 3-7$ are being formed in these oligomerizations. We have not been able to isolate and characterize all of the many species that comprise the oligomeric mixtures. However, to the extent that the structures of the oligomers are related to the isolated small molecules **3**–**5**, the oligomers contain molecular fragments resulting from hydrosilation (Scheme 3A) and normal olefin initiation (IN = initiator, Scheme 3C). In addition, radical recombination (Scheme 3B) is likely the process which accounts for the low molecular weights observed. A *model structure* exhibiting these constituents **6** is shown in Scheme 3.

Scheme 3

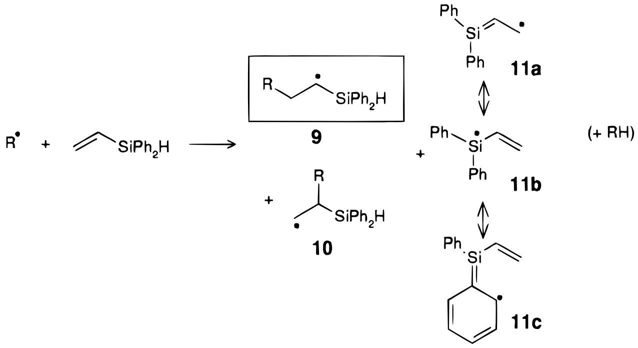


Scheme 4



Hydrosilation of Si—H Groups. The possibility exists that the preferential consumption of the Si—CH=CH$_2$ groups could have arisen because the Si—H groups are in some way protected during the reaction. To ascertain that the residual Si—H groups retain their reactivity after the radical reaction, the hydrosilation of these groups was performed. The H_2PtCl_6-catalyzed[25] reaction of **6** with HC≡CSiMe$_3$ led to complete conversion of the Si—H groups to an oligomeric vinylsilane species **7** (Scheme 4A, see Experimental Section). Similarly, vinyl-terminated silicones reacted quantitatively to form grafted polyolefin–silicone star polymers **8** (Scheme 4B), demonstrating that the Si—H groups remain available for reaction throughout the radical process.

Scheme 5



Discussion

The propagation and termination steps in the radical chain reactions of **1** involve a variety of possible radical entities such as **9**−**11** as shown in Scheme 5. The radicals may be divided into two classes, silicon- or carbon-based. The relative reactivity of these will be discussed in turn.

α- versus *β*-Addition to the Vinylsilane. Wilt[26] has demonstrated that α- and *β*-silyl carbon-based radicals are stabilized (3.0−4.0[27] and 2.6−3.0 kcal/mol,[28] respectively) with respect to the all-carbon systems whereas the *γ*-radical is of comparable reactivity. In the reaction of **1** with an initiating or propagating radical, addition to the *β*-silyl position of the olefin leading to an α-silyl carbon radical was preferred over the other regiochemical pathway via **10** (Scheme 5), as shown by the formation of **3** and the other products. In none of the products was the *β*-radical **10** implicated (aside from the methyl groups arising from AIBN, there were no methyl groups arising from $RCH_2^\bullet \rightarrow RCH_3$ in the products; none of the small molecules which could be completely characterized contained residues resulting from α-addition). The preference for *β*-addition to the vinyl group can be attributed to the stabilizing electronic effect of the silyl group, the greater relative stability of secondary *versus* primary radicals and the greater ease of radical addition to the *β*-silyl position on steric grounds.

Addition to the Vinyl Group versus Abstraction from the Si−H Group. Unlike benzylic radicals which achieve stability through resonance with the adjacent aromatic group, the analogous resonance in the silyl radical **11**, best represented by **11b**, does not provide a strong stabilizing effect; the silene bond is not nearly as strong as the analogous C=C bond.[29] It is, therefore, inappropriate to consider **11** to be an analogue of an allylic or benzylic radical (**11a**, **11c**).[30] The Si−H bond is, however, relatively weak,[2] and abstraction of $H^\bullet$ by initiator radicals (especially in the case of peroxide initiators) and by radicals such as **9** and homologues was evidenced by the formation of **3** and related products.

Radical Chain Lengths. Under even the most favorable of the conditions used, the radical chain lengths were shown to be very short. Product molecular weights were low in all cases and significant amounts of unreacted starting material were usually recovered even when the reaction was run without added solvent. This was not a result of rapid termination of chains due to high radical concentrations; adding the initiator over 12 h did not increase the conversion of **1**.

