Polycarbosilanes

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Radical Polymerization of the Silene $(Me_3Si)_2Si{=}CR_2$ by Hydrogen Transfer from a Trimethylsilyl Group**

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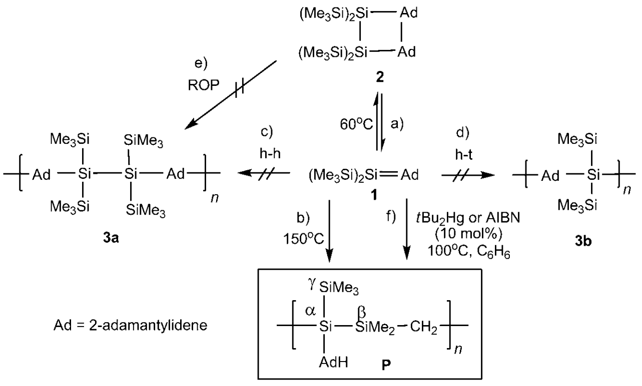
Dedicated to Professor Armin de Meijere on the occasion of his 70th birthday

Exciting progress has been achieved over the last two decades in the study of silenes — compounds with a Si=C bond -- and of other multiply bonded silicon compounds.[1] By analogy with the well-known polymerization of olefins, $R_2C{=}CR_2$, leading to polyolefins, it could be expected that silenes also polymerize to yield polycarbosilanes, $-(R_2Si-CR_2)_n-$. Polycarbosilanes have unique properties, and they are of significant practical interest.[2] It is therefore surprising that polymerization of a silene to form a polycarbosilane has not yet been reported.[3,4]

Herein, we report the polymerization of a silene, $(Me_3Si)_2Si{=}Ad$ (**1**; Ad = 2-adamantylidene), which was generated by thermal dissociation of its head-to-head dimer, the 1,2-disilacyclobutane **2**. The polymerization product has a Si–Si–C repeating moiety and 2-adamantyl side chains (structure **P** in Scheme 1). We provide evidence that the polymerization of **1** proceeds by a radical addition to the silicon terminus of the Si=C bond followed by hydrogen transfer from a trimethylsilyl group.

We reported previously the generation of silene **1** by the thermal dissociation of 1,2-disilacyclobutane **2** in hydrocarbons (Scheme 1, path a).[5] The conversion of **2** to **1** at 60 °C was demonstrated by NMR spectroscopy,[6] and by trapping **1** with various reagents.[7] Thermolysis at 150 °C of neat **2** yields a polymer **P** in 50 % yield (Scheme 1, paths a,b). Compound **P** was isolated by gel permeation chromatography (GPC) as an air- and water-stable white powder; a bimodal peak is observed in its chromatogram, corresponding to a molecular weight M_w of 11 400 $g\,mol^{-1}$ (Figure 1 a).[8]



Scheme 1. Possible polymerization modes of **1** and **2**. See text for details.

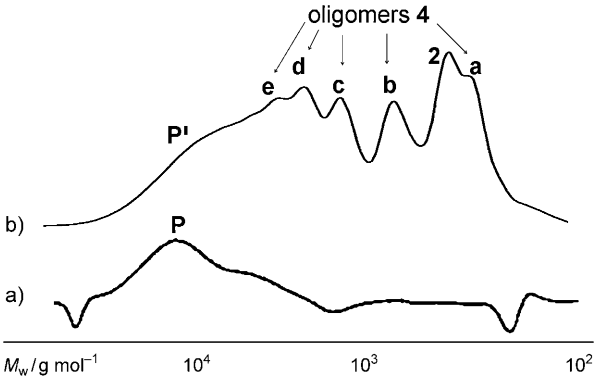


Figure 1. GPC curves (relative to a polystyrene standard) of a) polymer **P** obtained by thermolysis of neat **2** at 150 °C, and b) the crude mixture from the thermolysis of **2** in the presence of Na/K alloy.

The ^{29}Si NMR spectrum of **P** (Figure 2)[9] has three broad signals: at −11.2 and −15.5 ppm, corresponding to a silicon atom bonded to one silicon and three carbon atoms[10] (Si^β and Si^γ in **P**), and at −35.0 ppm, corresponding to a silicon atom bonded to two silicon and two carbon atoms[10] (Si^α in **P**). According to this NMR spectrum, the structure of **P** is different from that expected for a polycarbosilane resulting from either a head-to-head (h-h, **3a**) or a head-to-tail (h-t, **3b**) polymerization of **1** (Scheme 1, paths c and d, respectively). First, **3a** and **3b** are expected to give rise to only two ^{29}Si NMR chemical shifts (not three, as observed); second, the backbone silicon atoms in **3a** (each bonded to one carbon and

