# *Articles*

## Preparation of Soluble Polycarbosilane Polymers Using Group 4 Metallocene Catalysts

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The preparation of a series of carbosilane monomers of the form $H_3Si{-}R{-}SiH_3$ (primary carbosilane) and $H_2PhSi{-}R'{-}SiPhH_2$ (secondary carbosilane) ($R = {-}CH_2CH_2{-}$, $-{-}CH_2CH_2SiPh_2CH_2CH_2{-}$, ${-}CH_2CH_2CH_2SiPh_2CH_2CH_2CH_2{-}$; $R' = (CH_2)_n$ ($n = 1{-}3$), ${-}CH_2CH_2SiMe_2CH_2CH_2{-}$) is reported. Polymerization of the primary carbosilanes resulted in the formation of insoluble polycarbosilanes in less than 1 h. The secondary carbosilanes, however, yielded polymers that were soluble in common solvents (e.g., $CHCl_3$, $C_6H_6$, and THF). GPC analyses of the polymers indicated molecular weights as high as 12 000. The molecular weights were highly dependent on the structure of the monomer and the reaction conditions (temperature, solvent, catalyst concentration, and catalyst nature).

### Introduction

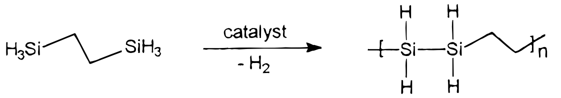
One of the methods used to prepare silicon carbide is the controlled pyrolysis of a polysilane or a polycarbosilane polymer precursor. A major advantage to this method is that one can control the structure of the precursor polymer during its synthesis, thereby affecting the outcome of the pyrolysis and the properties of the ceramic fiber.[1]

Since its discovery in the mid 1980s, catalytic dehydrocoupling has primarily been studied as an alternative method for the preparation of polysilanes.[2] However, extension to polymers that contained both silicon and carbon atoms in the backbone has also been reported. Tilley has studied the dehydropolymerization of a variety of bifunctional silanes of the type $H_3Si{-}Ar{-}SiH_3$[3] and $H_2RSi{-}C_6H_4{-}SiRH_2$.[4] Corriu has reported the condensation of the organosilane $H_2MeSiCH_2CH_2SiH_3$ in the presence of $Cp_2TiMe_2$ or $Cp_2TiCl_2$/2$^n$BuLi,[5] and Dunoguès has detailed the dehydrocoupling of $H_2MeSiCH_2CH_2SiMeH_2$ in the presence of group 4 catalysts.[6]

In this paper, we report the use of group 4 metallocene catalysts in the condensation of primary and secondary silyl-terminated carbosilanes. The first monomer chosen for study was 1,2-disilylethane, $H_3SiCH_2CH_2SiH_3$ (**1**), which when polymerized will contain a 1:1 ratio of silicon to carbon atoms. In order to vary the properties of the resultant polymers, the monomers $(H_3SiCH_2CH_2)_2SiMe_2$ (**2**), $(H_3SiCH_2CH_2)_2SiPh_2$ (**3**), $(H_3SiCH_2CH_2CH_2)_2SiPh_2$ (**4**), $H_2PhSiCH_2SiPhH_2$ (**5**), $H_2PhSiCH_2CH_2SiPhH_2$ (**6**), $H_2PhSiCH_2CH_2CH_2SiPhH_2$ (**7**), and $(H_2PhSiCH_2CH_2)_2SiMe_2$ (**8**) have been prepared and subjected to dehydrocoupling conditions.

### Results and Discussion

The first monomer studied was $H_3SiCH_2CH_2SiH_3$ (**1**), since the Si to C ratio matches that of SiC. Polymerization of **1** should ideally result in a linear polymer that contains alternating ${-}CH_2CH_2{-}$ and ${-}SiH_2SiH_2{-}$ units, as depicted in eq 1. Such a polymer, however, contains secondary silyl units in the backbone which could, in the presence of catalyst, undergo further dehydrocondensation with other similar units or with remaining monomer, leading to cross-linked material. Such cross-linked polymers generally exhibit lower solubility when compared to their linear analogs. For example, the soluble polysilane $H{-}[(MeH_2SiCH_2CH_2)SiH]_n{-}H$ undergoes further coupling at the secondary silyl sites, in the presence of the metallocene catalyst, to form a highly cross-linked, nonsoluble polymer.[5] Aromatic carbosilanes prepared by the catalytic dehydrocoupling of $H_3Si{-}Ar{-}SiH_3$ (e.g., Ar = 1,4-phenylene, 1,3-phenylene, biphenyl) were found to be insoluble in common solvents, and the insolubility was attributed to cross-linking (as determined by solid state-NMR spectroscopy).[3] In contrast, related polymers, prepared by