This result is consistent with previous work. Vinylsilanes do not polymerize easily under radical conditions, as judged by the relatively harsh conditions necessary even to get materials of low molecular weight. Vinyltrialkylsilanes react only sluggishly under radical conditions and even vinylsilanes bearing electron-withdrawing groups on silicon ($R_3Si-CH=CH_2$, R = Cl, OMe) are poor monomers.[7,31] Presumably, this results from (i) the preference for forming the α-silyl carbon radical such as **9**,[27] when compared to the *β*-silyl carbon radical **10**[28] or silyl radical **11**,[23] and (ii) its relatively low stability which allows it to act in essence as a radical trap via recombination at a faster rate than propagation processes can occur.

Relative Reactivity Si−H:Si−*CH*=*CH*$_2$. The experimental results outlined above indicated, on average, a relative reactivity of $Si-CH=CH_2/Si-H$ of about 2 at lower temperatures (Table 1, Figure 2) which is attenuated to about 1.2 at higher temperatures. We interpret this ratio, particularly at low conversion, to reflect the ratio of the rate constants ($k_{Si-CH=CH_2}/k_{Si-H} \approx 2$) for the two general pathways (vinyl addition, H-abstraction). This is clearly an oversimplification in that many radical species are present in solution, each of which will, for instance, abstract $H^\bullet$ with a different rate constant. This rate ratio is comparable to that of selected vinyl addition/radical abstraction rate constants when only one of the two functional groups is on a silicon atom.[23,32] We therefore conclude that the combined presence of both Si−H and $Si-CH=CH_2$ groups on a single silicon atom does not significantly affect the rates of the two radical reaction pathways, consistent with previous work. Although the group of Iwakura[17] observed that $PhSiH_2CH=CH_2$ underwent oligomerization with radical (AIBN) catalysis to give an oil, no characterization of the materials was reported. Hayakawa *et al.*,[16] however, have examined *γ*-ray-initiated polymerization of $Et_2HSiCH=CH_2$ and demonstrated, without quantitation, that both polymerization using hydrosilation (Scheme 3A) and vinylic oligomerization (Scheme 3B) were occurring.

Conclusion

Having two radically active groups, $Si-CH=CH_2$ and Si−H, on a single silicon nucleus does not dramatically affect the radical reactivity of the two functional groups. Preferential consumption of the vinyl group of **1** occurred with a reactivity ratio $Si-CH=CH_2/Si-H$ of about 2 although this ratio could be decreased somewhat by changing from an azo to a peroxide initiator and by varying the reaction conditions (Table 1). The reactivity ratio is similar to that of the analogous monofunctionalized compounds (e.g., $R_3Si-CH=CH_2$, R_3Si-H) under the same conditions. The products were Si−H-functionalized oligomers. The Si−H rich oligomers produced undergo normal reactions including transition metal-catalyzed hydrosilation, which can be used for the preparation of silicone star polymers.

Experimental Section

Apparatus, Materials, and Methods. The continuous wave ^1H NMR spectra were recorded on a Varian EM-390 (90-MHz) spectrometer, and the Fourier spectra, on a Bruker DRX-500 (500-MHz) spectrometer, Bruker AC-300 (300 MHz) spectrometer, or Bruker AC-200 (200 MHz) spectrometer. ^{13}C and ^{29}Si NMR were performed on a Bruker AC-200 (at 50.3 MHz for carbon) and Bruker AC-300 (at 75.5 MHz for carbon and 59.6 MHz for silicon, respectively). Chemical shifts are reported with respect to tetramethylsilane as standard, set to 0 ppm. Coupling constants (*J*) are recorded in hertz (Hz). The abbreviations s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, and m = multiplet are used in reporting the spectra.

Electron impact (EI) mass spectra were recorded at 70 eV with a source temperature of *ca.* 200 °C on a VG analytical ZAB-E mass spectrometer equipped with a VG 11-250 data system. Infrared spectra were run on a Perkin-Elmer 283 spectrometer, and Fourier spectra, on a BIO RAD FTS-40 spectrometer, as a neat film.

