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Synthesis and Characterization of Linear Siloxane–Diacetylene Polymers

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Polymers containing diacetylene units in the main backbone or in side chains have been the subject of much recent research.[1] The diacetylene groups can react by thermal or photochemical means to form a cross-linked polymer consisting of an extended conjugated network.[1c] Besides strengthening the host polymer, these cross-links can introduce novel optical properties into the polymer such as thermochromism,[1f,g] mechanochromism,[1h] and optical nonlinearity.[1a,2] In addition, diacetylene polymers have been used to make thermosetting fibers.[3] Our investigations have focused mainly on these polymers as precursors to high-temperature materials.

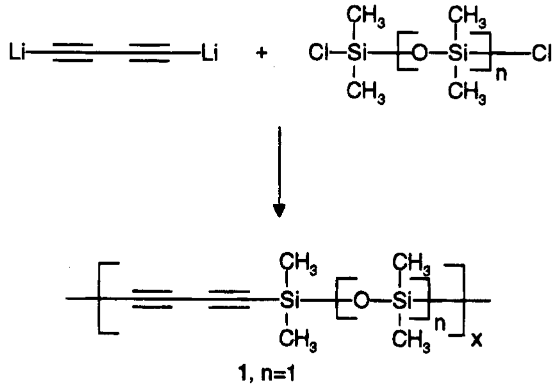
For practical purposes, the cross-linked polymers should possess certain physical properties such as thermal stability and good moisture resistance. While most reports have described purely organic polymers, combining inorganic elements with the diacetylene units should enhance the thermal and oxidative stability of the polymers. Siloxyl groups are a logical choice for inclusion in these polymers as they possess good thermal and oxidative stability and high hydrophobicity.[4] Furthermore, their flexibility should contribute favorably to the processability of the resulting polymers. A previous report from our laboratory described the synthesis and characterization of a novel poly(carborane–siloxane–acetylene).[5] This polymer cross-linked at 300 °C to produce a hard thermoset that exhibited superior thermal and oxidative stability. Polymers containing only siloxyl and diacetylene units should also afford thermosets of good stability. The polymer $(-C{\equiv}CC{\equiv}CSiMe_2OSiMe_2-)_n$ (**1**), obtained via the oxidative coupling of 1,3-diethynyltetramethyldisiloxane, was previously reported by Parnell and Macaione.[6] The authors reported obtaining only low molecular weight products in addition to some insoluble material. Herein, we report an alternative high-yield synthesis to **1** and the related polymer **2** and various thermal characteristics of these polymers.

The synthesis of the polymers is a simple two-step, one-pot reaction (Scheme 1) and is adapted from a previously reported synthesis of poly(silyldiacetylenes).[11] Treatment of hexachlorobutadiene with 4 equiv of *n*-butyllithium in THF/hexane at −78 °C generates 1,4-dilithio-1,3-butadiyne. After the mixture is stirred at room temperature for 2 h and then recooled to −78 °C, the appropriate dichlorosiloxane is added dropwise to the reaction mixture. Stirring at room temperature for 2 h followed by aqueous workup gives **1** and **2** in 85–95% yield. At room temperature, polymer **1** is a dark brown solid which liquefies at ~70 °C, while **2** is a slightly viscous dark brown liquid. This difference in properties can be attributed to the longer flexible siloxane spacer in **2**. Both polymers are completely soluble in common organic solvents such as ether, THF, acetone, toluene, and chloroform. The IR spectra for both polymers show strong acetylenic stretching bands (2071 cm^{-1}) and strong bands in the Si–O stretching region (1045–1055 cm^{-1}). ^{1}H and ^{13}C NMR spectral data for **1** and **2** are summarized in Table 1.

Table 1. ^{1}H and ^{13}C NMR Spectral Data for 1 and 2 (in CDCl$_3$)

	^{1}H NMR (ppm)	^{13}C NMR (ppm)
1 $(-Si(CH_3)_2-)$	0.30	1.68, 1.86
1 $(-C{\equiv}CC{\equiv}C-)$		84.9, 86.9
2 $(-Si(CH_3)_2-)$	0.11, 0.26	0.94, 1.79
2 $(-C{\equiv}CC{\equiv}C-)$		85.2, 86.8

Scheme 1



1, n=1
2, n=2

The polymers were also characterized using gel permeation chromatography (GPC) and elemental analysis. GPC analysis indicated broad molecular weight distributions, with peak maxima occurring at ~10 000 (relative to polystyrene) for both polymers. The presence of lower molecular weight species can be attributed to chain termination and formation of cyclic species during polymerization. Unreacted *n*-butyllithium from the formation of 1,4-dilithio-1,3-butadiyne could terminate a polymer chain by reaction with a Si–Cl bond. The discrepancies in the elemental analysis data for **1** and **2**[7] are likely a result of the relatively large amounts of end groups present. Besides butyl end groups, –SiOH groups resulting from hydrolysis of unreacted Si–Cl bonds during workup can terminate polymer chains. Similar elemental analysis variations were reported for poly[silylenediacetylenes].[8]

