Polycarbosilanes from Condensations of Cyclopentadienide with Dialkyl- and Diaryldichlorosilanes

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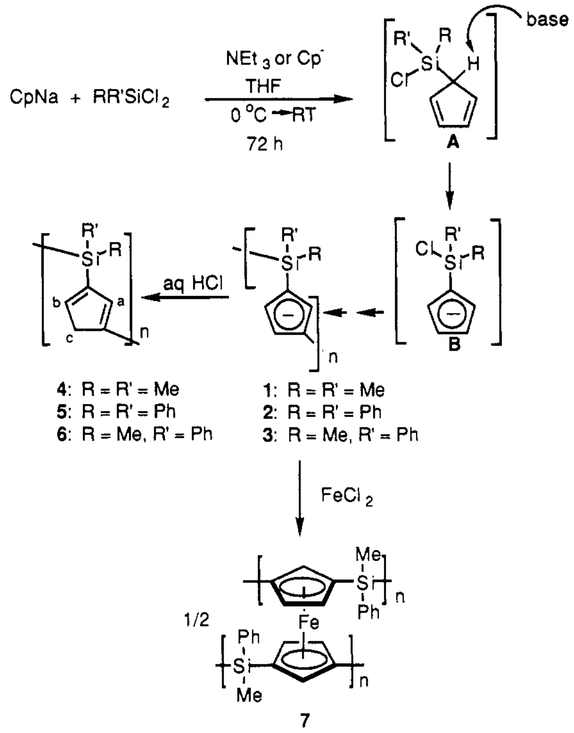
Organosilicon polymers having backbones composed of alkyl- or aryl-substituted silicon atoms bridged by organic groups are termed polycarbosilanes[1] and are viewed as carbon analogues of polysiloxanes.[2] Polycarbosilanes can be prepared by several different methods, including the reductive coupling of (halomethyl)halosilanes,[3] pyrolyses of monosilacyclobutanes,[4] thermolyses of 1,3-disilacyclobutanes,[5] transition-metal-catalyzed ring-opening polymerizations of 1,3-disilacyclobutenes,[6,7] thermal rearrangement of poly(dimethylsilylene),[8] and platinum-catalyzed hydrosilation polymerization of vinyldichlorosilane.[9] High molecular weight polymers of the type $[(CH_3)_2SiCH_2]_n$ are very stable thermally[7] and are unreactive toward concentrated mineral acids and strong base. Highly cross-linked polycarbosilanes are useful as precursors to SiC,[8] and some have found application as UV resists.[10]

We report that condensations of cyclopentadienylsodium (CpNa) with dialkyl- and diaryldichlorosilanes afford polycarbosilanes. Dropwise addition of 0.5–1.5 M solutions of CpNa in THF to dialkyl- and diaryldichlorosilanes in THF at 0 °C, followed by gradual warming to 20 °C, stirring for 72 h, and aqueous HCl workup provided polymers **4–6** (Scheme I).[11]

The polymerization mechanism we propose (Scheme I) is similar to that introduced[12] for condensations of CpNa with carbon dielectrophiles (dianhydrides and diacid chlorides) that afforded analogues of nylons having all carbon backbones (carlons). We assume that condensations of $RR'SiCl_2$ with CpNa initially generate the intermediate chlorosilylcyclopentadienes A, which are readily deprotonated by a base, either NEt_3 or excess CpNa, to form the aromatic anions B, and ultimately lead to the formation of the polyanions **1–3**. Addition to ice-containing HCl affords polymers **4–6**. The enhanced acidity of A is essential to the success of these polymerizations. Silicon adjacent to an X–H functionality is demonstrably stabilizing to R_3SiX^- anions, resulting in enhanced acidity.[13] In species A, the presence of a dialkyl- or diarylchlorosilyl group on an already acid cyclopentadiene ring is apparently sufficient for the ring to be deprotonated by NEt_3 or CpNa. The yields and molecular weights of polymers we obtained in reactions in which excess CpNa was used as base were slightly higher than those formed in reactions that contained NEt_3. We assume this was due to depletion of some of the CpNa in reactions containing NEt_3.