The molecular weight distributions of the oligomers were analyzed using a Waters gel permeation chromatograph equipped with a Waters 410 differential refractive index detector. Two Jordi mixed-bed columns in series were utilized with 1,1,1-trichloroethane as solvent flowing at 1.5 mL/min. Narrow molecular weight polystyrene standards from Polymer Laboratories were used for calibration of the chromatographic system.

All solvents were thoroughly dried before use. Diethyl ether was distilled over sodium/benzophenone. Benzene was washed with concentrated sulfuric acid, distilled, and then redistilled over sodium.

Due to the tendency of halo groups on silicon to hydrolyze easily, the Grignard reaction was carried out in dry apparatus under a nitrogen atmosphere with the use of septa and syringes for the transfer of reagents.

Sources of Material. Chloromethyldiphenylsilane (Lancaster, 97%), vinylmagnesium bromide (Aldrich, 1.0 M solution in tetrahydrofuran), benzoyl peroxide (Aldrich), di-*tert*-butyl peroxide (Fluka), dicumyl peroxide (Aldrich), (trimethylsilyl)acetylene (Aldrich, 98%), vinyldimethyl-terminated poly(dimethylsiloxane) (United Chemicals, viscosity = 4−6 centistokes), 1,2,4-trichlorobenzene (Aldrich), and tris(triphenylphosphine)rhodium(I) chloride (Aldrich) were used as received. Azobis(isobutyronitrile) (Eastman Kodak) was recrystallized from methanol prior to use. A 0.1 M solution of Speier's catalyst (hydrogen hexachloroplatinate(IV) hydrate, H_2PtCl_6, Aldrich) was prepared with anhydrous 2-propanol (Caledon, reagent grade) obtained by distillation under nitrogen after it was dried with sodium (BDH) overnight. Diethyl ether (BDH, reagent grade) was distilled from sodium/benzophenone (Aldrich) under a nitrogen atmosphere. Benzene (BDH, reagent grade) was washed with sulfuric acid (Fisher Scientific) and distilled from sodium under a nitrogen atmosphere. 1,1,1-trichloroethane (Caledon, reagent grade) was filtered using a Type HA 0.45 μm Millipore filter.

Preparation of Diphenylvinylsilane (1). Chlorodiphenylsilane (10 g, 45.9 mmol) was added dropwise to a stirred solution of vinylmagnesium bromide (1.1 equiv, 1.0 M in Et_2O, 50.5 mL, 50.5 mmol) in THF (50 mL) at 0 °C. Once addition was complete, the mixture was slowly warmed to room temperature and stirred for an additional 2 h. The reaction mixture was then slowly poured into an ice-water bath, extracted with diethyl ether, and washed with saturated brine. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. Distillation gave the silane as a colorless liquid.

Bp: 108 °C/1 mmHg. Yield: **1**, 90% (8.7 g, 41.4 mmol). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.11 (d, 1H, $J = 3.0$ Hz), 5.89 (dd, 1H, $J = 4.4$, 19.4 Hz), 6.24 (dd, 1H, $J = 4.4$, 14.5 Hz), 6.45 (ddd, 1H, $J = 3.0$, 14.5, 19.4 Hz), 7.30−7.60, 7.50−7.70 (m, 10H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 128.00, 129.71, 132.62, 133.25, 135.43, 136.99. ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ −21.60. IR (neat): ν 3051, 3003, 2971, 2124, 1590, 1485, 1428, 1404, 1304, 1115, 1007, 960, 816, 796 cm^{-1}. ^{29}Si NMR INEPT (with nonselective polarization transfer and no H decoupling during acquisition, *selected for Si−H peaks*, 1,2,4-trichlorobenzene, $CDCl_3$, DRX-500 MHz): δ −22.11 (d, $J_{Si-H} = 206.4$ Hz). MS (*m*/*z*): 210 (29, M$^+$), 181 (47), 155 (8), 132 (100), 105 (72), 91 (7), 79 (14), 53 (24).

General Procedure for Hydrosilation. A benzene solution of the monomer or oligomer (0.6 M) and 5 drops Speier's catalyst (H_2PtCl_6) were stirred at 50 °C for 12 h. The solvent was removed in vacuo, and the crude product was purified by precipitation. Precipitation involved dissolving the polymer in chloroform, precipitating the polymer with the addition of methanol, and then decanting the liquid. This process was repeated several times.