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Wurtz-type coupling were soluble, consistent with a linear structure.[7]

Polymerization reactions of **1** with the combination catalyst $Cp_2MCl_2$/BuLi (M = Ti, Zr) resulted in formation of completely insoluble polymer usually within 30 min to 1 h. Two strategies were employed to slow the condensation reaction: (a) adding solvent and (b) changing to a catalyst system known to promote dehydrocoupling more slowly (e.g., $(C_5H_4SiMe_3)_2HfCl_2/{}^nBuLi$).[2e] Condensation reactions run in solution (toluene) resulted in an increase in the level of consumption of starting material, but the polymer precipitated from solution and insoluble material was still formed when $(C_5H_4SiMe_3)_2HfCl_2/{}^nBuLi$ was used. The isolated polymers were probably cross-linked at the secondary silyl sites in the chain. Furthermore, some of the polymers were found to be pyrophoric in air. The reason for the pyrophoricity is not known but has been observed previously with alkyl-containing polysilanes.[8]

The structure of the polycarbosilane polymer backbone can have a significant effect on the solubility of the polymer. For example, the polymers of $[(R)_2Si-CH_2]_n$ are soluble in common organic solvents if R = alkyl (methyl through hexyl)[9,10] but not if R = aryl (phenyl or *o*-tolyl).[11] Our next strategy, therefore, was to modify the structure of the carbosilane monomer in order to obtain soluble material.

**Modified Primary Carbosilanes.** Compounds **2**−**4** represent the first set of modified monomers. The modifications were selected to minimize any change at the reactive primary silane center so that the monomer would react in essentially the same manner as the model, compound **1**. It was anticipated that an increase in the bulk of the monomer would increase the solubility of the polymer. In addition, the incorporation of the phenyl group was required to make detection of any soluble polymer possible by UV spectroscopy, thus allowing molecular weight measurements (using GPC with a UV detector) of only slightly soluble samples possible. The modifications did not yield a significant change in solubility, but molecular weight measurements of the material produced in the initial stages of the reaction were possible (Table 1).

Runs 1−7 (Table 1) involved monomer **3**, $(H_3SiCH_2CH_2)_2SiPh_2$. In runs 1−4, the reactions were performed neat at room temperature. After 10 min of reaction (run 1) the polymer was completely soluble in THF. GPC measurements indicated a multimodal polymer distribution with an average molecular weight of 14 100 and a polydispersity of 3.5. The polymer contained a high-molecular-weight component of almost 44 000. Twenty minutes (run 2) into the reaction, the polymer was only partially soluble. GPC analysis indicated the disappearance of most of the higher molecular weight components, resulting in a reduced average molecular weight of 2670 and a reduced polydispersity of 1.3. Thirty minutes into the reaction, the $M_w$ value had increased slightly to 3500 (run 3). After 1 h, the polymer was completely insoluble in THF (run 4). Infrared analysis of the polymer produced in run 4 (KBr pellet) verified the presence of Si−H ($\nu$ 2104 $cm^{-1}$), Si−Ph (1420, 1104 $cm^{-1}$), and Si−C (695 $cm^{-1}$).[12]

**Table 1. Condensation of $(H_3SiCH_2CH_2)_2SiPh_2$ (3) with $Cp_2ZrCl_2/{}^nBuLi$**

| run | conditions: soln/temp (°C)/time (h) | $M_w$/result[a] | PD |
|---|---|---|---|
| 1 | neat/25/0.167 | 14 100 (av);<br>43 400 (highest)[b] | 3.5 (2.2)[c] |
| 2 | neat/25/0.33 | 2670 | 1.3 |
| 3 | neat/25/0.50 | 3500 | 1.6 |
| 4 | neat/25/1 | insol solid | |
| 5 | Tol/25/0.33 | 10 000 | 2.7 |
| 6 | Tol/25/0.5 | >100 000 | |
| 7 | Tol/25/1 | 4000 | 1.8 |

[a] Three Waters Styragel GPC columns (500, $10^3$, and $10^4$ Å) were used connected in series (THF solvent); $M_w$ determined relative to polystyrene standards. [b] $M_w$ of a well-separated high-molecular-weight component observed in the GPC trace. [c] Polydispersity of the high-molecular-weight component.