Our depiction of polymers **4–6**, with 1,3-substitution of the cyclopentadienyl ring and having double bonds adjacent to –SiRR′, is consistent with literature reports of structures, determined by X-ray diffraction, of products of disubstitution of cyclopentadiene with SiR_3[14-16] and is predicted by molecular mechanics calculations.[17] The ^{13}C NMR spectrum[18] of **6** contains five major signals ($CDCl_3$, 20 °C, δ 61.8, 54.9, 48.6, 44.7, and 39.4) and four minor signals (δ 61.1, 53.0, 40.2, and 38.4) assigned to the disubstituted Cp ring, a complex multiplet (δ 146–128) assigned to the Ph and Cp moieties, and one major (δ 2.3) and two minor (δ 1.2, 0.1, and −1.1) signals assigned to the Si–Me moiety. Combinations of 1,1-, 1,2-, and 1,3-substitution of the Cp ring probably occur in our syntheses of **4–6**, but thermal rearrangements during the isolation of solid products presumably lead to predominantly 1,3-substitution.[19]

Scheme I
Sequence of Reactions Used To Prepare Polycarbosilanes 1–7



Polycarbosilanes **5** and **6** are soluble in organic solvents, and glassy, yellow–brown transparent films can be conveniently cast from solution. Polymer **4** is only partially soluble in THF and is insoluble in hexanes. Polymers **5** and **6** are thermoplastic, softening reversibly at 104 and 110 °C, respectively. The molecular weights of polymers **5** and **6** are in the range of 500–100 000 (DP < 540), as determined by GPC vs polystyrene standards.[20] The IR spectra of **4–6** confirm the presence of the intact Cp units ($\nu_{C=C}$ = 786, 746, and 698 cm^{-1}).

Preliminary experiments that included small amounts of $RSiCl_3$ in the reaction mixture indicated that cross-linked polymers were obtained. These polymers contained significant fractions of insoluble material. Thermal analyses (TGA, DTA) established that polymers **4–6** were stable thermally, losing only 40% of their initial mass on heating to 450 °C. Thermolyses of **4–6** at 900 °C under argon indicated that they retained mass consistent with the formation of SiC.[21]

The addition of $FeCl_2$ to polyanion **1** provides the cross-linked polymer **7** having intact disubstituted ferrocene units, as confirmed by elemental analysis and IR spectroscopy.[22]

We have also found that condensations of indenylsodium (IndNa) with dialkyl- and diarylsilanes afforded the related series of polymers **8** and **9** (Scheme II).[23] In this case, we draw the double bonds of the indenyl ring to allow conjugation of both rings. Polymers **8** and **9** were also soluble and film-forming and had molecular weights comparable to those of polymers **4–6**.

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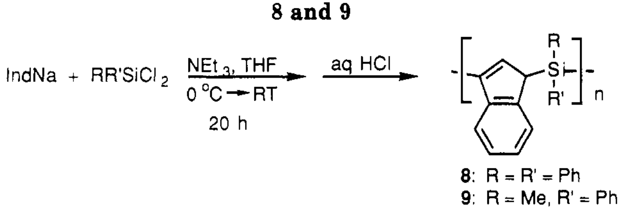
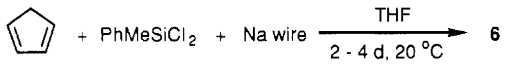
Scheme II
Sequence of Reactions Used To Form Polycarbosilanes 8 and 9



Experiments employing CpNa and IndNa with Ph_2GeCl_2 also afforded the analogous polycarbogermane polymers.[24] These polymers were soluble in organic solvents, from which light-yellow–brown, thermoplastic films could be cast.

Preliminary experiments also indicated that one-pot syntheses in which only sodium wire, phenylmethyldichlorosilane, and freshly-cracked cyclopentadiene were stirred for several days in THF produced oligomeric polycarbosilanes.



The essential step in the mechanism of this oligomerization probably involved the deprotonation of the initially-formed silane-substituted cyclopentadiene by sodium to afford substituted cyclopentadienide.