Homopolymerization of Diphenylvinylsilane by Hydrosilation. Diphenylvinylsilane (**1**) (1.0 g, 4.8 mmol), Speier's catalyst (5 drops, 0.1 M in 2-propanol), and benzene (7 mL) were reacted for 12 h at 50 °C. Yield: **2**, 50% (0.5017 g). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0−0.30, 0.20−1.65 (m, 3.8H), 4.42−5.10 (m, 0.05H), 5.20−6.48 (m, 0.15H), 6.60−8.00 (m, 10H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 1.03, 3.65, 7.41, 127.73, 129.11, 134.33, 134.95, 135.64, 135.86. ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ −9.55, −7.71, −3.86, 6.19, 8.75. IR (neat): ν 3067, 3044, 2910, 2879, 1589, 1485, 1427, 1261, 1110, 716 cm^{-1}; $\bar{M}_n$ 1800, $\bar{M}_w/\bar{M}_n$ 1.4.

General Procedure for Radical Polymerization. AIBN was recrystallized from methanol before use, and nitrogen was bubbled through the benzene for 1 h before beginning the reactions. BOOB and DCP were used as received.

A benzene or 1,2,4-trichlorobenzene solution of the monomer and a radical initiator, AIBN, BPO, BOOB, or DCP, was heated at 80 °C for 12 h (AIBN and BPO initiator), 150 °C for 1.25 h (DCP initiator), 160 °C for 10.5 h (BOOB initiator), and 100 °C for 6 h (BPO initiator) under an inert atmosphere (N_2, see Table 1). The reaction times were chosen to be greater than 10$t_{1/2}$ (half-lifetime of the initiator)[33] at the temperature values chosen for the reactions. The solvent was removed in vacuo, and the crude products were purified by radial chromatography using a hexane/ether (99:1 and 95:5) mixed solvent systems. For the neat polymerization reactions, the same procedure was followed with the following exception: diphenylvinylsilane was added to the pure initiator preweighed in a reaction flask thoroughly flushed with nitrogen. The crude mixtures of oligomers obtained were analyzed by ^{1}H, ^{13}C, and ^{29}Si NMR and separated by preparative TLC or radial chromatography using 99:1 and 95:5 hexane−ether mixtures, respectively.

Radical Polymerization of Diphenylvinylsilane. Thermal Initiation of 1. Diphenylvinylsilane (0.250 g, 1.2 mmol) was heated at 160 °C for 12 h, under a nitrogen atmosphere. ^{1}H NMR ($CDCl_3$, 200 MHz) shows only the presence of the starting material.

With 10 mol % AIBN. Diphenylvinylsilane (0.6 M, 1 g, 4.8 mmol), AIBN (0.1 equiv, 78.1 mg, 0.48 mmol), and benzene (7 mL) were reacted for 12 h at 80 °C. Crude: ^{1}H NMR ($CDCl_3$, 200 MHz, integration based on the 10 aromatic protons of $SiPh_2$) δ 0.20−2.80 (m, 2.66H), 4.66−4.95, 5.16−5.17 (m, 0.77H), 5.65−6.55 (m, 1.72H), 7.00−7.60, 7.30−7.80 (m, 10H); 50% (0.5 g) of diphenylvinylsilane recovered. From the ^{1}H NMR of the crude material: 43% vinyl and 23% Si−H reacted.

Products after removal of residual starting material, **6**: yield 50% (0.50 g); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.10−0.14, 0.10−2.3 (m, 3.52H), 4.20−4.87 (m, 0.27H), 5.65−6.57 (m, 0.21H), 6.60−8.00 (m, 10H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 4.25, 4.66, 4.84, 5.38, 5.75, 6.03, 12.16, 22.12, 23.43, 26.08, 36.09, 127.77, 127.91, 128.17, 129.30, 129.36, 129.50, 129.71, 129.89, 132.68, 133.31, 133.72, 134.27, 135.13, 135.45, 136.98; ^{29}Si NMR ($CDCl_3$, 59.6 MHz) δ −13.52, −12.50, −10.94, −3.46; IR (neat) ν 3089, 3048, 3014, 2914, 2116, 1589, 1485, 1427, 1108, 802, 725 cm^{-1}; $\bar{M}_n$ 770, $\bar{M}_w/\bar{M}_n$ 1.4.