In runs 5−7 the same condensation reaction was performed in toluene at room temperature. After 20 min (run 5) the polymer was completely soluble in THF and approached 10 000 in molecular weight. Thirty minutes into the reaction, the entire reaction mixture (containing toluene) began to gel. The material was partially soluble in THF at this point (run 6). The GPC trace showed the majority of the polymer was composed of a very high molecular weight component whose weight could not be determined, since it was far outside the range of the polystyrene standards employed in all measurements. After 40 min the entire reaction mixture had solidified. Analysis of the polymer after 1 h (run 7) indicated that it was mostly insoluble with only low-molecular-weight material (average of 4000) still soluble. Using a solvent (toluene) had two effects. First, the reaction was slower: 20 min was required to reach a molecular weight of 10 000 (run 5), whereas without solvent, it took less than 10 min to achieve a comparable molecular weight (run 1). Second, significant cross-linking (which is believed to be the cause of polymer insolubility) did not appear to occur until the polymer reached a higher molecular weight, since the material was still soluble at this point. It is speculated that, above some threshold of molecular weight, the polymers become insoluble, leaving only low-molecular-weight material in solution.

The presence of toluene in runs 5−7 served as an internal standard in the chromatographic (GPC) separations and allowed for an approximate determination of starting material consumption and polycarbosilane solubility (in THF). These data are presented in Table 2. At 20 min the data suggest that over 80% of the monomer has been consumed, and after 30 min, consumption was essentially complete (95%). Also after 30 min, only 46% of the polymer was soluble, and after 60 min, this number decreased to 23%.

Analysis of the polymer produced in run 4 (Table 1) by solid-state $^{13}C$ and $^{29}Si$ NMR was performed. The NMR data for the polymer and its precursor monomer are listed in Table 3. The data for the monomer (**3**)

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**Table 2. Monomer Consumption in Runs 5−7 (Table 1)**

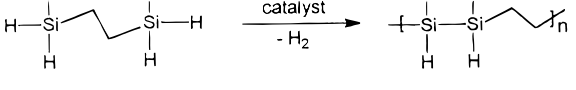
| reacn time (min) | mon consum[a] | % present[b] |
|---|---|---|
| 20 | 82% | ∼100% |
| 30 | 95% | ∼46% |
| 60 | 95% | ∼23% |

[a] Monomer consumption is equal to [1 − (monomer/toluene)] × 100. [b] % present is the percentage of the silanes that are soluble, equal to (all silane/toluene) × 100.

indicate little difference between the solid and solution NMR spectra. The $^{13}$C spectrum of the polymer exhibited broad signals in two regions, corresponding to the aryl and alkyl carbons. The $^{29}$Si spectrum also exhibited two broad signals, assigned to $CSiH_2SiH_2$ and $SiC_4$. A solution $^{29}$Si NMR spectrum of polymethylsilane, which contains primarily Si-H units, showed a broad Si−H signal centered at −64 ppm.[13] Solid-state $^{29}$Si NMR data of a polycarbosilane (made by thermolysis of polydimethylsilane) exhibited a signal at −16.7 ppm, assigned to $HSiC_3$. Solution NMR data of the same compound were similar.[14] The $^{29}$Si NMR spectrum of the polymer produced from $(H_3SiCH_2CH_2)_2SiPh_2$ exhibited only two broad resonances near 4.3 and −44.4 ppm (Table 3). The former is assigned to $-CH_2SiPh_2CH_2-$ and the latter to $-SiH_2-SiH_2-CH_2-$. If cross-linking occurred, a $-Si-Si(Si)CH_2-$ unit would be formed and a resonance further upfield would be expected.[15] It is possible that these peaks are either buried under the $CSiH_2SiH_2$ signals (this peak was broad and ranged from −32 to −60 ppm) or that the relative number of $CSi_3-H$ groups is small, compared to the other silicons, and therefore is not observed. Although cross-linking was not verified by solid-state $^{29}$Si NMR, on the basis of the published literature,[3−6] it is the most likely cause of the observed insolubility.