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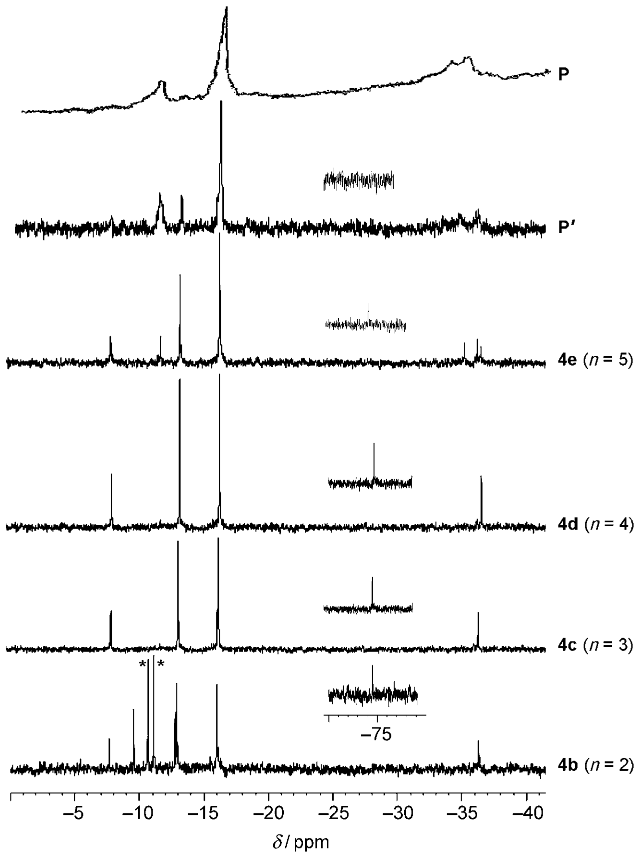
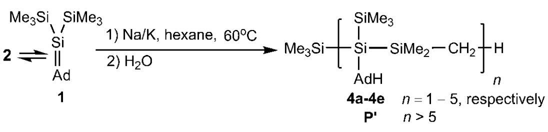


Figure 2. ^{29}Si NMR spectra of the oligomers **4b–4e** and the polymers **P′** and **P**. * Chemical shifts arising from precursor **2**.

three silicon atoms) are expected at $\delta \approx -70$ ppm;[10] such a signal is not observed. Thus, regular olefin-type polymerization of **1** and ring-opening polymerization (ROP)[11] of **2** (Scheme 1, path e) can be ruled out.

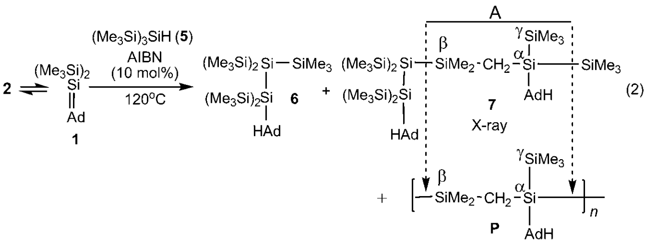
EPR analysis at room temperature of the reaction mixture of the thermolysis of neat **2** showed a broadened signal of an adamantyl-centered radical,[12] supporting a radical polymerization mechanism. Furthermore, when the thermolysis of **2** (0.02 M in C_6H_6) was carried out in the presence of catalytic amounts of radical initiators (0.002 M of $t\mathrm{Bu_2Hg}$ or 2,2′-azobisisobutyronitrile (AIBN)), **P** was obtained at a lower temperature of 100 °C (Scheme 1, path f).[13] In the presence of a stoichiometric amount of the radical initiators, polymerization is terminated.

To obtain strong evidence for the structure of the repeating unit of **P**, characterization of its short oligomers is required. To terminate the polymerization at an early oligomeric stage, **2** was heated in hexane in the presence of Na/K alloy [Eq. (1)]. In this case, the reaction occurred at 60 °C, which is significantly lower than the neat reaction (150 °C), and the yield of the low-molecular-weight fractions increased. The reaction products were separated by GPC (Figure 1b) and were identified by NMR and MS as oligomers **4a–e**, which have the $\mathrm{(Me_3Si)(AdH)SiSiMe_2CH_2}$ repeating unit, and trimethylsilyl and hydrogen as terminal groups.[14] An additional product is polymer **P′** with a molecular weight close to that of **P**. The ^{29}Si chemical shifts of **4b–e** and **P′** are very similar to those of **P** (Figure 2). Based on all these data, we conclude that the structure of polymer **P** is as shown in Scheme 1, and has a repeating unit similar to that of oligomers **4a–e**. This structure is unprecedented for a polycarbosilane, and it is different from that of regular olefin-type radical polymerization of **1** in which either (Si–C) or (Si–Si–C–C) repeating units are expected.