Fractions Isolated from above Material. AIBN adduct, **3**: yield 5% (0.05 g); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.24−1.65 (m, 10H), 4.87 (t, 1H, $J = 4$ Hz), 7.30−7.60, 7.50−7.70 (m, 10H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 7.78, 26.06, 34.25, 36.06, 124.90, 128.15, 129.86, 133.27, 135.04; IR (KBr) ν 3086, 2977, 2932, 2233, 2119, 1589, 1485, 1428, 1191, 1113, 906, 874, 807, 700 cm^{-1}; MS (*m*/*z*) 278 (7, M$^+$ − 1), 201 (25), 183 (100), 146 (11), 105 (45), 83 (31).

Dimer **4** yield 8% (0.08 g); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.11−1.42 (m, 4H), 4.83 (t, 1H), 5.74 (dd, 1H, $J = 4.0$, 20.0 Hz), 6.21 (dd, 1H, $J = 4.0$, 14.7 Hz), 6.48 (dd, 1H, $J = 14.7$, 20.0 Hz), 7.19−7.60, 7.40−7.62 (m, 20H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 4.59, 6.00, 126.73, 126.84, 126.93, 128.19, 128.30, 128.39, 128.49, 128.59, 128.84, 128.95, 129.05, 130.41, 130.50, 130.61, 134.10, 136.11, 136.20, 136.29, 136.38, 137.95; IR (KBr) ν 3085, 3067, 3049, 3011, 2914, 2119, 1589, 1486, 1428, 1405, 1112, 1053, 1009, 808, 758, 700 cm^{-1}; MS (*m*/*z*) 420 (8, M$^+$), 393 (10), 342 (20), 314 (18), 259 (40), 238 (10), 209 (74), 183 (100), 131 (9), 105 (43), 53 (8).

Trimer **5**: yield 4% (0.04 g); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.14, 0.78−2.33 (m, 7H), 4.55−4.82 (m, 2H), 5.71 (dd, 1H, $J = 3.8$, 20.2 Hz), 6.20 (dd, 1H, $J = 3.8$, 14.7 Hz), 6.46 (dd, 1H, J

Table 2. Conversion of Si—H and Si—CH=CH$_2$ Functional Groups in Ph$_2$SiHCH=CH$_2$ with Time[a]

hours	unreacted Si—Vinyl (of 3 H)	unreacted Si—H (of 1 H)
0	3.000	1.000
1	2.982	1.000
2	2.448	1.000
3	2.424	1.000
4	2.424	0.970
5	2.109	0.847
6	1.852	0.776
7	1.852	0.733
8	1.582	0.733
9	1.582	0.733
10	1.579	0.733
11	1.379	0.692
12	1.303	0.675

[a] Raw data for Figure 2.

= 14.7, 20.2 Hz), 7.15−7.61, 7.40−7.70 (m, 30H); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 4.60, 6.00, 8.20, 22.70, 34.90, 127.74, 127.91, 128.96, 129.08, 129.14, 129.45, 133.73, 134.28, 134.68, 134.85, 135.02, 135.08, 135.19, 135.26, 135.31, 135.38, 135.47, 135.51, 135.66, 135.72; IR (KBr) ν 3067, 2999, 2904, 2848, 2111, 1588, 1485, 1427, 1303, 1262, 1109, 1066, 998, 846, 800, 726 cm^{-1}; MS (*m/z*) 630 (2, M$^+$), 553 (4), 447 (4), 393 (8), 369 (4), 341 (4), 259 (46), 209 (9), 183 (100), 159 (12), 105 (34).

With 10 mol % AIBN, Neat. Diphenylvinylsilane (1.0 g, 4.8 mmol) and AIBN (0.1 equiv, 78.1 mg, 0.48 mmol) were reacted for 12 h at 80 °C. Crude: ^{1}H NMR (CDCl$_3$, 200 MHz, integration based on the 10 aromatic protons of SiPh$_2$) δ 0.20−2.80 (m, 3H), 4.60−5.00, 5.16−5.17 (m, 0.69H), 5.65−6.56 (m, 1.09H), 7.00−7.42, 7.30−7.80 (m, 10H); 23% (0.23 g) of diphenylvinylsilane recovered. From ^{1}H NMR of crude material: 64% of vinyl reacted and 31% of Si—H reacted. $\bar{M}_n$ 940, $\bar{M}_w/\bar{M}_n$ 1.4.