Polymerization of primary silane monomers **2** and **4** yielded essentially the same observable results as **3**; however, polymers formed from **2** were difficult to detect by GPC due to their relatively low UV activity.

**Secondary Carbosilanes.** As discussed in the previous section, the cross-linking of the polymers, which leads to insoluble material, is probably due to the presence of secondary silyl sites within the polymer chain. Our next strategy in attempting to prepare soluble polycarbosilanes was to eliminate the presence of these secondary silyl sites. Thus, secondary carbosilane monomers that contain a phenyl group on the silane end groups ($-CH_2SiPhH_2$) were prepared. When such a monomer is polymerized, the polymer backbone contains tertiary silyl sites which are less likely to undergo further coupling, thus reducing the possibility of cross-linking (e.g., eq 2 for monomer **6**).



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Four secondary carbosilane monomers, of differing lengths, were prepared and evaluated. The condensation of monomers **5**−**8** with zirconocene dichloride (and *n*-BuLi) resulted in polymers that were completely soluble in chloroform, benzene, and THF. The results are summarized in Table 4.

Experiments 8, 10, 14 and 15 for monomers **5**−**8** (in Table 4) deal with the relationship between monomer size and resultant molecular weight of polymer. The polymerization reactions were run at 90 °C (the temperature necessary to effectively couple the secondary silane $PhMeSiH_2$[2d]) under neat conditions and analyzed by GPC after 24 h of reaction time. With monomer **5** (containing a one-unit spacer) a $M_w$ value of 1870 was observed. Monomer **6** resulted in a significantly higher molecular weight of 11 800, while that for **7** dropped to 1195. Monomer **8** resulted in a $M_w$ value of 9060. From these data it is apparent that the size of the monomer has a significant effect on the molecular weight of the resultant polymer. However, there does not appear to be a simple relationship between monomer size and the ultimate $M_w$ value of the polymer produced. An optimum size for the monomer where the catalyst functions most effectively appears to be found in monomer **6**. Monomer **8** resulted in $M_w$ being almost as high as for **6**, but the average degree of polymerization (given approximately by ($M_w$ of polymer)/($M_w$ of monomer)) from **8** was 28 units after 24 h (it appeared to reach a maximum of 39 after 48 h) whereas that from **6** was 49 after 24 h, indicating considerably longer chain lengths for the latter.[16]

The catalyst to monomer ratio in the polymerization reactions (M/Si in Table 4) has been examined. With monomer **6**, a decrease in the catalyst to silane ratio from 1/20 to 1/60 did not greatly affect $M_w$, but decreasing the ratio further to 1/100 reduced the molecular weight by about 50% (runs 11−13, respectively). Therefore, the optimal M/Si ratio is around 1/60 (for monomer **6**).

The polymerization of monomer **6** was studied at room temperature and at 90 °C. At room temperature, $M_w$ reached only 2610 (run 9) after 24 h. However, if the temperature was raised to 90 °C, $M_w$ increased almost 5-fold (run 10) for the same time period. This result is consistent with previous observations made on the dehydrocoupling of secondary silanes.

**TGA Analysis.** TGA analysis of the polymer prepared from **1** (neat, zirconium catalyst) indicated only 11% weight loss after heating of the sample to 1200 °C, in argon. The same polymer, prepared in benzene, exhibited a 21% weight loss after heating to 1200 °C, probably reflecting a lower molecular weight of the sample. With both polymers, weight loss occurs primarily between 200 and 500 °C.[17] These data reveal relatively high conversion of polycarbosilane to SiC (81−89%). However, the purity of the SiC has not been determined. Future work will include TGA analyses of the polycarbosilanes presented in this paper and X-ray powder diffraction studies of the resultant ceramic.

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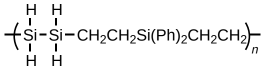
(16) These numbers are approximate and are considered primarily for comparison purposes, since the polymers under study do not possess the same structure as the polystyrene standards used in the GPC measurements.

(17) Samples used for analyses were prepared by F. Joslin. TGA analyses were performed at the University of Science and Technology of Languedoc. We thank Dr. Joel Moreau for obtaining these measurements.

