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Addition Polymerization of 1,1-Dimesitylneopentylsilene: Synthesis of a Polysilene

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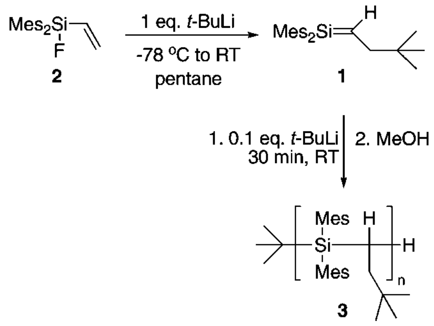
Addition polymerization of unsaturated, main group monomers has emerged as a promising route to inorganic polymers: phosphaalkenes (P═C) can be polymerized using radical and anionic initiators to yield poly(methylenephosphine)s,[1] and recently, the anionic polymerization of a solution stable germene (Ge═C) to give a polygermene has been demonstrated.[2] On the basis of these precedents, the addition polymerization of a silene (Si═C) appears to be a promising route to a poly(silylenemethylene),[3] $[\mathrm{SiC}]_n$, which, based on the nature of the monomer, can also be termed a polysilene. Although silenes have been studied extensively for many years, there are no reports on their polymerization reactions.[4]

The poly(silylenemethylene)s are of particular interest because of the stoichiometric ratio of silicon to carbon in the backbone, which has led to their use as effective thermal precursors to silicon carbide,[5,6] an important technological material.[7] High-molecular-weight poly(silylenemethylene)s are commonly obtained by the ring-opening polymerization of 1,3-disilacyclobutanes;[6] however, this method is limited by the availability of appropriate ring systems. Furthermore, the linear polymers obtained using this method generally give low to moderate ceramic yields upon pyrolysis. Alternatively, low molecular weight polymers with broad polydispersities can be synthesized by the reductive coupling of chloromethylchlorosilanes[8] or dihalosilanes with dihalomethanes.[9] The highly cross-linked polymers derived from chloromethylchlorosilanes have been shown to be excellent ceramic precursors.[8]

Scheme 1. Polymerization of 1,1-Dimesitylneopentylsilene (1)



With the high level of interest in the addition polymerization of main group alkene analogues and in the chemistry of poly(silylenemethylene)s, we now report on the addition polymerization of a solution stable silene, 1,1-dimesitylneopentylsilene (**1**), as a new approach to polymers with a $[\mathrm{SiC}]_n$ backbone.

A pentane solution of fluorovinylsilane **2** was converted to 1,1-dimesitylneopentylsilene (**1**) upon the addition of *t*-butyllithium (1 equiv).[10] Silene **1** is stable in pentane;[10] however, upon the addition of *t*-butyllithium (0.1 equiv) the color of the pale orange solution deepened and persisted until the reaction was quenched with methanol (Scheme 1).

The methanol adduct of the silene, $\mathrm{Mes_2Si(OMe)CH_2CH_2}t\mathrm{Bu}$, was not observed in the crude product mixture, indicative of complete consumption of silene **1**. The product (**3**) was isolated as a white, air-stable solid after precipitation from a $\mathrm{CH_2Cl_2}$ solution with methanol (50% yield). The ^{1}H NMR spectrum of the precipitate displayed several broad resonances consistent with polymeric material. The molecular weight of **3** was estimated by gel permeation chromatography (GPC) in THF. The number-average molecular weight (M_n) was determined to be 28 000 g mol^{-1} with a polydispersity index (PDI) of 1.2. DSC analysis of polymer **3** was performed; only a glass transition was observed (T_g = 153 °C) indicative of an

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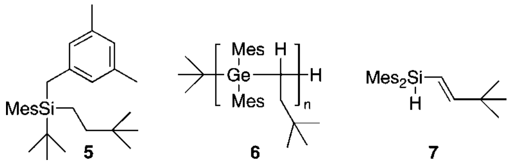
Chart 1



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amorphous polymer. The thermal stability of polymer **3** was determined using TGA; weight loss was observed between 325 and 525 °C. The weight of the residue remaining at 800 °C was 12% of the original weight and is composed primarily of carbon as demonstrated by EDX analysis. The high carbon content is not surprising given the large organic substituents on the polymer backbone.

Polymer **3** can also be synthesized directly by the addition of excess *t*-butyllithium (1.1 equiv) to fluorovinylsilane **2** at −78 °C. After warming to room temperature, the solution was pale orange and a precipitate formed (LiF), indicating the formation of silene **1**. Indeed, if methanol was added to the solution at this stage, the methanol adduct of the silene, $Mes_2Si(OMe)CH_2CH_2t$Bu, was isolated as the only product. Without the addition of methanol, a deep orange color developed, indicating formation of the polymer.

The polymer was isolated in 65% yield after precipitation and purification. The number-average molecular weight of polymer synthesized in one step was similar to that prepared from the addition of *t*-BuLi to silene **1** (M_n = 32 000 g mol^{-1}; PDI = 1.1). The one step method for the preparation of polymer **3** from silane **2** is preferred because the polymer was isolated in higher yield with fewer experimental manipulations.