With 100 mol % AIBN. Diphenylvinylsilane (0.6 M, 0.5 g, 2.4 mmol), AIBN (1 equiv, 390 mg, 2.4 mmol) and benzene (3.5 mL) were reacted for 12 h at 80 °C. Crude: ^{1}H NMR (CDCl$_3$, 200 MHz, integration based on the 10 aromatic protons of SiPh$_2$) δ 0.30−2.80 (m, 11H), 4.60−5.00, 5.12−5.13 (m, 0.65H), 5.67−6.56 (m, 1.06), 7.00−7.50, 7.45−7.80 (m, 10H). 15% (0.075 g) of diphenylvinylsilane recovered. From ^{1}H NMR of crude material: 65% vinyl reacted and 35% Si—H reacted. ; $\bar{M}_n$ 690, $\bar{M}_w/\bar{M}_n$ 1.5.

With Slow Addition of 20% AIBN (over 12 h). A mixture diphenylvinylsilane (2 g, 9.5 mmol), benzene (10 mL), and AIBN (0.2 equiv, 312.3 mg, 1.9 mmol) in benzene (4.8 mL) was added dropwise at a rate of 0.4 mL/h for a duration of 12 h using a Harvard Apparatus Syringe Infusion Pump 22. An aliquot (0.5 mL) was removed from the reaction mixture every hour, the solvent evaporated in vacuo, and a ^{1}H NMR taken. The data in the table are the integration of the Si—vinyl and Si—H regions based on 10 aromatic protons of SiPh$_2$ for each fraction. A total of 40% (0.8 g) of **1** was recovered. Thus, of the quantity of **1** which reacted, 96% of the Si—CH=CH$_2$ and 57% of the Si—H groups reacted. $\bar{M}_n$ 770, $\bar{M}_w/\bar{M}_n$ 1.4.

With 10 mol % BPO. Diphenylvinylsilane (0.6 M, 1 g, 4.8 mmol), benzoyl peroxide (0.1 equiv, 115.1 mg, 0.48 mmol), and benzene (7 mL) were reacted for 12 h at 80 °C. Crude: ^{1}H NMR (CDCl$_3$ 200 MHz, integration based on the 10 aromatic protons of SiPh$_2$) δ 0.2−2.80 (m, 1.47H), 4.63−4.95, 5.14−5.15 (m, 0.77H), 5.64−6.57 (m, 1.78H), 7.00−7.59, 7.50−7.80 (m, 10H); 50% (0.50 g) of diphenylvinylsilane recovered. From ^{1}H NMR of crude material: 43% vinyl reacted and 23% Si—H reacted.

Product after starting material was separated: **6** and related isomers; yield 50% (0.50 g); ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.1−0.14, 0.1−2.8 (m, 3.52H), 4.42−5.01 (m, 0.27H), 5.68−6.57 (m, 0.21H), 6.60−8.00 (m, 10H); ^{13}C NMR (CDCl$_3$, 50.3 MHz) δ 4.14, 4.67, 6.03, 14.20, 24.64, 29.70, 30.44, 127.81, 128.00, 129.33, 129.53, 129.69, 130.16, 132.64, 133.20, 135.10, 135.22, 135.43, 136.93; ^{29}Si NMR (CDCl$_3$, 59.6 MHz) δ −12.87, −12.04, −11.30, −9.16, −7.98, −3.85; IR (neat) ν 3067, 2910, 2112, 1589, 1483, 1427, 1262, 1110, 806, 728. $\bar{M}_n$ 770, $\bar{M}_w/\bar{M}_n$ 1.4.

Fractions isolated from the above material: dimer: **4** yield 9% (0.09 g); trimer: **5** yield 4% (0.04 g).