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(11) Polymer **4** was obtained as a light-brown powder. It was not sufficiently soluble to allow NMR spectrometry. Polymer **5** was obtained as a light-brown powder. ^{13}C NMR ($CDCl_3$, 20 °C): δ 137.1–135.3, 129.1–131.7, 128.8–130.0, 69, 65, 34, 2.8, 0.5. ^1H NMR ($CDCl_3$, 20 °C): δ 7.8–7.0 (m, Cp, Ph), 4.2–0.8 (m, Cp). UV: 239, 241, 258 nm. IR (KBr, cm^{-1}): 3071 (m), 3050 (m), 2927 (s), 2357 (w), 1958 (w), 1890 (w), 1821 (w), 1732 (m), 1588 (m), 1485 (m), 1430 (vs), 1258 (m), 1107 (vs), 997 (sh, m), 805 (m), 736 (s), 702 (vs), 509 (s). Anal. Calcd for polymer **5**, $C_{17}H_{14}Si$: C, 82.87; H, 5.73; Si, 11.40. Found: C, 79.14; H, 6.37; Si, 10.29. A reviewer has suggested that a significant amount of NaCl might be present as an impurity and proposed the following purification scheme. The samples submitted for elemental analysis were precipitated from THF by adding solutions dropwise to distilled water. The precipitated polymer was then redissolved in THF and dried with anhydrous sodium sulfate. The solution was then filtered and stripped in vacuo. This polymer was then washed with hexane and dried over P_2O_5 at 110 °C at 10^{-3} Torr for 12 h. Samples thus treated showed little change in their elemental analyses. We attribute the discrepancies in these analyses to the presence of –OH end groups which strongly bind water and prevent efficient drying. In a typical synthesis of polymer **6** using NEt_3, a solution of $MePhSiCl_2$ (0.50 g, 2.6 mmol) in ca. 50 mL of THF containing NEt_3 (1 mL, 7 mmol) was cooled to 0 °C and 1 equiv of CpNa (1.5 M, 1.7 mL) was added dropwise over 0.5 h. The solution was stirred and allowed to warm to room temperature. After stirring for 72 h, the mixture was added to 100 g of ice containing 2 mL of concentrated HCl. The THF was stripped from the mixture by rotary evaporation. Ether was added, and the organic layer was separated and dried over anhydrous magnesium sulfate. After filtration and removal of the ether in vacuo, the polymer was washed several times with hexanes and dried at 111 °C at 10^{-3} Torr over P_2O_5. This procedure afforded polymer **6** as a light-brown powder (0.39 g, 80%). Excess CpNa could also serve as the base. For example, a solution of $MePhSiCl_2$ (3.77 g, 14.9 mmol) in ca. 150 mL of THF was cooled to 0 °C, and 3 equiv of CpNa (1.49M, 30.0 mL) was added dropwise over 0.5 h. After a similar workup, polymer **6** was obtained as a dark-brown powder (3.67 g, 85.6%). ^1H NMR ($CDCl_3$, 20 °C): δ 7.7–5.8 (br m, Cp, Ph), 4.0–0.4 (br m, Cp, Me). UV: 243, 250, 258 nm. IR (KBr, cm^{-1}): 3047 (m), 2957 (s), 1956 (w), 1887 (w), 1817 (w), 1714 (br m), 1588 (m), 1428 (vs), 1254 (vs), 1108 (vs), 949 (s), 782 (s), 698 (s), 504 (s). Anal. Calcd for $C_{12}H_{12}Si$: C, 78.19; H, 6.56; Si, 15.24. Found: C, 73.09; H, 6.87; Si, 11.60.

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(20) The molecular weights of condensation polymers are very sensitive to exact proportions of dielectrophile and dinucleophile. In these experiments we have not taken particular care to ensure precise stoichiometry. The polymers prepared as described contain a broad distribution of molecular weights, extending as low as 500, with the major peak in the chromtograms usually falling in the 1000–3000 range.

(21) For example, complete pyrolysis of **6** to SiC would require a theoretical mass loss of 83.73%; our TGA indicated a mass loss of 84%.

(22) Anal. Calcd for $C_{24}H_{22}FeSi_2$: Fe, 13.22 (one iron/2 Cp rings). Found: Fe, 12.60. IR (KBr): 814 cm^{-1}.

(23) Deep-green THF solutions of indenylsodium (1.42 M) were prepared by refluxing indene over sodium wire for 2 days. The concentration of this solution was determined by titration. Dropwise addition of IndNa to solutions of dialkyldichlorosilanes containing excess NEt_3 at room temperature, followed by stirring for 72 h and aqueous HCl workup, produced **8** and **9** as dark-brown solids in 50–80% yields. Polymer **8**: ^{13}C NMR ($CDCl_3$, 20 °C): δ 134.4, 130.1, 127.8, 41.0, 36.2, 25.8. IR (KBr, cm^{-1}): 3071 (m), 3050 (m), 3022 (w), 1965 (w), 1896 (w), 1828 (w), 1704 (m), 1594 (m), 1429 (s), 1127 (vs), 997 (br s), 880 (sh, m), 839 (m), 743 (s), 722 (s), 701 (vs), 509 (s), 488 (sh, s).

(24) By a procedure analogous to that described for **6**, condensation of CpNa with Ph_2GeCl_2 afforded a brown, film-forming solid that was soluble in THF, toluene, acetone, etc., in 65% yield. ^{13}C NMR ($CDCl_3$, 20 °C): δ 135.19, 134.94, 131.66, 129.53, 129.17, 31.06. ^1H NMR ($CDCl_3$, 20 °C): δ 7.60 (m), 7.39 (m), 7.29 (m), 7.19 (m), 1.26 (s, Cp, aliphatic). IR (KBr): 3067.9 (sh, w), 3034.2 (w), 3026.8 (w), 1966.4 (w), 1891.2 (w), 1822.8 (w), 1774.9 (w, sh), 1706.5 (br w), 1487.6 (w), 1432.8 (m), 1097.6 (m), 844.5 (vs), 735.0 (m), 694.0 (s), 529.8 (m), 461.4 (s) cm^{-1}.