**Table 3. Solid-State $^{13}C$ and $^{29}Si$ NMR Data for 3 and the Resultant Polymer**

| material | $^{13}C$ NMR $\delta^{a,b}$ | assignt | $^{29}Si$ NMR $\delta^{a,b}$ | assignt |
|---|---|---|---|---|
| $(H_3SiCH_2CH_2)_2SiPh_2$ | 136.8 (135.4) | phenyl | 3.2 (−4.1) | $SiPh_2$ |
| | 136.4 (135.3) | phenyl | −43.3 (−54.1) | $SiH_3$ |
| | 130.8 (129.6) | phenyl | | |
| | 129.3 (128.2) | phenyl | | |
| | 9.6 (8.4) | $H_3SiCH_2$ | | |
| | 0.6 (−0.6) | $CH_2SiPh_2$ | | |
|  $-(SiH_2-SiH_2-CH_2CH_2Si(Ph)_2CH_2CH_2)_n-$ | 135.5 | phenyl | 4.3 | $SiPh_2$ |
| | 129.0 | phenyl | -44.4 | SiH |
| | 23.4 | $SiCH_2$ | | |
| | 14.7 | $CH_2SiPh_2$ | | |

[a] Chemical shift (ppm) for solid-state spectrum. [b] Chemical shift (ppm) in parentheses for solution spectrum.

**Table 4. Condensation Reactions Using $Cp_2ZrCl_2/2.2^nBuLi$**

| run no. | monomer[a] | conditions: soln/temp (°C)/time (h) | M/Si[b] | $M_w$/result | PD |
|---|---|---|---|---|---|
| 8 | **5** | neat/90/24 | 1/20 | 1870 | 1.51 |
| 9 | **6** | neat/25/24 | 1/20 | 2610 | 1.68 |
| 10 | **6** | neat/90/24 | 1/20 | 11800 | 3.93 |
| 11 | **6** | Tol/90/24 | 1/20 | 2390 | 1.69 |
| 12 | **6** | neat/90/24 | 1/60 | 11160 | 4.42 |
| 13 | **6** | neat/90/24 | 1/100 | 5800 | 2.52 |
| 14 | **7** | neat/90/24 | 1/20 | 2620 | 1.58 |
| 15 | **8** | neat/90/24 | 1/20 | 9060 | 2.74 |
| 16 | **8** | neat/90/48 | 1/20 | 12800 | 3.51 |

[a] $H_2PhSiCH_2SiPhH_2$ (**5**), $H_2PhSiCH_2CH_2SiPhH_2$ (**6**), $H_2PhSiCH_2CH_2CH_2SiPhH_2$ (**7**), and $(H_2PhSiCH_2CH_2)_2SiMe_2$ (**8**). [b] Catalyst to carbosilane ratio.

## Summary

The primary carbosilane, **1**, yielded insoluble polymers when polymerized in the presence of group 4 catalysts. The polymers were probably cross-linked along the secondary silyl sites present in the chain, producing highly insoluble material.

Solid-state $^{13}C$ and $^{29}Si$ NMR data were collected for one of the insoluble polymers in an attempt to provide evidence for cross-linking. The spectra indicated the presence of the expected units of the polymer chain (alkyl and aryl carbons, quaternary silanes, and probably secondary hydrosilanes). However, no discrete peaks which could be assigned to tertiary silanes (which should be present in the cross-linked polymer) were observed in the $^{29}Si$ NMR spectrum. The peaks were probably either buried beneath the $SiH_2$ signals (which were broad) or the number of Si−H units was small enough, compared to the other silane units, that the resonances could not be observed.

The monomer structure was further modified by the incorporation of a phenyl group onto each of the silyl end groups. Polymerization of the secondary carbosilanes (compounds **5**−**8**) yielded polymers that were soluble in common organic solvents. Characterization of the soluble polymers by GPC indicated that the molecular weight was highly dependent on the structure of the monomer. It was also found that the $M_w$ values of the soluble polymers was dependent on the reaction conditions. Maximum molecular weights were observed at elevated temperature (90 °C) in the absence of solvent.

TGA analyses of polymers produced from **1** indicated 81−89% conversion to SiC, although the nature of the ceramic has not yet been determined.