To aid in the spectroscopic analysis of **3**, we synthesized $Mes_2Si(t$Bu$)CH_2CH_2t$Bu (**4**) to model the repeating unit. When excess *t*-butyllithium (3 equiv) was added to silene **1** in ether at 0 °C followed immediately by the addition of aqueous ammonium chloride, compound **4** was produced quantitatively. In contrast, when the procedure for the synthesis of the analogous germanium compound was followed,[11] where excess *t*-butyllithium was added to silene **1** in ether at room temperature, isomeric *t*-butylsilane (**5**) was produced (Chart 1). It seems likely that the initial α-silyl anion, formed by the regioselective addition of *t*-butyllithium to silene **1**,[12] deprotonates an *o*-methyl group to form a benzylic anion, which undergoes an anionic 1,3-silyl shift. Presumably, the additional steric strain around silicon, relative to germanium, promotes this unusual anionic 1,3-C,C silyl shift.

The polymeric material (**3**) was characterized by one- and two-dimensional NMR spectroscopy. All of the signals in the ^{1}H NMR spectrum of **3** could be assigned based on their chemical shift and integration and were consistent with the proposed structure. However, the broadness of the signals leads to significant overlap between many of the resonances, so detailed structural information could not be extracted.

The ^{29}Si and ^{13}C NMR spectra of **3** were more useful in elucidating the structure of the polymer. The strongest ^{29}Si signal observed in the ^{1}H − ^{29}Si gHMBC spectrum of **3** (−7.5 ppm) showed a correlation to the ^{1}H signal at 6.5 ppm assigned to the aromatic hydrogen of the mesityl group (Mes-$\underline{H}$). No correlations to the Si−C$\underline{H}$ or Si-CHC$\underline{H}_2$ hydrogens were observed presumably because of the broadness of the ^{1}H signals. Two weaker ^{29}Si signals, at 2.1 and 10.1 ppm, correlated to the ^{1}H signals at 0.87 and 0.89 ppm, respectively. These ^{29}Si signals could represent the two different types of end group silicon environments: $\underline{Si}$-$C(CH_3)_3$ and $\underline{Si}$-CH_2CH_2tBu. The characteristics of the signal at 2.1 ppm are consistent with the ^{29}Si spectroscopic data of compound **4**, where the ^{29}Si signal (1.2 ppm) correlated strongly to the ^{1}H signal at 1.17 ppm, assigned to the Si−C(C$\underline{H}_3$)$_3$ hydrogens. The chemical shift of the ^{29}Si signal at 10.1 ppm is similar to that of **5** (4.0 ppm) indicating a rearranged terminal mesityl group. The difference in the steric bulk of the substituents may account for the observed difference in the chemical shift. The ^{13}C NMR spectrum of **3** was compared to that of compound **4** as well as to the ^{13}C NMR spectrum of the analogous germanium polymer **6**[2] (Chart 1). All of the signals could be assigned on the basis of their chemical shifts. For example, the Si-$\underline{C}$H and Si-CH$\underline{C}$H$_2$ carbons in **3** were observed to resonate at 14.0 and 38.2 ppm, respectively, compared to 16.3 and 38.7 ppm in germanium polymer **6** and 11.9 and 39.9 ppm in compound **4**. Also, two sets of mesityl signals were observed in both **3** and **6** because of the chirality of the backbone carbon. The assignments were confirmed by both ^{13}C−^{1}H correlation spectroscopy and DEPT spectroscopy. Both the ^{29}Si and ^{13}C NMR spectra of **3** are consistent with a dimesityl-substituted silicon within a regular alternating silicon−carbon backbone.

The polymerization of silene **1** most likely proceeds via an anionic mechanism initiated by the regioselective addition of *t*-butyllithium to the electrophilic silicon of the silene.[12] The regioselective addition of an anionic reagent to the silene is known to occur in ether, as observed in the synthesis of **4**; however, in pentane, the initial carbanion, $Mes_2Si(t$Bu$)CH(Li)CH_2t$Bu, appears to be more reactive and adds to the silicon of a second silene to propagate the growth of the polymer. The polymerization of silene **1** occurs rapidly, similar to the polymerization of 1,1-dimesitylneopentylgermene.[2] The rapid reaction is most likely due to the high reactivity of silene **1** toward nucleophilic addition.

Polymeric material was also produced when silene **1** was left in solution (C_6D_6) for 2 days in the absence of an anionic initiator; isomeric vinylsilane **7** (Chart 1) and several other unidentified compounds were produced in minor amounts. The polymer was isolated in 40% yield after precipitation from a CH_2Cl_2 solution with methanol. The molecular weight of the polymer was determined by GPC in THF (M_n = 37 000 g mol^{-1}; PDI = 1.2). The ^{1}H and ^{13}C NMR spectra of the polymer were identical to those of **3**, once again indicating a regular alternating silicon−carbon backbone. A radical polymerization mechanism is presumably occurring under these conditions; however, further investigation is required to confirm the mechanism of polymer formation.

In summary, we have reported the first addition polym-

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erization of a stable silene as a new route to a polymer with a $[SiC]_n$ backbone, a polysilene. We are currently investigating post polymerization modifications in an attempt to develop a polymer better suited for use as a ceramic precursor. We are also investigating whether the polymerization of silene **1** can be carried out under living anionic conditions for use in the synthesis of block copolymers containing this inorganic segment.

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Supporting Information Available: Experimental Procedures, ^1H and ^{13}C NMR spectra, TGA data, DSC data, GPC data, EDX data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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