With 10 mol % BPO in 1,2,4-Trichlorobenzene. Diphenylvinylsilane (0.6 M, 1 g, 4.8 mmol), benzoyl peroxide (115 mg, 0.48 mmol), and 1,2,4-trichlorobenzene (7 mL) were heated at 100 °C for 6 h ($t_{1/2}$ = 0.5 h at 100 °C).[33] Comparable ^{1}H NMR and ^{13}C NMR to those found for 10% BPO were found. Crude: ^{29}Si NMR (1,2,4-trichlorobenzene/Cr(acac)$_3$, 300 MHz) δ −22.11, −14.44, −13.03, −11.43, −9.19, −8.15, −4.16, 9.16 (recovered starting material); ^{29}Si NMR INEPT (with nonselective polarization transfer and no H decoupling during acquisition, *selected for Si—H peaks*, 1,2,4-trichlorobenzene, CDCl$_3$, DRX-500 MHz) δ −22.11 (d, $J_{\text{Si—H}}$ = 206.4 Hz, starting material), −14.44 (d, $J_{\text{Si—H}}$ = 198.6 Hz), −11.43 (d, $J_{\text{Si—H}}$ = 192.2 Hz). $\bar{M}_w$ 580, $\bar{M}_w/\bar{M}_n$ 1.31.

With 10 mol % BOOB in 1,2,4-Trichlorobenzene. Diphenylvinylsilane (0.6 M, 1.0 g, 4.8 mmol), di-*tert*-butyl peroxide (0.070 g, 0.48 mmol), and 1,2,4-trichlorobenzene (7 mL) were heated with stirring under a nitrogen atmosphere at 160 °C for 10.5 h ($t_{1/2}$ = 13.4 min at 160 °C).[33] Comparable spectra to those shown for 10% BPO were obtained. Crude: ^{29}Si NMR (CDCl$_3$/ Cr(acac)$_3$, 59.6 MHz) δ −22.34 (starting material), −16.29, −14.94, −12.44, −11.64, −9.41, 9.19.

With 10 mol % BOOB Neat. Diphenylvinylsilane (0.6 M, 1.0 g, 4.8 mmol) and di-*tert*-butyl peroxide (0.070 g, 0.48 mmol) were heated with stirring under nitrogen atmosphere at 160 °C for 10.5 h ($t_{1/2}$ = 13.4 min at 160 °C). Crude: ^{1}H NMR (CDCl$_3$, 200 MHz, integration based on the Si—H at 4.82 ppm) δ 0.29−1.9 (m, 3.5H), 3.94−4.28 (m, 0.34H), 4.65 (m, 0.06H), 4.82 (m, 0.1H), 7.15−7.57 (m, 10H); ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ 3.62, 4.15, 5.10, 6.14, 6.57, 7.40, 8.13, 13.80, 14.71, 21.88, 24.66, 25.69, 26.63, 29.97, 31.23, 32.03, 127.77, 129.14, 129.35, 134.42, 134.97, 135.66; ^{29}Si NMR (CDCl$_3$/Cr(acac)$_3$, 59.6 MHz) δ −11.36, −9.99, −9.09, −8.24, −3.80, 2.80, 9.76.

With 10 mol % DCP in 1,2,4-Trichlorobenzene. Diphenylvinylsilane (0.6 M, 1.0 g, 4.8 mmol), dicumyl peroxide (0.13 g, 0.48 mmol), and 1,2,4-trichlorobenzene were heated with stirring under nitrogen atmosphere at 150 °C for 1.25 h ($t_{1/2}$ = 6 min at 150 °C). ^{1}H NMR and ^{13}C NMR spectra were comparable to those for 10% BPO. Crude: ^{29}Si NMR (1,2,4-trichlorobenzene, Cr(acac)$_3$, 59.6 MHz) δ −22.11 (starting material), −14.74, −13.03, −11.43, −9.19, −4.03. $\bar{M}_n$ 590, $\bar{M}_w/\bar{M}_n$ 1.36.