## Experimental Section

**General Considerations.** Solvents were dried using standard techniques (THF and diethyl ether dried over sodium/benzophenone; hexanes over calcium hydride; chloroform and methylene chloride over phosphorus pentoxide after prepurification by washing with sulfuric acid and water). Glassware was either dried in an oven at 110−120 °C or flame-dried prior to use. All reactions were conducted under an inert atmosphere of nitrogen or argon.

Commercial compounds (*n*-BuLi in hexanes, metallocene dichlorides, chlorosilanes, vinylmagnesium bromide, phenyl bromide, and allyl bromide), unless otherwise noted, were used as supplied. Literature methods were used to prepare $H_3SiCH_2CH_2SiH_3$,[18] $Me_2SiVin_2$,[19] $Ph_2SiVin_2$,[19] $MePhSiVin_2$[19] ($PhMeSiCl_2$ was used as the chlorosilane), $(allyl)_2SiPh_2$,[20] $PhVinSiCl_2$,[22] and $H_2PhSiCH_2SiPhH_2$.[6] $(allyl)(Ph)SiCl_2$[23] and $PhSiHCl_2$[23] were prepared by a modification of Corriu's synthesis of $Vin(Ph)SiCl_2$.[21]

$^1H$ and $^{13}C$ NMR spectra were collected on a Varian XL-300 or a Unity 300 spectrometer at frequencies of 300 and 75 MHz, respectively. $^{29}Si$ NMR spectra were collected on a Varian Unity 300 instrument at 59.6 MHz or a Bruker ARX-500 at 99 MHz. Unless otherwise noted, $^1H$ and $^{13}C$ NMR spectra were referenced to the residual protons of the solvent. $^{29}Si$ spectra were referenced to TMS. $^{13}C$ and $^{29}Si$ CP-MAS NMR spectra were obtained on a Varian Unity plus 300 MHz NMR spectrometer equipped with either a narrow bore (for $^{13}C$ experiments, 75.4 MHz) or a wide bore (for $^{29}Si$ experiments, 59.6 MHz) Varian solid MAS probe for 7 mm o.d. rotors, with spinning speeds of 2.5 kHz. Silicon nitride ($Si_3N_4$) rotors were used to obtain the $^{13}C$ spectra, and zirconia rotors were used for collection of the $^{29}Si$ spectra. $^{13}C$ and $^{29}Si$ cross polarization−magic angle spinning NMR experiments were recorded at room temperature and were carried out using a 4.5 $\mu$s pulse width for both $^{13}C$ and $^{29}Si$. Relaxation times of 2−5 s were used. Optimized cross-polarization contact times of 2.5 ms for $^{13}C$ and 3.2 ms for $^{29}Si$ were utilized for the experiments. Chemical shifts are reported in ppm and are relative to external hexamethylbenzene for $^{13}C$ (132.1 ppm) and talc for $^{29}Si$ (−90 ppm). Infrared spectra were collected on a Perkin-Elmer 1600 Series FTIR spectrometer. Gas chromatographic separations were performed on a Shimadzu GC-14A gas chromatograph using a J&W Scientific DB-5 capillary column. Mass spectral data were collected on a Hewlett-Packard 5988A GC/MS instrument equipped with an RTE-A data system. Preparative gas chromatographic separa-

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(22) Allylmagnesium bromide (1 equiv) was added to phenyltrichlorosilane (2 equiv).

(23) Phenylmagnesium bromide (1 equiv) was added to trichlorosilane (2 equiv).

**Table 5. Starting Materials Used in the Preparation of 2−4 and 6−8**

| product[a] | hydrosilane (amt: g, mol) | vinyl (or allyl) silane (amt: g, mol) |
|---|---|---|
| $(H_3SiCH_2CH_2)_2SiMe_2$ (**2**) | $HSiCl_3$ (10.6, 0.0780) | $Me_2SiVin_2$ (4.00, 0.0360) |
| $(H_3SiCH_2CH_2)_2SiPh_2$ (**3**) | $HSiCl_3$ (11.5, 0.0850) | $Ph_2SiVin_2$ (9.10, 0.0380) |
| $(H_3SiCH_2CH_2CH_2)_2SiPh_2$ (**4**) | $HSiCl_3$ (16.9, 0.130) | $Ph_2Si(allyl)_2$ (15.0, 0.0570) |
| $H_2PhSiCH_2CH_2SiPhH_2$ (**6**) | $PhSiHCl_2$ (7.3, 0.041) | $PhVinSiCl_2$ (7.0, 0.034) |
| $H_2PhSiCH_2CH_2CH_2SiPhH_2$ (**7**) | $PhSiHCl_2$ (5.4, 0.030) | $(allyl)(Ph)SiCl_2$ (5.5, 0.025) |
| $(H_2PhSiCH_2CH_2)_2SiMe_2$ (**8**) | $PhSiHCl_2$ (10.5, 0.0593) | $Me_2SiVin_2$ (3.0, 0.027) |