$$\mathbf{2} \rightleftharpoons \underset{\mathbf{1}}{\mathrm{(Me_3Si)_2Si{=}Ad}} \xrightarrow[\text{2) } \mathrm{H_2O}]{\text{1) Na/K, hexane, 60°C}} \mathrm{Me_3Si}\!\left[\!\!\begin{array}{c}\mathrm{SiMe_3}\\ |\\ \mathrm{Si{-}SiMe_2{-}CH_2}\\ |\\ \mathrm{AdH}\end{array}\!\!\right]_n\!\!\mathrm{H} \quad \begin{array}{ll}\mathbf{4a\text{-}4e} & n = 1-5\text{, respectively}\\ \mathbf{P'} & n > 5\end{array} \qquad (1)$$

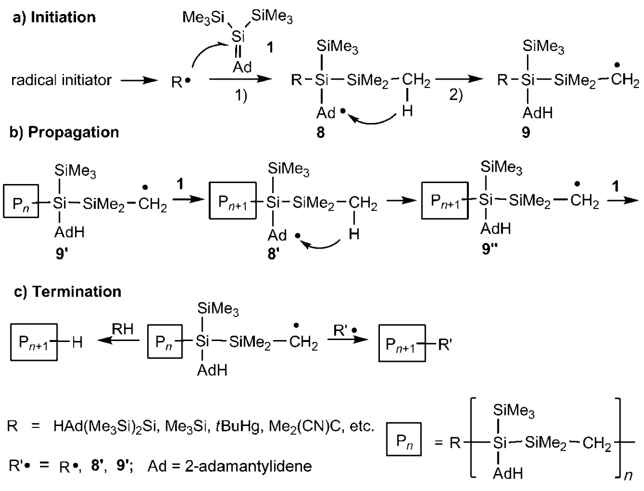
To obtain information on the initiation step of the polymerization, **2** was heated at 120 °C in the presence of AIBN (10 mol %) with an excess of $\mathrm{(Me_3Si)_3SiH}$ **5**. The reaction produced, in addition to **P**, two new compounds: **6** (10 %) and **7** (30 %) [Eq. (2)].[15] Compound **6** is formally a product of addition of the Si–H bond of **5** to the Si=C bond of **1**.[16] The structure of **7** was determined by X-ray crystallography, revealing that it is a product of two reactions: addition of a $\mathrm{(Me_3Si)_3Si^{\bullet}}$ radical to the silicon terminus of the Si=C bond, and radical hydrogen abstraction from the trimethylsilyl group.[17] We suggest that similar two reactions take part in the initiation step of the polymerization of **1** (see Scheme 2, paths 1 and 2). In addition, the structure of the repeating unit of **P** is strongly supported by the similarity of the ^{29}Si chemical shifts of **P** and those of fragment A in **7** (Si$^{\alpha}$: −34.9 vs. −35.0, Si$^{\beta}$: −9.4 vs. −11.2, Si$^{\gamma}$: −16.0 vs. −15.5 ppm for **7** and **P**, respectively).



(2)

The suggested mechanism for the formation of **P** is given in Scheme 2, and is based on the following points: 1) observation by EPR spectroscopy of a 2-adamantyl-centred radical in the thermolysis of **2**;[12,13b] 2) a decrease in the polymerization temperature by radical initiators, leading to the same polymer **P**; 3) termination of the polymerization by a stoichiometric amount of radical initiators; and 4) the structures of **P** and **7**.

The initiation step for the polymerization of silene **1** involves the following reactions: a radical R$^{\bullet}$, produced from a radical initiator,[18] attacks **1** to form the sterically protected radical **8** with the spin localized on the 2-adamantyl group.[13b] Radical **8** then rearranges by a 1,4-hydrogen shift to the more reactive radical **9** with the spin localized on the CH_2 group (Scheme 2a).[19,20] The propagation step involves attack of radical **9** (or **9′** in the consecutive steps) on **1** to form an elongated 2-adamantylidenyl-centred radical **8′**, which rear-



Scheme 2. Suggested mechanism for the polymerization of silene **1**.

ranges to **9''** (Scheme 2b), and so forth. Termination can result from the coupling of two radicals or from hydrogen abstraction; for example, from a trimethylsilyl substituent of one of the compounds (Scheme 2c).