With 10 mol % DCP, Neat. Diphenylvinylsilane (1.0 g, 4.8 mmol) and dicumyl peroxide (0.13 g, 0.48 mmol) were heated with stirring under a nitrogen atmosphere at 150 °C for 1.25 h. The reaction mixture was separated using preparative TLC and a 95:5 hexane:diethyl ether solvent system. After the removal of the starting material, several fractions were obtained, including a major fraction shown to be **5** (0.20 g, 20% yield). Crude: ^{1}H NMR (CDCl$_3$, 500 MHz, integration based on the Si—H of the starting material) δ 0.32−2.28 (m, 64H), 4.59−4.82 (m, 5.2H), 5.11 (d, 1H, J = 3.0 Hz), 5.72 (dd, 0.67H, J = 3.6, 20.4 Hz), 5.89 (dd, 1H, J = 3.4, 19.9 Hz), 6.17 (d, 0.38H, J = 3.6 Hz), 6.24 (dd, 1H, J = 3.6, 14.5 Hz), 6.42 (m, 1.7H), 7.20−7.54 (m, 179.6H), 7.93 (d, 1.62H, J = 7.1 Hz); ^{13}C NMR (CDCl$_3$, 125.8 MHz) δ 3.75, 4.29, 4.65, 4.80, 5.42, 6.00, 6.15, 13.81, 14.69, 17.84, 17.97, 21.88, 24.67, 26.56, 29.97, 31.75, 128.30, 128.56, 129.16, 129.36, 129.50, 129.72, 132.65, 133.06, 133.29, 134.24, 134.41, 134.99, 135.14, 135.46, 136.07, 136.99, 137.13; ^{29}Si NMR (CDCl$_3$/Cr(Acac)$_3$, 59.6 MHz) δ −22.11 (starting material), −14.62, −12.83, −11.34, −11.33, −10.09, −9.82, −9.09, −5.58, −3.87, 9.65.

Reaction of Si—H Groups with *N*-Bromosuccinimide. Fraction 4 (20 mg in 0.5 mL of CDCl$_3$) was mixed with 0.5 mL of 0.1 M *N*-bromosuccinimide in CDCl$_3$ in an NMR tube. ^{1}H NMR spectrum showed the disappearance of the signals at 4.78 ppm, indicating that this is a signal of the Si—H type.

Hydrosilation of Oligomer 6. Oligomer **6** (0.3222 g), Me$_3$SiC≡CH (1 mL, 0.695 g, 7.08 mmol), Speier's catalyst (H$_2$PtCl$_6$, 5 drops, 0.1 M in 2-propanol), and benzene (10 mL) were reacted for 12 h at 50 °C. Yield: **7**, 0.1305 g. ^{1}H NMR (CDCl$_3$, 200 MHz): δ −0.20−0.00, −0.10−0.20 (m, 9H), 0.10−2.30 (m, 3H), 6.54 (d, 1H), 6.71 (d, 1H), 6.50−8.00 (m, 10H). ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ −1.56, −1.06, −0.21, −13, 4.08, 4.79, 8.52, 22.60, 23.25, 25.70, 25.97, 29.67, 34.19, 35.58, 127.68, 127.82, 127.99, 128.24, 129.16, 129.27, 129.39, 129.54, 134.12, 134.38,134.48, 134.59, 134.81, 134.93, 134.98, 135.13, 135.25, 135.45, 135.54, 135.66, 135.87, 136.05, 136.34, 143.56, 144.04, 145.96, 157.43. ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ −15.32, −13.88, −10.48, −7.28, −6.91, −2.70. IR (KBr): ν 3068, 2954, 2899, 1589, 1427, 1404, 1248, 1173, 1107, 1014, 837 cm^{-1}. $\bar{M}_n$ 1000, $\bar{M}_w/\bar{M}_n$ 1.5.

Oligomer **6** (0.3534g), vinyldimethyl-terminated poly(dimethylsiloxane) (1 mL, 0.93 g, 4.6 cs, $\bar{M}_n \approx 750$), Speier's catalyst (5 drops, 0.1 M in 2-propanol), and benzene (5 mL) were reacted for 12 h at 50 °C. Yield: **8**, 0.1718 g. ^{1}H NMR ($CDCl_3$, 200 MHz): δ −0.20−0.60, (m, 32H), 0.10−2.00 (m, 9H), 6.60−8.00 (m, 20H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ −0.478, 0.268, 1.04, 1.55, 9.94, 15.29, 127.72, 129.04, 135.00, 135.65. ^{29}Si NMR ($CDCl_3$, 59.6 MHz) δ −22.44, −20.79, −9.80, −9.50, −3.39, −3.100, 8.01. IR (KBr): ν 3070, 2963, 2909, 1595, 1428, 1408, 1261, 1100, 1024, 801 cm^{-1}. $\bar{M}_n$ 6700, $\bar{M}_w/\bar{M}_n$ 2.9.

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(32) Direct comparison is rather difficult as very few examples exist of either competitive studies or absolute rate determinations of a given radical adding to $Si-CH=CH_2$ and abstracting $H^\bullet$ from $Si-H$.

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