The thermal behaviors of **1** and **2** were examined using thermogravimetric (TGA) and differential calorimetric (DSC) analysis. As expected, polymer **1** possesses a higher char yield than **2** in nitrogen (**1**, 74%; **2**, 58%). Polymer **2**, having a higher concentration of siloxane groups in its backbone, is more susceptible to degradation at higher temperatures via formation of monomeric cyclic siloxanes.[9] The DSC data for both polymers are shown in Figure 1. Large exotherms are observed at 289 and 315 °C for **1** and **2**, respectively. These exotherms can be attributed to the diacetylenic cross-linking reactions.[10] Polymer **1**, a solid, reproducibly exhibits two small endotherms between 50 and 80 °C. When **1** is heated to 100 °C, recooled to room temperature, and then reheated, the endotherms are again observed. These likely indicate that different degrees of crystallinity exist in the solid. A similar phenomenon has been observed in poly(urethane–diacetylene) copolymers.[1f]

Both **1** and **2** can be cured thermally via the diacetylene cross-linking reaction.[11] A degassed sample of **1** was heated in argon at 200, 300, and 400 °C for 2 h at each temperature to give a hard, void-free thermoset (**3**) with 94% mass recovery. Some shrinkage of the

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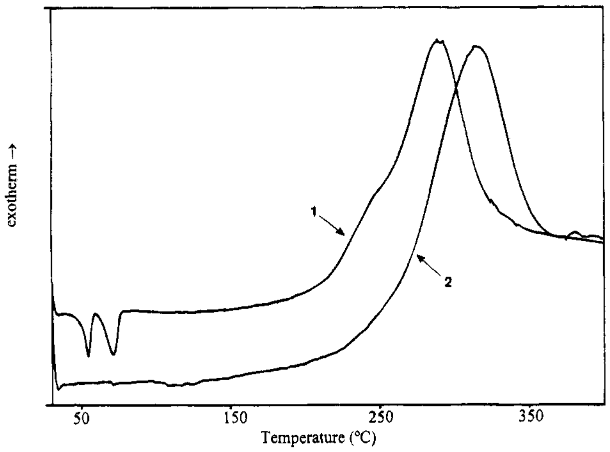

Figure 1. DSC data for **1** and **2**. Heating rate = 10 °C/min in nitrogen.

sample was observed. An IR spectrum of **3** showed almost total disappearance of the diacetylenic absorption, indicating that cross-linking was complete. In a similar manner, polymer **2** was cured by heating in argon at 225, 325, and 400 °C for 2 h at each temperature. A hard, void-free thermoset (**4**) was obtained with 90% mass recovery. Again, some shrinkage was observed. For both samples, curing in air resulted in lower mass retention. The glass transition temperatures for **3** and **4** were found to be 144 and 170 °C, respectively. The greater chain flexibility in **2** due to the longer siloxane spacer perhaps contributes to an enhancement in the amount of cross-linking in **4**, resulting in a higher T_g. By heating a sample of **3** at 450 °C for 4 h, the T_g of **3** can be elevated to 195 °C. These values are comparable to those of other cross-linked silicone resins.[12]

Thermosets **3** and **4** both exhibit excellent thermooxidative stabilities. When heated in air to 1000 °C (rate = 10 °C/min), **3** and **4** exhibit no weight loss to approximately 400 °C. Unlike conventional organic thermosets, **3** and **4** do not lose all their mass at higher temperatures. The overall char yields after heating to 1000 °C were approximately 60% for both **3** and **4**. When **3** was heated to 1000 °C in an inert atmosphere, a char representing only 26% weight loss was recovered. This char also possesses excellent thermooxidative stability. On heating to 1000 °C in air, the char remained stable to ~600 °C, at which point gradual weight loss was observed. The overall weight loss was only 15% (Figure 2). As a comparison, the char from our previously reported poly(carborane–siloxane–acetylene) actually gained weight when heated to 1000 °C in air.[5] Boron is oxidized at high temperatures, and the resulting oxidized layer serves to protect the internal components from oxidation. This effect has been observed previously.[13]

In summary, linear siloxane–diacetylene polymers can be prepared efficiently in high yields. Cross-linking via the diacetylene groups occurs on heating, and the resulting materials have excellent thermal and thermooxidative stabilities. Current investigations are focusing on the fundamental requirements for high-temperature material design.

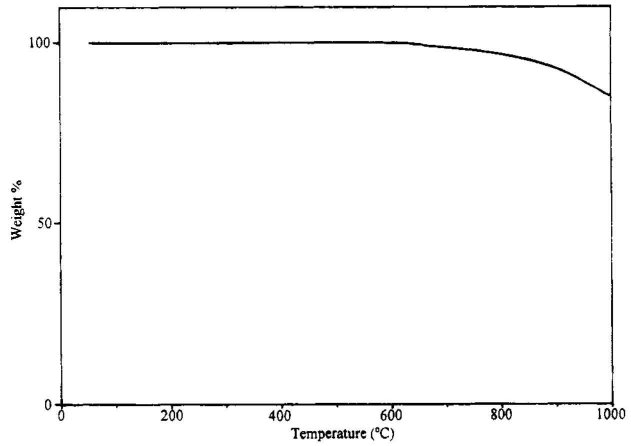

Figure 2. TGA data for char (from **3**). Heating rate = 10 °C/min in air.

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