In summary, we report the direct polymerization of silene **1** to produce a polycarbosilane with an unprecedented $(Me_3Si)(AdH)Si{-}SiMe_2CH_2$ repeating unit. We provide evidence that the polymerization of **1** proceeds by a radical addition to the silicon terminus of the Si=C bond of **1**, followed by hydrogen transfer from a trimethylsilyl group. We are continuing studies on this unique polymerization mechanism and on the properties and possible applications of the novel polycarbosilane.

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[6] A solution of **2** in C_6D_6 was heated to 60 °C for 1 h in a sealed NMR tube. The NMR spectrum recorded immediately after cooling the solution to room temperature exhibited a 5% conversion of **2** to **1**. After 30 min at room temperature, only **2** was observed. ^{29}Si NMR of **1**: $\delta = -14.3$ (Me_3Si), 53.8 ppm (Si=C).

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[8] a) The relatively low polydispersity index (M_w/M_n) of 1.4 indicates that **P** is a one dimensional (linear or macrocyclic) polymer with a small degree of branching or cross-linking. This conclusion is consistent with the high solubility of **P** in hydrocarbons; b) Kinetically stabilized isolable silenes tBuMe$_2$Si-(Me$_3$Si)Si=Ad and (tBuMe$_2$Si)$_2$Si=Ad[8c] do not undergo polymerization upon any of the conditions reported in this paper; c) Y. Apeloig, M. Bendikov, M. Yuzefovich, M. Nakash, D. Bravo-Zhivotovskii, D. Blaser, R. Boese, *J. Am. Chem. Soc.* **1996**, *118*, 12228.

[9] Additional spectroscopic and physical data for **P** are given in the Supporting Information.

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[11] Ring-opening polymerization of sila- and disilacyclobutanes was reported: a) H. Yamashita, M. Tanaka, K. Honda, *J. Am. Chem. Soc.* **1995**, *117*, 8873; b) E. D. Babich in *Polymeric Materials Encyclopedia*, *Vol. 10* (Ed.: J. C. Salamone), CRC, New York, **1996**, p. 7621; c) S. Greenberg, S. B. Clendenning, K. Liu, I. Manners, S. Aouba, H. E. Ruda, *Macromolecules* **2005**, *38*, 2023.

[12] The EPR spectrum is presented in Figure S4 of the Supporting Information. For a related EPR study of a 2-adamantyl radical see: M. Kira, M. Akiyama, M. Ichinose, H. Sakurai, *J. Am. Chem. Soc.* **1989**, *111*, 8256.

[13] a) Thermolysis of **2** at 100 °C in the absence of the radical initiators, and in the presence of anionic initiators (MeLi or H_2PtCl_6), does not lead to polymerization; b) The R(SiMe$_3$)$_2$Si-Ad$^•$ radical was detected by EPR spectroscopy of the reaction mixture from the thermolysis of **2** at 100 °C for 10 min with tBu$_2$Hg (10 mol%) in hexane. See Figure S5 in the Supporting Information.

[14] The source of the terminus Me$_3$Si group is probably **1** or **2**; these compounds undergo partial decomposition upon reduction by Na/K. Details are given in the Supporting Information.

[15] Experimental and spectroscopic data for **6** and **7** are given in the Supporting Information.

[16] A similar radical-induced addition reaction of the Si–H bond of **5** to olefins has been reported; see C. Chatgilialoglu, C. Ferreri, T. Gimisis in *The Chemistry of Organic Silicon Compounds*,

Vol. 2 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, p. 1539.

[17] Compound **7** may also be described by the formal insertion of the Si=C bond of **1** into a C–H bond of a $SiMe_3$ group of **6**. The insertion of a Si=C bond into a C–H bond has been reported for a number of radical-induced intramolecular reactions.[1f] A possible radical chain mechanism for the formation of **7** and a graphical comparison of the ^{29}Si NMR spectra of **7** with that of **P** are presented in the Supporting Information.

[18] In the absence of an external radical initiator, the source of $R^{\bullet}$ is probably **2**, which upon thermolysis (150 °C) dissociates to yield radical species.[1f,12]

[19] Intramolecular hydrogen shifts have been observed in many radical reactions: a) U. Wille, G. Heuger, C. Jargstorff, *J. Org. Chem.* **2008**, *73*, 1413; b) J. Robertson, J. Pillai, R. K. Lush, *Chem. Soc. Rev.* **2001**, *30*, 94; c) Z. Cekovic, *Tetrahedron* **2003**, *59*, 8073; d) D. P. Curran, W. Shen, *J. Am. Chem. Soc.* **1993**, *115*, 6051.

[20] The EPR spectrum of radical **9** generated upon UV irradiation of **4a** dissolved in $(tBuO)_2$ at 270 K is given in Figure S6 of the Supporting Information.