[a] After reduction with $LiAlH_4$ in diethyl ether.

tions were performed on a Varian Aerograph Model 700 instrument using a 5% SE-30 on Chrom 6 40/60 aluminum column (10 ft. × 3/8 in.) at the following temperatures (isothermal): 65 °C for compound **2**, 138 °C for **3**, 188 °C for **4**, 150 °C for **6** and **7**, and 180 °C for **8**. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

The syntheses of the new carbosilane monomers **2**−**4**, and **6**−**8** were essentially the same; therefore, only the synthesis of **4** is described in detail. The spectroscopic data and elemental analyses for all the new compounds are presented following the description of **4**. Starting materials for the syntheses of the various monomers are shown in Table 5.

**Preparation of $(H_3SiCH_2CH_2CH_2)_2SiPh_2$ (4).** Trichlorosilane (16.9 g, 0.130 mol) was added dropwise to diallyldiphenylsilane (15.0 g, 0.0570 mol) containing a catalytic amount of $H_2PtCl_6$ (solution in 2-propanol). After a few drops of the chlorosilane were added, the reaction was initiated with a sun lamp, the lamp was then removed, and the remainder of the chlorosilane was added. The reaction mixture was heated to approximately 90 °C for 5 h, cooled, and then dissolved in ether (30 mL) and added dropwise to a dispersion of $LiAlH_4$ (3.56 g, 0.0940 mol) in ether (200 mL). After complete addition, the mixture was refluxed for 5 h. The solid was then removed by filtration and the solvent removed. The residue was extracted three times with pentane; the pentane extracts combined and then washed with water. The organic layer was dried over sodium sulfate and the pentane removed (rotavaporator). The product was distilled at 65 °C/0.1 mmHg (5.03 g, 52.7% yield; 97% pure by GC). Further purification can be effected by passing the product through a silica gel column (3 cm diameter, 7 cm height with $CH_2Cl_2$ as solvent) prior to isolation of the analytical sample by preparative gas chromatography. $^1H$ NMR ($\delta$; $C_6D_6$; $Me_4Si$ at 0.00 ppm): 0.614 (m, 4, $CH_2$), 1.08 (m, 4, $CH_2$), 1.49 (m, 4, $CH_2$) 3.57 (t, $SiH_3$), 7.17, 7.47 (m, 10, SiPh). $^{13}C$ NMR ($\delta$; $C_6D_6$): 10.8, 16.5, 21.5, 128.1, 129.5, 135.2, 136.5. $^{29}Si$ NMR ($\delta$; $C_6D_6$): −60.8 ($SiH_3$), −7.38 ($SiPh_2$). Anal. Calcd for $C_{18}H_{28}Si_3$: C, 65.78; H, 8.59. Found: C, 65.20; H, 8.55.

**$(H_3SiCH_2CH_2)_2SiMe_2$ (2).** The product was distilled at 60 °C/30 mmHg (2.81 g, 42.0%; isomeric mixture as indicated by the multiplet in the Si−H region of the $^1H$ NMR spectrum). $^1H$ NMR ($\delta$; $C_6D_6$): −0.148 (s, SiMe), 0.394 (m, $CH_2$), 3.40 (m, $SiH_3$). $^{13}C$ NMR ($\delta$; $C_6D_6$): −4.07, −0.70, 10.9. $^{29}Si$ NMR ($\delta$; $C_6D_6$): −54.3 ($SiH_3$), 7.54 ($SiMe_2$). Anal. Calcd for $C_6H_{20}Si_3$: C, 40.83; H, 11.42. Found: C, 40.32; H, 11.17.

