Preparation of Poly(dichlorosilaethylene) and Poly(silaethylene) via Ring-Opening Polymerization[1]

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Polymeric precursors to SiC that have the requisite properties for fiber spinning, preparation of SiC coatings, etc., and that will produce this ceramic product in high yield and purity on pyrolysis have been the subject of much attention during the past ca. 10 years.[2,3] In this context, polymers that possess a nominal 1:1 ratio of Si to C and that undergo pyrolysis so as to preserve this 1:1 stoichiometry have been of particular interest.[3] The general rule-of-thumb in this search for high-yield SiC precursors has been that linear polymers exhibit a low ceramic yield due to thermally induced "chain-unzipping" processes that lead to volatile, low molecular weight fragments and, consequently, that cross-linked structures are a virtual requirement for suitable precursors.[4]

Our recent work on linear poly(silapropylene) obtained via ring-opening polymerization (ROP) of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane has suggested that the presence of H attached to Si in linear polycarbosilanes may provide an effective thermosetting mechanism for overcoming this depolymerization tendency.[5] We now report an extension of this ROP process that permits the preparation of high molecular weight, linear poly(silaethylene), $(-SiH_2CH_2-)_n$, a polymer that exhibits remarkably high ceramic yields on pyrolysis to 1000 °C. This paper also reports the basic NMR and IR characterization data for this silicon analogue to polyethylene.

Prior reports of the preparation of poly(silaethylene) have been limited to the claim, in a patent, that the synthesis of this polymer was accomplished by the ring-opening polymerization of disilacyclobutane.[6] However, other than its conversion to SiC in 85% ceramic yield, no basic characterization data for this polymer was given nor was the yield of the ROP reaction specified. Indeed, it is well-known in silicon chemistry that the Si–H bond is easily activated by the Pt catalysts employed in this patent, and it appears likely that the polymer so obtained would be extensively cross-linked by Si–Si interchain bonding.[7] Our attempts to repeat this preparation have resulted in an extremely low conversion efficiency (20%) with even lower yields of hydrocarbon-soluble polymer (8%) whose IR and NMR spectra indicate branching at Si.

We have found that 1,1,3,3-tetrachloro-1,3-disilacyclobutane (I) is a much more satisfactory starting point for the preparation of poly(silaethylene) and that high yields of a high molecular weight precursor to this polymer can be obtained by ROP of I. Moreover, this intermediate, poly(dichlorosilaethylene) (II), $(-SiCl_2CH_2-)_n$, is a novel polymer in its own right that holds considerable potential as a precursor to a wide range of new substituted polycarbosilanes.

Poly(dichlorosilaethylene) (II) was prepared by ROP of I catalyzed by chloroplatinic acid or a platinum–divinyltetramethyldisiloxane complex in benzene as described in detail elsewhere.[1] ^{1}H NMR: 1.17 ppm. ^{13}C{H} NMR: 18.03 ppm. ^{29}Si{H} NMR: 18.5 ppm.

Direct reduction of this product in benzene leads to the corresponding poly(silaethylene) (III) as a hydrocarbon-soluble, viscous liquid.[1] Gel permeation chromatography indicated a monomodal molecular weight distribution (M_n = 12 300, M_w = 33 000 vs polystyrene). The quintets observed in the ^{1}H NMR spectrum of this polymer (Figure 1) at 4.158 and −0.098 ppm and their 1:1 integration ratio are consistent with the expected structure, $(-SiH_2CH_2-)_n$.[8] The ^{29}Si NMR spectrum of III showed the proper splittings when coupled with the protons and gave one major singlet at −34.4 ppm when proton decoupled. A small peak at −62.3 ppm was attributed to the end group $-SiH_3$ and another even smaller peak at −12.3 ppm was presumed to be due to −SiH. The ^{13}C NMR spectrum showed one major singlet at −9.21 ppm as expected for the $-CH_2-$ group and another small peak at −4.85 ppm due to the $-CH_3$ end group. Elemental analysis of this polymer is consistent with the expected structure. (Found: C, 27.21; H, 9.09. Calcd: C, 27.27; H, 9.09.)

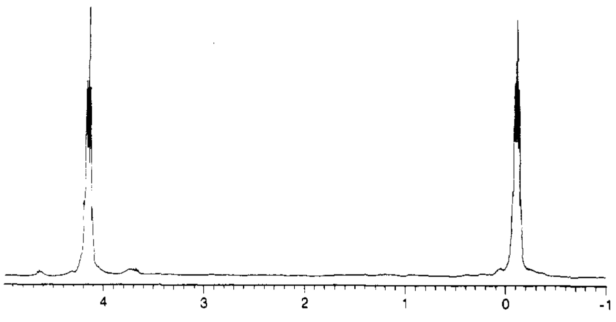

Figure 1. ^{1}H NMR spectrum of poly(silaethylene), $(-SiH_2CH_2-)_n$.

The IR spectrum of III indicates well-defined narrow absorption bands at 1046, 950, 851, and 760 cm^{-1}. This is in contrast to the branched hydridopolycarbosilane prepared in our laboratory by Grignard coupling of trichloro(chloromethyl)silane followed by reduction with $LiAlH_4$, which shows broad absorption in the 1050–750-cm^{-1} region.[3a]

The TGA study of III in N_2 gave a remarkably high ceramic yield (calcd, 90.9; obsd, 87). Weight loss started at about 100 °C, and there was almost no weight loss after 600 °C. The infrared spectrum of the ceramic product obtained after pyrolysis to 1200 °C showed only one absorption at 823 cm^{-1}, consistent with the formation of SiC.[9] The powder X-ray diffraction study of the ceramic product, obtained after pyrolysis to 1000 °C in N_2 and holding at that temperature for 1 h, indicated the formation of β-SiC. The average crystallite size of this material, calculated by the line broadening of the XRD pattern, was 2.5 nm.[10] This represents an unusually low crystallization temperature for SiC obtained from organometallic precursors[2,3] and suggests, along with the observed weight loss, a high level of purity for the SiC so obtained. Further heating under N_2 at 1800 °C for 2 h, resulted in a sharpening of the XRD pattern, indicating an increase in the average crystallite size to 24.3 nm.

These results, along with those obtained in our earlier study of poly(silapropylene),[5] show clearly that an initially cross-linked structure is by no means a requirement for high ceramic yields. The studies suggest further that high molecular weight linear polycarbosilanes, when substituted with H on Si, can undergo relatively facile thermally-induced cross-linking prior to, or accompanying, chain scission. The mechanism for this cross-linking process is currently under study; however, it is perhaps notable that the decomposition of methylsilanes (Me_nSiH_{4-n}, n = 1–4)

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is also facilitated by increasing substitution of H on Si.[11] In this case 1,1-H_2 elimination from the methylsilanes with $n = 1$ and 2 leads to a silylene (=Si:) intermediate. This highly reactive species is known to insert into Si–H or even C–H bonds;[12] thus in a condensed polymer, cross-linking and branching would be expected to result from the attack of such silylene species on adjacent polymer chains. Even in the case of polycarbosilanes such as poly(silapropylene), which have only one H per Si, H transfer from Si to the adjacent C atom, accompanied by Si–C bond scission,[11] could generate such silylene species with a similar consequence in terms of interchain cross-linking and/or branching.

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References and Notes

(1) This work was presented in the Polymer Chemistry Division program at the 4th International Chemical Congress in New York in Aug 1991, and a brief description of the preparation method has appeared in the proceedings (*Polym. prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1991**, *32* (3), 588–589).

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