**$(H_3SiCH_2CH_2)_2SiPh_2$ (3).** The product was distilled at 120 °C/0.1 mmHg (5.42 g, 44.1%) to give an oil that solidified at room temperature. The product was crystallized from pentane at −50 °C; mp 33−35 °C. $^1H$ NMR ($\delta$; $C_6D_6$): 0.523 (m, 4, $CH_2$), 1.01 (m, 4, $CH_2$), 3.63 (t, $SiH_3$), 7.18, 7.41 (m, 10, SiPh). $^{13}C$ NMR ($\delta$; $C_6D_6$): −0.550, 8.40, 128.2, 129.6, 135.3, 135.4. $^{29}Si$ NMR ($\delta$; $C_6D_6$): −54.1 ($SiH_3$), −4.10 ($SiPh_2$). Anal. Calcd for $C_{16}H_{26}Si_3$: C, 63.93; H, 8.05. Found: C, 63.93; H, 8.04.

**$H_2PhSiCH_2CH_2SiPhH_2$ (6).** The product was distilled at 110 °C/0.1 mmHg (6.10 g, 66.4%). $^1H$ NMR ($\delta$; $C_6D_6$, TMS): 0.85 (m, 4H, $CH_2$), 4.43 (m, 4H, $SiH_2$), 7.14, 7.42 (m, 10H, phenyl). $^{13}C$ NMR ($\delta$; $C_6D_6$, TMS): 4.63, 128.0, 129.6, 132.1, 135.3. $^{29}Si$ NMR ($\delta$; $C_6D_6$): −27.5. Anal. Calcd for $C_{14}H_{18}Si_2$: C, 69.35; H, 7.48. Found: C, 69.84; H, 7.47.

**$H_2PhSiCH_2CH_2CH_2SiPhH_2$ (7).** The product was distilled at 117 °C/0.1 mmHg (3.50 g, 54.6%). $^1H$ NMR ($\delta$; $C_6D_6$, TMS): 0.87 (m, 4H, $CH_2$), 1.58 (m, 2H, $CH_2$), 4.42 (t, 4H, $SiH_2$), 7.14, 7.45 (m, 10H, phenyl). $^{13}C$ NMR ($\delta$; $C_6D_6$): 13.9, 21.2, 128.3, 129.8, 132.5, 135.5. $^{29}Si$ NMR ($\delta$; $C_6D_6$): −31.6. Anal. Calcd for $C_{15}H_{20}Si_2$: C, 70.24; H, 7.86. Found: C, 70.42; H, 7.80.

**$(H_2PhSiCH_2CH_2)_2SiMe_2$ (8).** The product was distilled at 170 °C/0.5 mmHg (8.87 g, 54.8%). $^1H$ NMR ($\delta$; $C_6D_6$, TMS): 0.07 (s, 6H, $CH_3$), 0.55 (m, 4H, $CH_2$), 0.74 (m, 4H, $CH_2$), 4.55 (t, 4H, $SiH_2$), 7.21, 7.56 (m, 10H, phenyl). $^{13}C$ NMR ($\delta$; $C_6D_6$): −4.29, 2.96, 8.83, 128.3, 129.8, 132.9, 135.5. $^{29}Si$ NMR ($\delta$; $C_6D_6$): −26.4 ($SiPhH_2$), 0.16 ($SiMe_2$). Anal. Calcd for $C_{18}H_{28}Si_3$: C, 65.78; H, 8.59. Found: C, 64.71; H, 8.59.

**Condensation Reactions**. In a typical experiment the metallocene dichloride (0.07 mmol) was weighed into a Schlenk tube, the carbosilane (1.4 mmol) was added at room temperature, and the polymerization initiated by the addition of 2.2 equiv of *n*-butyllithium. In most cases, a yellow color developed and hydrogen gas evolution was observed. Heated samples turned dark brown. After the appropriate time had elapsed, the reaction was quenched by addition of bulk hexanes or an aliqout was removed (e.g., runs 1−7, Table 1) and dispersed in the appropriate solvent (THF for GPC analysis). The air sensitivity of the active catalysts renders them easily oxidizable upon exposure to air and dispersion in HPLC grade THF. The insoluble metal complexes were removed by filtration prior to collection of the GPC data. Reaction conditions and molecular weight data are provided in Tables 1 and 4.

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